United States Patent Office 2,905,542
Patented Sept. 22, 1959

2,905,542

STABLE DISTILLATE FUEL OIL COMPOSITIONS

Ralph I. Gottshall, Willow Grove, and Mark L. Hill, Jr., Springfield, Pa., assignors to Gulf Oil Corporation, Pittsburgh, Pa., a corporation of Pennsylvania

No Drawing. Application December 7, 1953
Serial No. 396,755

5 Claims. (Cl. 44—72)

This invention relates to stable distillate fuel oil compositions inhibited against sludge deposition by means of ashless improvement agents having good water separation properties and other desirable characteristics. More particularly, the invention relates to distillate fuel oil compositions containing certain alkyl amine dialkyl orthophosphates.

Sludge deposition in distillate fuel oils is known to be detrimental for the reason that sludge particles may cause clogging of fuel filters or screens, conduit lines, burner nozzles or injection ports through which the fuel oil is passed. An acceptable distillate fuel oil should therefore possess low sludging tendencies.

The sludge depositing tendencies of different specific distillate fuel oils vary principally according to the processing treatments to which the distillates have been subjected and to some extent according to the composition of the original crude. Thus, incompletely refined or improperly refined, straight run fuel oil distillates containing naphthenic acids not completely removed by caustic washing, or distillates having a high sulfur content, either as the result of materials added during refining of the oil as in "doctor-treating," or as a result of certain sulfur-bearing components of the original crude, may exhibit appreciable sludging tendencies. The sludging tendencies of such straight run oils are normally attributable to the insolubility of oxidized degradation products.

A high degree of instability is evidenced in cracked distillate fuel oils, both of the thermally cracked and catalytically cracked types, by the substantial amount of color darkening during storage, even in instances where large amounts of precipitated sludge particles are not formed. The instability and/or the sludging tendencies of cracked distillate fuel oils are normally attributable to polymerization of the olefinic and olefinic-aromatic compounds in the oils. The relatively small amount of insoluble sludge occurring in some cracked distillate oils during storage is believed to be due to the solvent action of the cracked distillate oil for its polymerized degradation products.

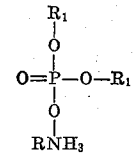
Mixed fuel oil distillates containing both straight run and cracked (especially catalytically cracked) components, blended to produce a distillate fuel oil having better burning characteristics than cracked distillate alone and to balance refinery production, are particularly troublesome in that such oils not only possess the cumulative sludging characteristics of each of the component oils but in addition exhibit greatly aggravated sludging tendencies. This effect is believed to be due to the antisolvent action of the predominantly paraffinic straight run distillate oil components for the polymeric degradation products of the cracked fuel oil distillate.

The present invention relates to novel distillate fuel oil compositions containing minor concentrations, effective to inhibit sludge deposition, of certain alkyl amine dialkyl orthophosphates. Specifically, the class of alkyl amine salts included by the invention are the substantially neutral salts of primary amines having a t-alkyl substituent containing from 12 to 15 carbon atoms with dialkyl

esters of o-phosphoric acids whose alkyl substituents each contain from 3 to 10 carbon atoms. We have found that the foregoing class of t-alkyl amine salts are extraordinarily effective in inhibiting deposition of sludge in distillate fuel oils, even in those distillate fuel oils which exhibit most severe sludging tendencies.

The invention includes distillate fuel oil compositions containing mixtures of straight run and catalytically cracked fuel oil distillates. The inhibitors of the present invention are especially useful in connection with mixtures of catalytically cracked and straight run fuel oil distillates in which the ratio of catalytically cracked distillate to straight run distillate is from about 4:1 to about 1:4, since such mixtures characteristically exhibit extremely severe sludging tendencies, and since the herein disclosed inhibitors retain their remarkable effectiveness in combination with such oils. Representative of distillate fuel oils containing one or more of the foregoing components is the so-called No. 2 fuel oil, a distillate fuel oil cut boiling within the range of 350° to 750° F. and having a minimum API gravity of 26°. Such oils are commonly used as domestic furnace oil, diesel fuel or light industrial fuel oil.

