ABSTRACT OF THE DISCLOSURE

Alkylamine salts, suitable for use as stabilizers for liquid hydrocarbons are provided, containing alkyl substituent groups and being salts of either phosphoric acids, phosphoric acid alkyl esters, boric acid, carboxylic acid, aminocarboxylic or hydroxymethyl aminocarboxylic acids.

CROSS-REFERENCE TO RELATED APPLICATIONS

Application Ser. No. 395,933, filed Sept. 11, 1964 (parent application).

BACKGROUND OF THE INVENTION

Field of the invention

This invention, which is a division of our application Ser. No. 395,933, filed Sept. 11, 1964, 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.

Description of the prior art

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, the boiling point of at least one of the above liquids has been suggested as antilizers, carburetor detergents and anticorrosives; 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.

SUMMARY OF THE INVENTION

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:

\[
R_1 \quad [R_2 - N - R_3 - X]
\]

where:

- \( R_1, R_2, \) and \( R_3 \) are selected from the group consisting of hydrogen and alkyl groups having from 1 to about 22 carbon atoms, and preferably, from about 8 to about 18 carbon atoms. X is an acid radical selected from the group consisting of (a) phosphoric acids having from 2 to 8 phosphorus atoms per molecule, (b) phosphoric acid alkyl esters having 2 to 8 phosphorus atoms per molecule and containing from 1 to 4 alkyl groups having from 1 to 22 carbon atoms per alkyl group, (c) boric acid, (d) carboxylic acid, (e) aminocarboxylic acids and hydroxymethyl 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), tripolyphosphoric acid, hexa phosphoric acid and polynuosphoric acid. Aminocarboxylic acids of the type indicated under (e) may include ethylenediamine tetraacetic acid, nitrilotriacetic acid, diaminocyclohexane-N,N',N'-tetraacetic acid, and diethylenetriamine pentaacetic acid. Hydroxymethyl aminocarboxylic acids indicated under (e) may include N-hydroxymethyl ethylenediaminetriacetic 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 antiscreen 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 containing petroleum distillates, which are hydrocarbon fractions, having an initial boiling point of about 30° F. and an end boiling point not more 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, or thermally cracked (including hydrocracked) distillate fuel oils, or mixtures of straight-run distillate fuel oils, naphtha and the like, with cracked distillate stocks. Moreover, such fuel oils can be treated in accordance with well known commercial methods, such as, acid 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 properties which characterize 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 gasoline, Nos. 1, 2 and 3 fuel oils used in heating, diesel fuel oils, and the jet combustion fuels. The gasoline generally boil within the range from about 90°F to about 450°F. The domestic fuel oil generally contains 0.7% of aromatics as determined 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 additives 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 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, dimethylpolysiloxane, dialkyl tarate, metal sulfonates, and the like.

DESCRIPTION OF SPECIFIC EMBODIMENTS

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 to 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% catalytically cracked, 40% reformate and 20% alkylate components), was treated with 10 ml. of 0.8 N NaOH (as a soap compound, particularly mercaptan, removing agent), 6 ml. of distilled water and 20 ml. of 13 g./L. of ZnCl₂ 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 fifteen uniform, moderate, shakings and allowed to settle for one 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 show adverse effects on 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, under such conditions the additives of the present invention reduced, to a very significant degree, the tendency of the uninhibited gasoline and uninhibited gasoline containing an alkylamine monophosphate (as a typical antiscratter, antirust and carburetor detergent multifunctional additive) to form emulsions.

The additives of the following table were prepared as follows:

**EXAMPLE I**

Preparation of Primene 81R salt of triplyphosphoric acid

A mixture comprising: 74 grams (0.2 mol) sodium triplyphosphate (Na₅P₃O₁₀), 200 grams water and 36.7 grams hydrochloric acid (100 grams of 36.7% hydrochloric acid solution) was stirred for a period of one hour at 60°C and then heated to 115°C to form the free triplyphosphoric acid. To this mixture were then added 200 grams (1 mol) of Primene 81R (a commercially available mixture of branched chain amines of 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 one 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 81R salt of triplyphosphoric acid.

**EXAMPLE II**

Preparation of tetra Primene 81R salt of ethylenediamine tetraacetic acid

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

Another group of useful additives of the aforementioned type are the Primene 81R salts of alkyl phosphoric acid esters having from 2 to 8 phosphorus atoms, an acid number from about 200 to about 750 and from 1 to 12 carbon atoms per alkyl group. Examples III and IV illustrate two typical types of this group.

**EXAMPLE III**

Preparation of Primene 81R salt of Phosphonol H

A mixture comprising: 100 grams of mixed alkyl polyphosphoric acid esters (commericially available under the tradename Phosphonol H, 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 81R to form the Primene 81R salt of Phosphonol H.

**EXAMPLE IV**

Preparation of Primene 81R salt of Strodex P-100

A mixture comprising 110 grams of mixed alkyl polyporphosphoric acid esters (commercially available under the
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tradename Strodex P-100, falling within the descriptive properties indicated above and having an acid number of 240, was stirred for a period of about two hours at a temperature of 150° C. with 94 grams of Primene 81R to form the Primene 81R salt of Strodex P-100.

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phosphoric acid wherein said acid corresponds to the acid form of Na₅P₂O₁₀, the primary alkyl amine is a mixture of branched chain amines having from about 8 to 18 carbon atoms, the primary amine group is directly attached to a tertiary carbon atom.

<table>
<thead>
<tr>
<th>TABLE</th>
<th>Demulsification Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>Concentration layer, percent emulsified</td>
</tr>
<tr>
<td>blank gasoline</td>
<td>100</td>
</tr>
<tr>
<td>blank gasoline a commercial alkylamine monophosphate</td>
<td>100</td>
</tr>
<tr>
<td>blank gasoline Primene 81 R salt of tri-polyphosphoric acid</td>
<td>100</td>
</tr>
<tr>
<td>blank gasoline tern Primene 81 R salt of ethylenediamine tetrasulfate</td>
<td>100</td>
</tr>
<tr>
<td>blank gasoline Primene 81 R salt of phosphoric acid</td>
<td>100</td>
</tr>
<tr>
<td>blank gasoline Primene 81 R salt of Strodex P-100.</td>
<td>100</td>
</tr>
</tbody>
</table>

1 A commercial type catalytically cracked-reformer-alkylate gasoline blend containing 5 lb./1,000 barrel 2,6-dimercaptopentane; 1 lb./1,000 barrels N,N-diallylendecyl-1,2-propanediamine; and 3 cc. tetraethyllead/gal.

While this 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. The neutral primary alkyl amine salt of an alkyl phosphoric acid ester having from 2 to 8 phosphorus atoms, an acid number from about 200 to about 750 and from 1 to 12 carbon atoms per alkyl group, wherein the primary amine al mine is a mixture of branched chain amines having from about 8 to 18 carbon atoms, having the primary amine group directly attached to a tertiary carbon atom.

2. The neutral primary alkyl amine salt of tripolyphos-

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A. H. SUTTO, Assistant Examiner

U.S. Cl. X.R.

23—59, 106; 44—72; 260—501.1, 501.11, 583
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,504,055 Dated March 31, 1970

Inventor(s) Harry J. Andress, Jr. and Julius Capowski

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 71, for "more" read --higher--

Column 3, line 74, for "13 g/l" read --13.6 g/l--

Column 4, line 2, "of" should be omitted

Column 4, lines 3 and 4, for "one one minute" read --one minute--

SIGNED AND SEALED
JUL 28 1970

(SEAL)
Attest:
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