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OXO-OCTYL AMINE SALTS OF DIOXO-OCTYL PHOSPHORIC ACID ESTERS

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This invention relates to a novel class of amine salts of dialkyl orthophosphates. More particularly, the invention relates to substantially neutral salts of primary, secondary, or tertiary oxo-octyl amines and to the use of these salts in hydrocarbon oils.

Combustion gas turbine fuels, especially aviation turbine fuels, that is, "jet" fuels, have been found to form deposits under service conditions, which deposits tend to clog the fuel nozzles or orifices through which the fuel is introduced into the combustion chambers of engines in which the fuel is consumed. The formation of these deposits is usually attributed to the use of the fuel as a cooling medium to remove heat from lubricating oil that has absorbed heat developed by the compression of combustion air, by fuel combustion, and by friction. Under these service conditions the fuel is subjected to service temperatures of the order of 300 to 400° F. for substantial periods of time, and to even higher temperatures, of the order of 500° F. or more, for shorter periods of time in the region of the fuel nozzles or orifices. The less stable components of the fuel tend to undergo degradation as a result of polymerization, oxidation, and/or thermal decomposition reactions, and to form solid or semisolid deposits that interfere with proper functioning of jet engines.

The present invention relates to improving the thermal stability of combustion gas turbine fuels, such as aviation turbine fuels, and to reducing the tendency of such fuels to form deposits in the fuel inlet regions of the combustion zones of the engines in which the fuels are consumed, whereby such fuels are rendered more suitable for use in such engines. The thermal stability characteristics of the above-indicated fuels, as well as other characteristics of these and other hydrocarbon oils, can be improved by incorporation therein of a small amount of a substantially neutral salt of a primary, secondary, or tertiary oxo-octyl amine and dioxo-octyl acid orthophosphate. In especially preferred embodiments the amine salts are the substantially neutral salts of di- and trioxo-octyl amine and dioxo-octyl acid orthophosphate. The class of amine salts disclosed herein can be employed in varying amounts. Preferably, the proportions in which the amine salts are employed are small. For example, good results will usually be obtained by the use of the amine salts in proportions of 10 to 50 pounds of salt per 1,000 barrels of fuel, but other proportions can be used. Thus, proportions in the range of 0.001 to 1.0 percent or more by weight of the fuel can be used. The present invention includes not only the above-indicated amine salts as such, but also improved hydrocarbon oil compositions containing the same.

The exact manner in which the amine salts disclosed herein function to improve the thermal stability of aviation turbine fuels has not been definitely determined. It is presumed that the amine salts function at least in part as detergents and/or dispersants for the solid or semisolid deposits formed in the fuel at high temperatures. However, the fact that improved color stability will also be obtained at elevated temperatures by the use in the oil of the hereindisclosed amine salts would suggest that the salts also function in part by inhibiting the chemical reactions that characterize thermal degradation of the oils.

The amine salts of this invention can be prepared in any suitable manner. According to a preferred procedure, a dioxo-octyl acid orthophosphate is substantially neutralized by the addition thereto of an approximately equimolar amount of a primary, secondary, or tertiary oxo-octyl amine. The neutralization reaction proceeds spontaneously at room temperature with evolution of heat. The temperature of the reaction is maintained below about 200° F. and preferably below about 180° F. in order to prevent splitting out of water from the addition salt reaction product. Control of the reaction temperature is conveniently achieved by controlling the rate of addition of the amine or by external cooling or both. The over-all time required to complete the reaction can vary somewhat according to the method by which the temperature is controlled and according to the temperature at which the reaction is carried out. Normally, it is preferred to continue agitation of the reaction mixture after addition of the amine has been completed for about the same length of time required to add the amine in order to assure completion of the reaction. It is usually most convenient to measure the pH of the reaction product near the end of the period required for addition of the amine and to control the amount of additional amine added thereafter, in order to assure that the reaction product will be substantially neutral, that is, that it will have a pH of about 5.5 to about 7.5, preferably about 7.0.

The dioxo-octyl ester of orthophosphoric acid employed in the preparation of the amine salts of this invention can be prepared in any suitable way. For example, in accordance with one preferred method, phosphorus pentoxide is added to oxo-octyl alcohol, preferably in an oil diluent, in a mole ratio of about 1:4, while maintaining the reaction temperature below about 180° F., through control of the rate of addition of phosphorus pentoxide and/or by external cooling, the reaction mixture being stirred after completing addition of phosphorus pentoxide, until the product is clear. Some external heating of the reaction product to a temperature not exceeding about 180° F., is sometimes advantageous toward the end of the reaction period in order to accelerate completion of the reaction.