The t-alkyl amine dialkyl orthophosphates of the present invention are the substantially neutral addition salts of primary amines having a t-alkyl substituent containing from 12 to 15 carbon atoms and dialkyl esters of o-phosphoric acids whose alkyl substituents each contain 3 to 10 carbon atoms. These salts may be represented by the generic formula:



where R is a t-alkyl radical containing from 12 to 15 carbon atoms and the R_1 substituents are alkyl radicals containing from 3 to 10 carbon atoms.

The above-identified class of amine salts are formed by neutralizing the selected dialkyl o-phosphoric acid with substantially equimolar proportions of one or more of the aforesaid t-alkyl amines. In practice it is generally more convenient merely to neutralize the dialkyl o-phosphoric acid to a pH of from about 6.5 to about 7.5 with the t-alkyl amine. The reaction normally takes place spontaneously at room temperature, sometimes with the evolution of heat. However, additional heat may in some instances be desirable in order to accelerate the reaction. The temperature of the reaction should not be allowed to exceed substantially the boiling point of water and preferably the reaction temperature should not exceed about 180° F., in order to avoid decomposition or partial decomposition of the t-alkyl amine salt reaction products. The reaction is normally complete in less than thirty minutes.

The preparation of the above-indicated dialkyl o-phosphoric acids is effected, as is known, by esterification of o-phosphoric acid with the desired saturated aliphatic, primary monohydric alcohol or alcohols, either simultaneously or consecutively, the mol ratio of reactants being such as to esterify only 2 of the 3 acidic hydroxyl groups of the o-phosphoric acid. The preparation of these compounds is conventional and is fully understood by those skilled in the art. Accordingly, no detailed discussion is necessary.

The preparation of the t-alkyl amine salt inhibitors of this invention can be further illustrated by the following specific examples:

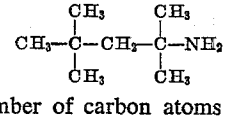
EXAMPLE I

To 182 parts by weight of a di-n-propyl o-phosphoric

acid ester were added about 217 parts by weight, or an amount sufficient to raise the pH of the reaction mixture to about 7.3, of a commercial mixture of C_{12-15} t-alkyl amines having a mol combining weight of 217, an average molecular weight of from about 185 to about 227, a neutralization equivalent of 217, and a pour point below −85° F. The temperature of the reaction mixture was kept below 180° F. The product of the reaction was a straw-colored, non-viscous liquid consisting essentially of the t-C_{12-15} alkyl amine di-n-propyl orthophosphates and having the following properties:

Gravity, ° API	26.4
Physical state at room temperature	Liquid
Color, ASTM Union	4.5
Odor	Amine
pH value, Gulf 416 glass, calomel electrodes	7.3
Phosphorus, percent	7.6

The commercial mixture of amines referred to in this example is described in detail under the trade name "Primene 81–T" in the brochure entitled Tertiary-Alkyl Primary Amines, published by Rohm & Haas Company of Philadelphia, Pennsylvania, in December 1951. As pointed out in this brochure, all of the amines described therein are characterized by the "tertiary-alkylamine (tertiary-carbinamine) structure in which the primary amino nitrogen is directly attached to a teritary carbon atom." The brochure further describes Primene 81–T as a technical grade mixture of highly branched primary amines having a tertiary-alkyl structure of the same type as that in tertiary-octyl amine having the formula:



but with the number of carbon atoms varying from 12 to 15. The brochure further states that Primene 81–T may be represented approximately by the formula

$$t\text{-}C_{12-15}H_{25-31}NH_2$$

EXAMPLE II

Approximately 217 parts by weight of the mixed C_{12-15} t-alkyl amines of Example I were added with stirring to about 210 parts by weight of di-n-butyl o-phosphoric acid, until the pH of the mixture was 7.0. The temperature of the reaction mixture was kept below 180° F. The reaction product was a red-colored, non-viscous liquid consisting essentially of the t-C_{12-15} alkyl amine di-n-butyl orthophosphates and having the following properties:

