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AVIATION TURBINE FUELS

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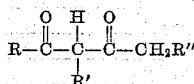
5 Claims. (Cl. 44-73)

This invention relates to thermally stable aviation turbine fuels. More particularly, the invention relates to aviation turbine fuel compositions that contain small amounts of a combination of certain high molecular weight 1,2,3-substituted 1,3-diones and N,N'-di(orthohydroxyarylmethylidene)alkylenepolyamines, and that have a reduced tendency to form solid deposits at very high service temperatures.

Aviation turbine fuel is presently employed as a cooling medium, or "heat sink" in combustion gas turbine powered aircraft to remove heat from lubricating oil that has absorbed heat developed in the engine by the compression of combustion air, by fuel combustion, and by friction of moving parts. As a result the fuel is subjected to service temperatures of the order of 300 to 400° F. for relatively substantial time intervals. In addition, aviation turbine fuel is subjected to even higher temperatures, of the order of 500° F., for short periods of time in the area of the nozzles or orifices from which the fuel is introduced into the combustion chamber of the engine. As a result, certain components of the fuel tend to undergo decomposition due to polymerization, oxidation, and thermal decomposition, and to form solid or semi-solid degradation products that clog the fuel orifices and thereby interfere with proper combustion of the fuel. Ordinary stabilizing agents, antioxidants, and the like of the kind that are employed to stabilize the fuels during storage have been found inadequate to inhibit deterioration of the fuels at the high service temperatures encountered in aviation turbine engines.

The use of high molecular weight 1,2,3-substituted 1,3-diones has been proposed to improve the thermal stability of aviation turbine fuels. Although these materials are excellent inhibitors of deposits in the fuel nozzle and combustion zone inlet area, when used alone they are not entirely satisfactory as thermal stabilizers in aviation turbine fuels, because they fail to inhibit deposits due to thermal degradation in the fuel line or heat-exchange section of the fuel supply system.

It has now been found that the tendency of aviation turbine fuels to form deposits in the fuel inlet area of the combustion zone and in the heat-exchange section of the fuel supply system of an aviation turbine engine can be substantially improved by incorporation in the fuel of a small amount of a combination of (a) an N,N'-di(orthohydroxyarylmethylidene)alkylenepolyamine that contains 2 to 3 amino groups and whose alkylene groups contain 2 to 6 carbon atoms each, and (b) a beta-diketone having the general formula:



where R is an aromatic hydrocarbon group having a nuclear carbon atom thereof connected directly to the adjacent carbonyl carbon atom and containing 6 to 22 carbon atoms, and R' and R'' are like or unlike open-chain saturated or unsaturated aliphatic hydrocarbon radi-