The dioxo-octyl acid orthophosphates from which the amine salts of this invention are derived are obtained from oxo-octyl alcohols, that is, a mixture of highly branched octyl alcohol isomers, chiefly dimethylhexanols, mostly 4,5-, 3,5-, 3,4-, and 5,5-dimethylhexanols, prepared by the well-known oxo-synthesis process. Briefly, as applied to the production of oxo-octyl alcohol, the oxo-synthesis process involves the hydroformylation, that is, reaction with carbon monoxide and hydrogen, of a mixture of heptene isomers obtained by the fractionation of the product of polymerization of a mixture of propylene and butylene isomers in the presence of a phosphoric acid or other polymerization catalyst to obtain a mixture of branched-chain octyl aldehydes, and by hydrogenating the resulting mixed aldehydes to obtain the mixture of isomeric octyl alcohols commonly referred to as oxo-octyl alcohols.

The dioxo-octyl orthophosphates disclosed herein need not be pure and can contain appreciable amounts of monooxo-octyl orthophosphate and free oxo-octyl alcohol without detrimental results. If desired, however, the dioxo-octyl orthophosphate can be separated from the monooxo-octyl orthophosphate by the use of selective immiscible solvents therefor, as described in British Patent No. 778,081. Alternatively, the dioxo-octyl orthophosphates can be separated from the monooxo-octyl orthophosphate by reaction with lime and equili-

brating the resulting calcium salts between oil and water, the dioxo-octyl orthophosphate being relatively more soluble in oil.

Amines that form addition salts suitable for the purposes of this invention with dioxo-octyl acid orthophosphates include primary, secondary, and tertiary oxo-octyl amines. It is not necessary that the amine be absolutely pure and small amounts of other amines can be present. The use of mixtures of primary, secondary, and tertiary oxo-octyl amines is also contemplated. The oxo-octyl amines that form amine salts included by this invention can be prepared in any suitable way. Thus, primary oxo-octyl amine can be prepared by reacting the oxo-octyl aldehydes, prepared as described above, with excess anhydrous ammonia to form the corresponding imine, which can then be hydrogenated under pressure and in the presence of a catalyst to produce the corresponding primary oxo-octyl amine. Dioxo-octyl amine can be conveniently derived from oxo-octyl alcohol by reacting the latter with ammonia in a mole ratio of about 2:1 with refluxing. Trioxo-octyl amine can be prepared similarly as the secondary amine by reaction of oxo-octyl alcohol with ammonia in the mole proportion of 3:1.

The amine addition salts included by this invention and the preparation thereof are further illustrated by the following specific examples:

EXAMPLE I

To a mixture of 25 grams of a light, diluent oil and 75 grams of dioxo-octyl acid orthophosphate, prepared by reacting phosphorus pentoxide with oxo-octyl alcohol in the mole ratio of 1:4 as described above, there is added 29 grams of primary oxo-octyl amine, with stirring, while maintaining the temperature of the reaction mixture below about 180° F. The addition of the amine is completed in about 15 to 20 minutes and stirring of the mixture is continued for about an equal length of time thereafter. The product of the reaction is the substantially neutral salt of primary oxo-octyl amine and dioxo-octyl acid orthophosphate.

A typical sample of the primary oxo-octyl amine, prepared as indicated above, and employed in the above-described reaction had the following properties:

Specific gravity, 20°/20° C	0.8794
Refractive index, n^{20}/D	1.4312
Neutralization value, ASTM D664	430
Boiling range: ° C. at 760 mm. Hg	160–170

A typical sample of the oxo-octyl aldehydes of the kind from which the above-described oxo-octyl amine was obtained—and of the kind from which the hereinafter-described oxo-octyl alcohol was obtained—was found to contain the following approximate composition in percent by weight:

	Percent
4,5-dimethylhexanal	38
3,5-dimethylhexanal	30
5-methylheptanal	10
3,4-dimethylhexanal	19
5,5-dimethylhexanal	3

The proportions of the primary oxo-octyl amine or oxo-octyl alcohol isomers present in a mixture of primary oxo-octyl amines or oxo-octyl alcohols derived from the mixture of aldehydes described above all will correspond to the proportions of the aldehyde isomers.