Gravity, ° API	3.02
Physical state at room temperature	Liquid
Color, ASTM Union	7.5
Odor	Amine
pH value, Gulf 416 glass, calomel electrodes	7.0
Phosphorus, percent	7.1

EXAMPLE III

To 322 parts by weight of di-n-capryl o-phosphoric acid were added with stirring about 220 parts by weight of the mixed C_{12-15} t-alkyl amines of Example I, until the pH of the mixture was 7.5. The temperature of the reaction mixture was kept substantially below 180° F. The product of the reaction consisted essentially of the t-C_{12-15} primary alkyl amine salts of di-n-capryl o-phosphoric acid and was a red-colored, non-viscous liquid having the following physical properties:

Gravity, °API	30.4
Physical state at room temperature	Liquid
Color, ASTM Union	8.0
Odor	Amine
pH value, Gulf 416 glass, calomel electrodes	7.5
Phosphorus, percent	5.1

Other t-alkyl amine salts of the class included by the invention may be prepared in substantially identical fashion.

The inhibitors of the present invention may be incorporated in a distillate fuel oil base in any desired manner. Thus, for example, the preformed inhibitors may be dissolved in the ultimate distillate fuel oil which is to be inhibited, or a mineral oil concentrate containing a relatively high concentration of the inhibitor, i.e., up to the solubility limit, may be added to the desired base fuel oil in amounts sufficient to provide the desired ultimate inhibitor concentration. The latter procedure often facilitates more rapid solution of the inhibitor in the oils. Alternatively, the t-alkyl amine salts of this invention may be formed in situ in the distillate fuel oil composition by addition of the required reacting proportions of t-alkyl amine and dialkyl o-phosphoric acid.

As indicated, the inhibitors herein described are employed in an amount sufficient to inhibit sludge deposition in the fuel oil. It is generally desirable from an economic standpoint to employ a concentration no greater than that which is adequate to produce the desired degree of improvement. The concentration necessary to produce the desired degree of improvement will of course vary somewhat for different specific fuel oils. Normally from about 0.001 to about 0.1 percent by weight of the fuel oil composition of the combined additives is sufficient to accomplish major improvement in the sludging characteristics of the fuel oil. However, in some instances it may be desirable to employ the disclosed inhibitors in concentrations of up to about 0.5 percent by weight of the fuel oil composition. Although some improvement in sluding characteristics may be achieved with less than the minimum concentration indicated, amounts within the above-mentioned range of proportions are normally desirable in order to obtain major improvement.

The highly beneficial results achieved by incorporation of the herein disclosed inhibitors in distillate fuel oils tending to deposit sludge has been demonstrated by subjecting distillate fuel oils containing minor concentrations of the inhibitors to accelerated tests designed to determine the stability of the oils with respect to sludge deposition under the action of ultraviolet light and heat. The extraordinary results brought about by the use of the herein disclosed t-alkyl amine salts as opposed to corresponding n-alkyl amine salts were demonstrated by subjecting a distillate fuel oil containing an equivalent dosage of mixed n-alkyl amine salts of a dialkyl o-phosphoric acid of the herein disclosed class to the same test.

Stability to ultraviolet light was tested by exposing a 100 ml. sample of the oil to be tested to a light source rich in ultraviolet rays for a period of 4 hours alternated with periods of 20 hours during which the oil was stored in the dark. The test was complete after 40 hours exposure to the light. At the end of each dark storage period the samples undergoing the test were examined for the presence of precipitated sediment or sludge. Exposure to light was accomplished by placing the test samples of the fuel oil in 4 oz. unstoppered glass bottles to allow free access of air. These bottles were placed in a circular metal enclosure at a distance of 22 inches from the light source (a Westinghouse 400 watt type 2–8–1 mercury vapor lamp mounted vertically on the center of the housing). A temperature rise of about 20° F. was found to occur during the exposure period. The interval of dark storage is permitted to allow any dispersed sludge to settle and to permit oxygen to replace any used in the light induced reaction. The effect of exposure to light was judged by swirling the bottle and estimating the quantity of precipitate which had settled. The results are recorded in terms of the number of hours of exposure to light required to produce a trace of sludge and light, medium and heavy sludge.