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cals containing 8 to 22 carbon atoms. Orthohydroxyarylmethylidene-substituted alkylenepolyamines whose orthohydroxyaryl substituents are either unsubstituted or substituted only with hydrocarbon substituents are preferred, but orthohydroxyarylmethylidene-substituted alkylenepolyamines that are substituted with other groups such as alkoxy, halo, cyano and carboxy can be used. An example of a particularly outstanding orthohydroxyarylmethylidene-substituted alkylenepolyamine for the purposes of this invention is N,N'-disalicylidene-1,2-propylenediamine. Examples of other N,N'-(orthohydroxyarylmethylidene)alkylenepolyamines are N,N'-di(2-hydroxy-6-methylbenzylidene) - 2,3-butylenediamine, N,N'-di(orthohydroxynaphthylidene) - 1,3 - propylenediamine, N,N'-di(2-hydroxy - 3 - methoxybenzylidene) - 3,4 - diaminoheptane, N,N'-di(2 - hydroxy-5-chlorobenzylidene) - 1,2-propylenediamine, N,N'-di(2 - hydroxy - 3 - cyano-benzylidene)ethylenediamine, N,N' - di(2-hydroxy-3-carboxylbenzylidene)ethylenediamine and N,N'-disalicylidenediethylenetriamine. Beta-diketones having the formula indicated above where R is a mononuclear aromatic radical containing 6 to 12 carbon atoms, such as phenyl, tolyl, xylyl, and isobutylphenyl, R' and R'' are aryl groups containing 12 to 18 carbon atoms, such as octadecyl, hexadecenyl, and hexadecadienyl are preferred, but beta-diketones where R is some other aromatic hydrocarbon substituent and where R' and R'' are other acyclic hydrocarbon radicals can be used. Especially good results are obtainable when the beta-diketone is 1-phenyl-2-hexadecyl-1,3-eicosanedione. Examples of other 1,2,3-substituted 1,3-diones are 1-tolyl-2-octyl-1,3-hexadecanedione, 1-xylyl-2-decyl - 1,3 - tetradecanedione, 1 - tolyl-2-decyl-1,3-hexadecanedione, and 1-tolyl-2-hexadecadienyl-1,3-tetradecanedione. The N,N'-di(orthohydroxyarylmethylidene)alkylenepolyamines and the 1,2,3-substituted 1,3-diones disclosed herein can be employed in varying proportions with respect to one another. It is generally preferred to add them to aviation turbine fuels in about equal proportions by weight, but other proportions can be used provided the compound present in the smaller amount is present in an amount corresponding to at least about five pounds per thousand barrels of fuel. In general, it is preferred to employ the respective compounds in weight ratio in the range of about 1:4 to 4:1, but other weight ratios, for example 1:10 to 10:1, can be used.

The exact mechanism by which the compounds disclosed herein function to improve the thermal stability of aviation turbine fuels has not been definitely established. It may be that the respective compounds tend to form stable complexes with traces of metals in the fuels that normally tend to catalyze high temperature instability, thereby inhibiting any catalytic effect such metals may have upon the oils. This possibility might seem to be borne out by the fact that both beta-diketones of the class disclosed herein, that is, beta-diketones that contain high formula weight substituents in the 1, 2, and 3 positions, as well as N,N'-di(orthohydroxyarylmethylidene)alkylenepolyamines have been found to form stable metallic complexes. However, this mechanism is somewhat negated by the fact that neither the beta-diketones nor the N,N'-di(orthohydroxyarylmethylidene)alkylenepolyamines disclosed herein as such is capable of inhibiting formation of deposits in both the heat exchange section, or fuel conduit section, of the fuel supply system and in the fuel inlet orifices in the combustion zone of aviation turbine engines. Although the exact functioning of the respective classes of compounds disclosed herein is not known, available experimental data clearly indicate that the respective classes of compounds disclosed herein coact with one another, as it has been found that deposits in both the heat ex-

change section of the fuel supply line and the fuel inlet orifices of the combustion chambers of aviation turbine engines are not inhibited by combinations of N,N'-di-(orthohydroxyarylmethylidene)alkylenepolyamines and other materials that alone are capable of inhibiting deposits in the fuel inlet orifices of the combustion chambers of aviation turbine engines.

The preparation of the beta-diketones and the N,N'-di-(orthohydroxyarylmethylidene)alkylenepolyamines disclosed herein forms no part of this invention. Thus, the N,N' - di-(orthohydroxyarylmethylidene)alkylenepolyamines can be prepared conveniently in known fashion by condensation of an aromatic aldehyde with an alkylenepolyamine in molar proportions of 2:1, respectively. The beta-diketones disclosed herein can be prepared as described in copending application Serial No. 783,730, filed in the name of Robert J. Hartle, now U.S. Patent No. 3,004,070, which application is directed to the beta-diketones as such. Briefly, that application discloses that the beta-diketones can be prepared by condensation of a suitable disubstituted ketene dimer or codimer, in the presence of a Friedel-Crafts catalyst, with an equivalent proportion of a suitable aromatic hydrocarbon.

