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[54] LIQUID HYDROCARBON FUELS CONTAINING ALKYLAMINE SALTS

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[51] **Int. Cl.** **C10l 1/26**

[58] **Field of Search** ..... 44/71, 76, 72, 69 P, 56 D; 252/389

[56] **References Cited**

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[57] **ABSTRACT**

Liquid hydrocarbon fuels are provided which contain, as stabilizing agents, neutral primary alkylamine salts of an alkyl phosphoric acid ester having from two to eight phosphorous atoms, an acid number from about 200 to about 750 and from one to 12 carbon atoms per alkyl group, wherein the primary alkylamine comprises a mixture of branched chain amines having from about eight to about 18 carbon atoms and having the primary amine groups attached to a tertiary carbon atom.

7 Claims, No Drawings

LIQUID HYDROCARBON FUELS CONTAINING ALKYLAMINE SALTS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a division of our copending application Ser. No. 395,933, filed Sept. 11, 1964, now abandoned.

This invention relates to liquid hydrocarbon fuels. More particularly, the invention relates to liquid hydrocarbon combustion fuels that are stabilized against screen-clogging, filter plugging, sediment formation, icing and corrosion, and the novel additive compounds useful for such purposes.

As is well known to those skilled in the art, liquid hydrocarbon fuels, particularly hydrocarbon combustion fuels, such as fuel oils, diesel fuels, jet fuels and gasolines, tend to exhibit certain deleterious characteristics either after long periods of storage or under the conditions of operational use. Thus, it has been found that in such fuels, apart from the fact that under storage or operational conditions they may exhibit icing, corrosion and sediment formation, a particularly serious problem is encountered in the clogging of screens and plugging of filters. This tendency to clog screens and plug filters results from the caustic treatment of catalytically refined petroleum distillate fuels for the removal of sulfur-containing materials.

More specifically, this condition occurs when certain polar materials (surface-active additives and trace constituents) in the fuel contacted by the caustic agents, break down and form, as part of the product, water-soluble alkali metal compounds. When, subsequently, these fuels contact water such as might be present in fuel tank bottoms, these alkali metal compounds are leached out of the hydrocarbon phase into the water phase to greater or lesser degrees. There, by replacement of the alkali metals, corresponding compounds of dissolved metals having normal valences greater than one (for e.g., calcium, magnesium, zinc, copper, iron, aluminum, barium or lead) may be formed. Because of their surface activity, and reduced water and product solubility, these compounds may cause emulsification and gel formation particularly in the hydrocarbon layer, as well as in the water layer, with consequent serious detrimental effects on the clogging of screens and the plugging of filters. Heretofore, certain organic amine monophosphates have been suggested as anti-icers, carburetor detergents and anti-rust agents; however, these additives have, nevertheless, been found to cause serious problems with respect to the aforementioned screen clogging and filter plugging conditions. Accordingly, a means for stabilizing such fuels and protecting them against the aforementioned screen clogging, filter plugging, as well as other undesirable storage conditions normally encountered, is highly desirable.

It is, therefore, an object of the present invention to provide improved liquid hydrocarbon fuels.

Another object of the invention is to provide improved liquid hydrocarbon combustion fuels and means for protecting them, which are effective not only against sediment formation, icing and corrosion, but also against screen-clogging and filter plugging.

Other objects and advantages inherent in the invention will become apparent to those skilled in the art from the following description.

In accordance with the present invention, as more fully hereinafter described, it has been found that the above objects can be attained by the addition of small amounts of additive compositions having the formula:



where:

R_1, R_2 and R_3 are selected from the group consisting of hydrogen and alkyl groups having from one to about 22 carbon atoms, and preferably, from about eight to about 18 carbon atoms, X is an acid radical selected from the group consisting of (a) phosphoric acids having from two to eight phosphorous atoms per molecule, (b) phosphoric acid alkyl esters having from two to eight phosphorus atoms per molecule and containing from one to four alkyl groups having from one to 22 carbon atoms per alkyl group, (c) boric acid, (d) carbonic acid, (e) aminopolycarboxylic acids and hydroxyethyl aminocarboxylic acids, in which the amine nitrogen atom is separated from the carboxylic carbon atom by a methylene or ethylene linkage and in which when more than one nitrogen atom is present they are separated from each other by ethylene or propylene linkages, and *n* is a whole number from 1 to 5, the maximum value of n being limited by the number of replaceable hydrogen atoms in the acid molecule of which X is an acid radical.