A typical sample of the oxo-octyl alcohol from which the dioxo-octyl orthophosphate was derived had the following properties:

Specific gravity, 20°/20° C	0.8324
Viscosity, kinematic, cs., 20° C	12.43
Refractive index, n^{20}/D	1.4313
C_8 alcohol content, percent by wt	99.3
C_8 carbonyl content, percent by wt	0.06

Distillation, isooctyl alcohol, ASTM D1078, ° C.:	
Over point	184.0
Dry point	188.5
10%	185.5
50%	186.4
90%	187.5

An oil solution of a substantially neutral salt of primary oxo-octyl amine and dioxo-octyl acid orthophosphate, prepared as described above had the following properties:

Gravity, ° AP I	19.6.
Color, ASTM union	<0.5.
Appearance	Bright.
Physical state, room temperature	Liquid
Phosphorus, percent	5.58.
pH value	7.4.

EXAMPLE II

To a mixture of 78 grams of a light hydrocarbon dilution oil and 233 grams of dioxo-octyl acid orthophosphate, prepared as described in Example I, are added 280 grams of dioxo-octyl amine, prepared from oxo-octyl alcohol of the kind described in Example I, while stirring and maintaining the temperature of the reaction below about 180° F. As in Example I the addition of the amine is completed in about 15 to 20 minutes and stirring of the reaction mixture is continued for about an equal length of time thereafter. The product of this reaction is an oil solution of the dioxo-octyl amine salt of dioxo-octyl acid orthophosphate. A reaction product prepared as described had the following properties:

Gravity, ° API	22.7.
Color, ASTM union	<1.0.
Appearance	Bright.
Physical state, room temperature	Liquid.
Phosphorus, percent	4.5.
pH value	7.2.

EXAMPLE III

To a mixture of 125 grams of a light hydrocarbon diluent oil and 375 grams of dioxo-octyl acid orthophosphate, prepared as described in Example I, are added 753 grams of trioxo-octyl amine, prepared from oxo-octyl alcohol of the kind described in Example I, while stirring and maintaining the reaction temperature below about 180° F. As in the preceding examples the addition of the amine is completed in about 15 to 20 minutes. An additional 85 grams of light hydrocarbon diluent oil is then added. Stirring of the mixture is then continued for an additional 15 to 20 minutes. The product of this reaction is an oil solution of the trioxo-octyl amine salt of dioxo-octyl acid orthophosphate. A product prepared as described had the following properties:

Gravity, ° API	29.0.
Color, ASTM union	<1.0.
Appearance	Bright.
Physical state, room temperature	Liquid.
Phosphorus, percent	2.67.
pH value	7.3.

The addition salts of this invention are useful when incorporated in hydrocarbon oil compositions in various amounts. Thus, the salts can be employed in hydrocarbon oil aviation turbine fuels in any amount sufficient to improve the thermal stability characteristics of the oils. The addition salts of this invention are preferably employed in small amounts. Thus, excellent results are obtained by the use of such salts in hydrocarbon oil aviation turbine fuels in proportions of about 10 to 50 pounds of salt per 1,000 barrels of fuel, but larger or smaller proportions can be used. Thus, good results can be obtained by the use of proportions in the range of about 0.002 to about 0.2 percent by weight of the oil composition and in some instances amounts as low as 0.001 or as large as 1.0

percent by weight of the composition will be advantageous.