EXAMPLE IV

To separate samples of a typical run of the refinery

No. 2 fuel oil containing 72.0 percent straight run fuel oil distillate and 28.0 percent of fluid catalytically cracked fuel oil distillate were added respectively 0.01 percent by weight of the inhibitors prepared according to Examples I, II and III. To another sample of the same No. 2 fuel oil was added a substantially equivalent dosage of n-alkyl amine salts of isoamyl octyl o-phosphoric acid. These n-alkyl amine salts were prepared substantially identically with the procedure described in Examples I, II and III, using approximately equimolar proportions of 3-methyl-butyl,2-ethylhexyl o-phosphoric acid and cocoamine, the latter being a commercial mixture of primary amines composed predominantly of lauryl amine but in addition containing C_8, C_{10}, C_{14}, C_{16} and C_{18} n-alkyl amine homologues, and having a molecular weight of about 206 and a melting point of 21° C.

These samples, together with an uninhibited sample of the No. 2 fuel oil mentioned above, were then subjected to the ultraviolet light stability test procedure described above. The results obtained in these tests are presented in the table below:

Table A

[U.V. light stability, time to formation of sludge, hrs.]

	Trace	Light	Medium	Heavy	Sludge at 40 Hrs.
Uninhibited No. 2 Fuel Oil Base.	4	16	20	40	Heavy.
Base Oil plus 0.01% by Wt. Additive of Example I.	4	16	--------	--------	Light.
Base Oil plus 0.01% by Wt. Additive of Example II.	4	16	--------	--------	Light.
Base Oil plus 0.01% by Wt. Additive of Example III.	4	16	--------	--------	Light.
Base Oil plus 0.009% by Wt. n-Alkylamine Salts of Isoamyl Octyl o-Phosphoric Acid.	8	16	32	--------	Medium.

The inhibitors of this invention have also exhibited sludge deposition in unstable distillate fuel oils tested according to the procedure of another standard accelerated stability test. This test was carried out by heating a 600 gram sample of the test fuel oil for 40 hours at 210° F. in a loosely-stoppered, clear glass bottle. Following the heating period, the sample was cooled to room temperature and filtered by suction through a tared, medium porosity, fritted glass, Gooch-type crucible. The sludge in the crucible was washed with heptane. Complete removal of the sludge adhering to the inside of the bottle was accomplished by means of a rubber policeman and heptane. The crucible was dried in an oven at 210° F. for 1 hour, cooled in a desiccator and reweighed. The increase in the weight of the crucible was recorded as mg. sludge per 600 grams of oil.

EXAMPLE V

Separate samples of the No. 2 fuel oil of Example IV, made up identically as in Example IV above, together with an uninhibited example of the same fuel oil, were subjected to the stability test described immediately above. The results obtained are presented in the table below:

Table B

[Stability test, 40 hrs., 210° F.]

	Insoluble sediment, Mg./600 grams oil sample
Uninhibited No. 2 fuel oil base	43.5
Base oil plus 0.01% by wt. additive of Example I	1.0
Base oil plus 0.01% by wt. additive of Example II	2.2
Base oil plus 0.01% by wt. additive of Example III	1.2
Base oil plus 0.009% by wt. n-alkylamine salts of isoamyl octyl o-phosphoric acid	16.9

Other inhibitors of the herein disclosed class may be similarly incorporated in low concentrations in unstable distillate fuel oils tending to deposit sludge with similar beneficial results. Representative of such other inhibitors are the substantially neutral t-lauryl, t-tridecyl, t-myristyl and t-pentadecyl primary amine salts of the di-n-amyl, di-isoamyl, di-n-octyl, diisooctyl, and isoamyl isooctyl, o-phosphoric acids.