More specifically, with respect to the aforementioned substituents for the acid radical X, phosphoric acids of the type indicated under (a) may include pyrophosphoric acid (diphosphoric acid), triphosphoric acid, hexaphosphoric acid and polyphosphoric acid. Aminopolycarboxylic acids of the type indicated under (e) may include ethylenediamine tetraacetic acid, nitrilotriacetic acid, diaminocyclohexane - N,N'-tetracetic acid, and diethylene-triamine pentaacetic acid. Hydroxyethyl aminocarboxylic acids indicated under (e) may include N-hydroxyethyl ethylenediamine triacetic acid and dihydroxyethyl glycine.

As will become hereinafter apparent, these additive compositions are particularly effective not only as stabilizers against icing, corrosion and sediment formation, but also as anti-screen clogging and filter plugging agents in liquid hydrocarbon fuels.

These beneficial effects result from the fact that in the previously described replacement of the alkali metals, those metals having valences greater than one are tied up and rendered unavailable. As a result of such action, the aforementioned detrimental effects are prevented from occurring.

The alkylamine salt additives are, in general, prepared by reacting one equivalent of the selected amine with one equivalent of the selected acid, in accordance with the above-described general formula, preferably at elevated temperature, for example, from about 50° C. to about 120° C.

The aforementioned alkylamine salt additives may be used to improve liquid hydrocarbon fuels, generally. Of particular significance is the use of these additives to improve liquid hydrocarbon fuels comprising petroleum distillates, which are hydrocarbon fractions, having an initial boiling point of at least about 90° F. and an end boiling point not higher than about 750° F., and boiling substantially continuously throughout their distillation range. Such fuels are generally referred to as distillate fuel oils. It will be understood, however, that this terminology is not restricted to straight run distillate fractions. The distillate fuel oils may comprise straight run distillate fuel oils, catalytically or thermally cracked (including hydrocracked) distillate fuel oils, or mixtures of straight run distillate fuel oils, naphthas and the like, with cracked distillate stocks. Moreover, such fuel oils can be treated in accordance with well known commercial methods, such as, acid or caustic treatment, hydrogenation, solvent refining, clay treatment and the like.

The distillate fuel oils are characterized by their relatively low viscosities, pour points and the like. The principal property which characterizes the contemplated liquid hydrocarbon fuels of the present invention, however, is their distillation range. As previously indicated, this range will lie between about 90° F. and about 750° F. Obviously, the distillation range of each individual fuel oil will cover a narrower boiling range, falling, nevertheless, within the above-specified limits. Likewise, each fuel oil will boil substantially continuously throughout its distillation range.

Particularly contemplated among the aforementioned liquid hydrocarbon fuel oils are gasolines, Nos. 1, 2 and 3 fuel oils used in heating, diesel fuel oils, and the jet combustion fuels. The gasolines generally boil within the range from about 90° F. to about 450° F. The domestic fuel oils generally conform

to the specifications set forth in ASTM Specifications D396–62T. Specifications for diesel fuels are defined in ASTM Specifications D975–60T. Typical jet fuels are defined in Military Specifications MIL–F–5624B.