The thermal stabilizing, detergent and dispersant properties of the addition salts of this invention in hydrocarbon oil aviation turbine fuels were demonstrated by incorporating the addition salts of Examples I, II, and III into separate samples of an uninhibited military-grade JP–5 type jet engine fuel in the proportion of 16 pounds of active ingredient per 1,000 bbls. of fuel and by subjecting the test samples of aviation turbine fuel to an accelerated thermal stability test. In accordance with this test method, aviation turbine fuels to be tested are subjected to the Proposed Method of Test for Thermal Stability of Aviation Turbine Fuels (ASTM Standards on Petroleum Products and Lubricants, December 1958, page 1135). This test is used to determine the high temperature stability of aviation turbine fuel in an apparatus commonly referred to as the CFR fuel coker. In general, the test is designed to subject the test fuel to temperatures and conditions similar to those occurring in some aviation turbine engines. Briefly, the test apparatus comprises a fuel system containing two heated sections: (1) a preheater section that simulates the hot fuel line sections of a jet engine as typified by an engine fuel-lubricating oil cooler and (2) a filter section that simulates the nozzle, or fuel inlet zone of the combustion chamber of an aircraft jet engine, wherein fuel degradation products may be trapped. A precision, sintered, stainless-steel filter is employed in the filter section to trap fuel degradation particles formed during the test. The extent of the build-up of fuel degradation particles in the fuel section is indicated by the pressure differential across the test filter, and this is used as an index of the high temperature stability of the aviation turbine fuel. In these specific tests the fuel flow through the test apparatus was maintained at the rate of about six pounds per hour, the preheater temperature was maintained at about 400° F. and the filter temperature was maintained at about 500° F. The maximum test length was five hours.

The test fuel employed in the above-described tests had the following properties:

Gravity, ° API	43.7.
Existent gum, mg./100 ml	1.
Sulfur, percent	0.02.
Mercaptan sulfur, percent	0.001.
Freezing point, F	—64.
Aniline-gravity constant	6358.
Aromatics, vol. percent	12.9.

The results of the above-described tests were as set forth in the following table:

Table A

	Blank	1	2	3
Sample Make-up, percent by Vol.:				
JP–5 Aviation Turbine Fuel	100	100	100	100
Addition Agent, Active Material Added, Lb./1,000 Bbls.—				
Oxo-octyl Amine Salt of Dioxo-octyl Acid Orthophosphate (Example I)		16		
Dioxo-octyl Amine Salt of Dioxo-octyl Acid Orthophosphate (Example II)			16	
Trioxo-octyl Amine Salt of Dioxo-octyl Acid Orthophosphate (Example III)				16
Inspections:				
Pressure drop at 300 Min., In. Hg	[1] >25	0.7	0.1	0.2

[1] Pressure drop reached 25 in. Hg after 140 min., after which test was discontinued.

As demonstrated by the great reduction in pressure drop across the filter obtained with test samples 1, 2, and 3 in the preceding table, the thermal stability of hydrocarbon oil aviation turbine fuels is greatly improved by the amine salts of this invention.

The addition salts of this invention also impart valuable rust and corrosion-inhibiting properties to hydrocarbon oils in which they are employed. The rust and corrosion-inhibiting properties of the addition salts of this invention were demonstrated by incorporating the salts of Examples I, II, and III in various proportions in separate samples of a highly paraffinic hydrocarbon turbine lubricating oil and isooctane and by subjecting the thus-prepared test samples to standard accelerated corrosion test procedures. The results of these tests were as set forth in the following table:

Table B

	1	2	3	4	5
Sample Make-up, percent by Vol.:					
Paraffinic Turbine Lubricating Oil	100	------	100	------	100
Depolarized Isooctane	------	100	------	100	------
Addition Agent, Active Component Added.—					
Oxo-octyl Amine Salt of Dioxo-octyl Acid Orthophosphate (Example I Salt), percent by Wt	------	------	0.12	------	------
Dioxo-octyl Amine Salt of Dioxo-octyl Acid Orthophosphate (Example II Salt), Lb./1,000 Bbls	------	------	------	7.5	------
Trioxo-octyl Amine Salt of Dioxo-octyl Acid Orthophosphate (Example III Salt), percent by Wt	------	------	------	------	0.05
Inspections:					
Rust Test, ASTM D665–54, Procedure B (Salt Water), 24 Hrs., percent Rust	100	------	0	------	------
Rust Test, MIL–L–25017 ASG, Method 4011–B, 10% Distilled Water Washed, 100° F., 20 Hrs., percent Rust	------	100	------	0	------
Rust Test, ASTM D665–54, Procedure A (Distilled Water), 24 Hrs., percent Rust	100	------	------	------	0

Aviation turbine fuels of the type whose use is included by the present invention are liquid hydrocarbon oil mixtures whose properties are defined fully in the following specifications: MIL–J–516E (Referee JP–4 Fuel), MIL–J–5624D (JP–4, JP–5 Fuel), MIL–F–25656 (JP–6 Fuel), MIL–F–25524A, MIL–F–2558B (RJ–1 Fuel), MIL–F–25576A (RP–1 Fuel), and American Airlines Specification No. M6–4A. In general, typical hydrocarbon oil aviation turbine fuels are characterized by the following common properties.