Examination of the results presented in Table A above indicates that the t-alkyl amine salt inhibitors of this invention are especially outstanding in that they permit only light sludge to form during the entire 40-hour test period, and in that they completely arrest sludge formation after sixteen hours. In contrast, the data presented in Table A indicate that corresponding n-alkyl amine salts permit sludge formation during twice as great a portion of the test period.

Examination of the results presented in Table B indicates that the fuel oils inhibited by the t-alkyl amine salt inhibitors of this invention produce from about 87 percent to about 94.1 percent reduction on the amount of sludge formed as compared with that produced by an equivalent dosage of the corresponding n-alkyl amine salts. An indication of the significance of this improvement is the fact that fuel filters or screens in systems employing distillate fuel oils inhibited in accordance with this invention could be expected to function from 8 to 17 times as long without clogging on account of sludge formation.

The t-alkyl amine salts of this invention are further unexpectedly advantageous as compared with the corresponding n-alkyl amine salts in that they have a reduced viscosity and pour point, thus facilitating blending of the additives with the fuel oil carriers. Moreover, the t-alkyl amine salts of this invention possess superior water separation characteristics, i.e., oils containing these salts show little tendency to form table water-containing emulsions or suspensions. This property is especially important in cold climates since entrained ice particles may hamper loading and delivery operations. In addition to the desirable properties mentioned above the inhibitors of the present invention are advantageous in that they are ashless on combustion and in that they possess excellent corrosion inhibiting properties. Fuel oils containing the additives of this invention also exhibit improved color stability.

The expression "t-alkyl" is used herein in its usual sense to indicate an alkyl groups of the type



where R is itself an alkyl radical.

If desired, the stable fuel oil compositions of this invention may contain, in addition to the t-alkyl amine salt inhibitors disclosed herein, anti-oxidants, flash point control agents, anti-foam agents, ignition quality improvers, combustion improvers, cetane number 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 numerous modifications and variations of the herein disclosed subject matter may be resorted to without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. A stable fuel oil composition comprising a major amount of a mixture of catalytically cracked and straight run fuel oil distillates tending to deposit sludge and a minor amount, sufficient to inhibit sludge deposition, of a substantially neutral salt of a primary amine having a t-alkyl substituent containing from 12 to 15 carbon atoms and a dialkyl ester of o-phosphoric acid whose alkyl substituents each contain from 3 to 10 carbon atoms.

2. The composition of claim 1 wherein said substan-

tially neutral salt is present in an amount of from about 0.001 to about 0.5 percent by weight of the composition.

3. A stable fuel oil composition comprising a major amount of a mixture of catalytically cracked and straight run fuel oil distillates tending to deposit sludge and a minor amount, sufficient to inhibit sludge deposition, of a substantially neutral salt of a primary amine having a t-alkyl substituent containing from 12 to 15 carbon atoms and di-n-propyl o-phosphoric acid.

4. A stable fuel oil composition comprising a major amount of a mixture of catalytically cracked and straight run fuel oil distillates tending to deposit sludge and a minor amount, sufficient to inhibit sludge deposition, of a substantially neutral salt of a primary amine having a t-alkyl substituent containing from 12 to 15 carbon atoms and di-n-butyl o-phosphoric acid.

5. A stable fuel oil composition comprising a major amount of a mixture of catalytically cracked and straight run fuel oil distillates tending to deposit sludge and a minor amount, sufficient to inhibit sludge deposition, of a substantially neutral salt of a primary amine having a t-alkyl substituent containing from 12 to 15 carbon atoms and di-n-capryl o-phosphoric acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,297,114	Thompson	Sept. 29, 1942
2,371,851	Smith et al.	Mar. 20, 1945
2,408,232	Smith et al.	Sept. 24, 1946
2,441,295	Smith et al.	May 11, 1948
2,550,982	Eberz	May 1, 1951
2,602,049	Smith et al.	July 1, 1952

FOREIGN PATENTS

654,968	Great Britain	July 4, 1951