The amount of the aforementioned alkylamine salt additive contemplated for use herein which is added to the liquid hydrocarbon fuel will depend, of course, upon the intended and the particular additives selected, inasmuch as these additives may necessitate being used in greater concentrations than others to be effective. In most cases, in which it is desired to obtain the aforementioned beneficial results in the liquid hydrocarbon fuels, viz prevention of clogging of screens and plugging of filters, in addition to stabilization against sediment formation, icing and corrosion, additive concentrations varying from about 1 to about 200 pounds per thousand barrels of the fuel will be employed. Preferably, it will vary from about 5 to about 25 pounds per 100 barrels of fuel. If so desired, the aforementioned liquid hydrocarbon fuel compositions of the present invention can contain other additives for the purpose of achieving other results. Thus, for example, there may be present foam inhibitors, ignition and burning quality improvers, and others. Examples of such additives are silicones, dinitropropane, amyl nitrate, metal sulfonates, and the like.

The following examples and comparative data are intended to illustrate the novel additive compositions of the present invention and also to demonstrate their effectiveness in improving the properties of liquid hydrocarbon fuels. It will be understood, of course, that it is not intended the invention be limited to the particular compositions shown or to the operations or manipulations involved. Various other additive compositions, and other fuels, can be utilized as those skilled in the art will readily appreciate.

In carrying out the comparative experimentation, previously referred to, laboratory bench tests were made in which 40 ml. of an average commercially available gasoline blend, (comprising, by volume, 40 percent catalytically cracked, 40 percent reformate and 20 percent alkylate components), was treated with 10 ml. of 0.8 N. NaOH (as a sulfur compound, particularly mercaptan, removing agent), 6 ml. of distilled water and 20 ml. of 13.6 g./l. of $ZnCl_2$ solution (a component providing zinc ions which are often present in the field in tank water bottoms as a result of chemical actions on galvanized metal surfaces) in a 100 ml. mixing graduate. This mixture was given 15 uniform, moderate, shakings and allowed to settle for 1 minute. The mixture was then examined for indications of colloidal states. The following table indicates the results obtained in such examinations. With regard to this table, it should be noted that the laboratory tests simulate the most severe conditions of commercial use that would normally be expected to result in emulsion and gel formation, which would otherwise cause handling difficulties in product distribution systems and in vehicle fuel lines, with particular emphasis residing in encountering screen clogging and filter plugging. As will be seen from the table, u nder such conditions the additives of the present invention reduced, to a very significant degree, the tendency of the uninhibited gasoline and the uninhibited gasoline containing an alkylamine monophosphate (as a typical anti-icer, anti-rust and carburetor detergent multifunctional additive) to form emulsions.

The additives of the following table were prepared as follows:

EXAMPLE I

Preparation of Primene 81 R Salt Of Tripolyphosphoric Acid

A mixture comprising: 74 grams (0.2 mol) sodium tripolyphosphate ($Na_5P_3O_{10}$), 200 grams water and 36.7 grams hydrochloric acid (100 grams of 36.7 percent hydrochloric acid solution) was stirred for a period of one hour at 60° C. and then heated to 115° C. to form the free tripolyphosphoric acid. To this mixture were then added 200 grams (1 mol) of Primene 81 R (a commercially available mixture of branched chain amines of from about 12 to about 15 carbon atom chain lengths having the primary amine group directly attached to a tertiary carbon atom) and 100 grams of benzene. The resulting mixture was then heated to 100° C. and maintained at this temperature for a period of 1 hour. The resulting water layer was then removed from the mixture by the use of a separatory funnel. The remaining mixture was then topped at 180° C. under reduced pressure and filtered to yield the desired product of the Primene 81 R salt of tripolyphosphoric acid.

EXAMPLE II

Preparation of Tetra Primene 81 R Salt Of Ethylenediamine Tetraacetic Acid

A mixture comprising: 200 grams (1 mol) Primene 81 R, 73 grams (0.25 mol) ethylenediamine tetraacetic acid and 273 grams of xylene as a diluent was stirred for a period of about 2 hours at a temperature from about 125° C. to about 130° C. to form the tetra Primene 81 R salt of ethylenediamine tetraacetic acid, diluted with 50 percent xylene.

Another group of useful additives of the aforementioned type are the Primene 81 R salts of alkyl phosphoric acid esters having from two to eight phosphorus atoms, an acid number from about 200 to about 750 and from one to 12 carbon atoms per alkyl group. Examples III and IV illustrate two typical types of this group.