Inspections:

Gravity, ° API	32.5–57.
Existent gum, mg./100 ml. (max.)	5–7.
Potential gum, mg./100 ml. (max.)	4–14.
Sulfur, percent (max.)	0.07–0.04.
Mercaptan sulfur, percent (max.)	0.001–0.005.
Freezing point, ° F	—74 to —40.
Thermal value, B.t.u./lb. (min.)	18,300–18,500.
Aniline - gravity constant (max.)	>4,500, usually >5,250.
Aromatics, vol. percent (max.)	5–25.
Olefins, vol. percent (max.)	1–5.

In addition to hydrocarbon oil aviation turbine fuels and the gasoline distillate and lubricating oils discussed above, the salts of this invention are also useful and will produce good results when incorporated in other hydrocarbon oil compositions such as motor-grade gasoline, aviation-grade gasolines, other lubricating oils, kerosenes, diesel fuels, furnace oils, grease compositions, synthetic lubricants, and the like.

In addition to the properties previously indicated hereinabove, the addition salts of this invention are also considered to exhibit preignition control characteristics and

tetraethyl lead stabilizing properties in gasolines containing tetraethyl lead, combustion-improving properties in distillate fuels, antistalling properties in gasolines that normally tend to promote carburetor icing, and induction system deposit-reducing properties in gasolines.

To the hydrocarbon oil compositions containing the amine salts disclosed herein there can also be added singly or in combination one or more additional, compatible agents adapted to improve one or more properties of the composition. Thus, there can be added metal deactivating agents such as N,N'-disalicylidene-1,2-propylenediamine, antiknock agents, lead scavengers, pour-point depressants, ignition-control agents, antioxidants, thickeners, viscosity index improvers, dyes, and other antirust agents, stabilizers, deicing agents, detergents, and dispersants.

Many other modifications of the herein described invention will suggest themselves to those skilled in the art and such modifications can be resorted to without departing from the spirit or scope of this invention. Accordingly, only such limitations are to be imposed on the invention as are found in the claims appended hereto.

We claim:

1. A substantially neutral salt of an amine selected from the group consisting of oxo-octyl amine, dioxo-octyl amine, and trioxo-octyl amine, and dioxo-octyl acid orthophosphate.

2. A substantially neutral salt of oxo-octyl amine and dioxo-octyl acid orthophosphate.

3. A substantially neutral salt of dioxo-octyl amine and dioxo-octyl acid orthophosphate.

4. A substantially neutral salt of trioxo-octyl amine and dioxo-octyl acid orthophosphate.

5. A hydrocarbon oil composition comprising a major amount of a hydrocarbon oil and containing 0.001 to 1.0 percent by weight of the oil of a substantially neutral salt of an amine selected from the group consisting of oxo-octyl amine, dioxo-octyl amine, and trioxo-octyl amine and dioxo-octyl acid orthophosphate.

6. A combustion gas turbine fuel comprising a major proportion of a hydrocarbon oil combustion gas turbine fuel containing a small amount, sufficient to improve the thermal stability characteristics of the fuel, of a substantially neutral salt of an amine selected from the group consisting of oxo-octyl amine, dioxo-octyl amine, and trioxo-octyl amine, and dioxo-octyl acid orthophosphate.

7. The composition of claim 6 wherein said small amount is 10 to 50 pounds of said salt per thousand barrels of said fuel.

8. A combustion gas turbine fuel comprising a major proportion of a hydrocarbon oil combustion gas turbine fuel containing a small amount, sufficient to improve the thermal stability characteristics of the fuel, of a substantially neutral salt of oxo-octyl amine and dioxo-octyl acid orthophosphate.

9. A combustion gas turbine fuel comprising a major proportion of a hydrocarbon oil combustion gas turbine fuel containing a small amount, sufficient to improve the thermal stability characteristics of the fuel, of a substantially neutral salt of dioxo-octyl amine and dioxo-octyl acid orthophosphate.

10. A combustion gas turbine fuel comprising a major proportion of a hydrocarbon oil combustion gas turbine fuel containing a small amount, sufficient to improve the thermal stability characteristics of the fuel, of a substantially neutral salt of trioxo-octyl amine and dioxo-octyl acid orthophosphate.

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