EXAMPLE III

Preparation of Primene 81 R Salt of Phosphonol H

A mixture comprising: 100 grams of mixed alkyl polyphosphoric acid esters (commercially available under the trade name Phosphonol H, manufactured by Beacon Chemical Industries, Inc., Cambridge, Mass.) falling within the descriptive properties indicated above and having an acid number of 302, was stirred for a period of about one hour at a temperature of 100° C. with 108 grams of Primene 81 R to form the Primene 81 R salt of Phosphonol H.

EXAMPLE IV

Preparation of Primene 81 R Salt of Strodex P–100

A mixture comprising 110 grams of mixed alkyl polyphosphoric acid esters (commercially available under the trade name Strodex P–100, manufactured by Dexter Chemical

TABLE

				Demulsification test	
			Concentration, lbs./1,000 bbls.	Gasoline layer, percent emulsified	Water layer, observations
1	Blank gasoline [1]		0	40	Cloudy with heavy precipitate.
2	do	+ A commercial alkylamine monophosphate	100	80	Cloudy with moderate precipitate.
3	do	+ Primene 81 R salt of tripolyphosphoric acid	100	10	Cloudy with slight precipitate.
4	do	+ Tetra Primene 81 R salt of ethylenediamine tetraacetic acid.	100	0	Cloudy with moderate precipitate.
5	do	+ Primene 81 R salt of Phosphonol H	100	10	Cloudy with slight precipitate.
6	do	+ Primene 81 R salt of Strodex P–100	100	0	Cloudy with moderate precipitate.

[1] A commercial type catalytically cracked/reformate/alkylate gasoline blend containing 5 lb./1,000 barrels 2,6-ditertiary butyl paracresol; 1 lb./1,000 barrels N,N'-disalicylidene-1,2-propanediamine; and 3 cc. tetraethyl lead/gal.

Corp., New York, N.Y.) falling within the descriptive properties indicated above and having an acid number of 240, was stirred for a period of about 2 hours at a temperature of 150° C. with 94 grams of Primene 81 R to form the Primene 81 R salt of Strodex P–100.

While the present invention has been described with preferred embodiments, it should be understood that modifications and variations thereof may be resorted to without departing from the spirit of the invention as will be obvious to those skilled in the art.

We claim:

1. A liquid hydrocarbon fuel containing, as a stabilizer, a small amount of the neutral primary alkyl amine salt of an alkyl phosphoric acid ester having from two to eight phosphorous atoms, an acid number from about 200 to about 750 and from one to 12 carbon atoms per alkyl group, wherein the primary alkyl amine is a mixture of branched chain amines having from about eight to 18 carbon atoms, having the primary amine group directly attached to a tertiary carbon atom.

2. A fuel as defined in claim 1 wherein the stabilizer is the neutral primary alkyl amine salt of tripolyphosphoric acid wherein said acid corresponds to the acid form of $Na_5P_3O_{10}$, the primary alkyl amine is a mixture of branched chain amines having from about eight to 18 carbon atoms, the primary amine group is directly attached to a tertiary carbon atom.

3. A fuel as defined in claim 1 wherein the alkylamine salt is present in an amount from about 1 to about 200 pounds per 1,000 barrels of fuel.

4. A fuel as defined in claim 1 wherein the alkylamine salt is present in an amount from about 5 to about 25 pounds per 1,000 barrels of fuel.

5. A composition as defined in claim 1 wherein said liquid hydrocarbon fuel comprises a petroleum distillate having an initial boiling point of at least about 90° F. and an end boiling point not higher than about 750° F.

6. A fuel as defined in claim 1 wherein said alkylamine salt is a t-alkyl primary amine salt of tripolyphosphoric acid.

7. A fuel as defined in claim 1 wherein said alkylamine salt is a tetra t-alkyl primary amine salt of ethylenediamine tetraacetic acid.

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