The beta-diketones and the N,N'-di-(orthohydroxyarylmethylidene)alkylenepolyamines disclosed herein can be incorporated in aviation turbine fuels in any suitable manner. For example, they can be added singly or in combination, either as such, or in diluted form to the aviation turbine fuels either promptly after distillation of the latter or after storage of the fuels. Alternatively, the addition agents disclosed herein can be added to aviation turbine fuels in admixture with other addition agents adapted to improve one or more characteristics of the fuels. For example, the addition agents disclosed herein can be added to the fuels in admixture with corrosion inhibitors, such as amine salts of organic orthophosphates, antioxidants such as 2,6-di-*tert*-butyl-4-methylphenol, or 2,4-dimethyl-6-*tert*-butylphenol.

The addition agents disclosed herein can be employed in aviation turbine fuels in any proportions sufficient to improve the thermal stability of the fuels. Normally a noticeable improvement in thermal stability will be obtained by the use of as little as five pounds of beta-diketone per thousand barrels of aviation turbine fuel and as little as five pounds of N,N'-(orthohydroxyarylmethylidene)alkylenepolyamines per thousand barrels of the fuel, but it is usually desirable to employ at least seven pounds per thousand barrels of fuel of the respective additives in order to obtain a substantial improvement in thermal stability. A major improvement will ordinarily be obtained by the use of proportions in the range of about 10 to 20 pounds per thousand barrels of the respective addition agents and accordingly such proportions are preferred. Normally it is not necessary to exceed 20 pounds per thousand barrels of fuel but in instances of aviation turbine fuels having very poor thermal stability characteristics, or in instances of relatively less effective members of the respective classes of addition agents disclosed herein, the agents can be employed in proportions of as much as 50 to 250 pounds or more per thousand barrels of fuel.

Aviation turbine fuels of the type whose use is included by this invention are liquid hydrocarbon mixtures whose properties are defined fully in the following specifications: MIL-J-5161E (Referee JP-4 Fuel), MIL-J-5624D (JP-4, JP-5 Fuel), MIL-F-25656 (JP-6 Fuel), MIL-F-25524A, MIL-F-25558B (RJ-1 Fuel), MIL-F-25576A (RP-1 Fuel), and American Airlines Spec. No. M6-4A. In general, typical 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. (max.) - -75 to -40.
Thermal value, B.t.u./lb.
(min.) ----- 18,300-18,500.
Aniline-gravity constant -- >4500, usually >5250.
Aromatics, vol. percent
(max.) ----- 5-25.
Olefins, vol. percent (max.) - 1-5.

The ability of the combinations of beta-diketones and orthohydroxyarylmethylidene-substituted alkylenepolyamines disclosed herein to reduce formation of solid deposits in aviation turbine fuels at high service temperatures has been demonstrated by subjecting fuel compositions of the kind disclosed herein to the CFR Fuel Coker test procedure. This test procedure is described in detail in the Manual of ASTM Standards on Petroleum Products and Lubricants for 1957, Appendix XV. In accordance with this test method, aviation turbine fuels are subjected to flow conditions and temperature stresses similar to those in jet aircraft engines.

Schematically, 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 which simulates the nozzle, or fuel inlet, area of the combustion zone of a jet engine where fuel degradation particles 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 filter section is indicated by the pressure differential across the test filter and is used as an index of the high temperature stability of the aviation turbine fuel. The extent of deposit formation in the preheater section is determined by inspection and is used as an index of the high temperature stability of the aviation turbine fuel in the hot fuel line section, or heat exchange section, of an aviation turbine engine. Preheater deposits are rated according to the following scale: 0=no visible deposits; 1=visible haze or dulling, but no visible color; 2=barely visible discoloration; 3=light tan to peacock stain; 4=heavier than 3. In carrying out the test, the temperature of the fuel at the outlet of the preheater section is maintained at 400° F. and the filter section temperature is maintained at 500° F. During the test, fuel is caused to flow through the test apparatus at the rate of six pounds per hour and the test duration is five hours.

In the particular test reported below the test fuel, hereinafter referred to as Aviation Turbine Fuel A, was a blend of straight run distillates having the following characteristics.

Gravity, ° API ----- 43.3
Freezing point, ° F. ----- -60
Sulfur, l., percent ----- 0.058
Mercaptan sulfur, percent ----- <0.001
Existent gum, mg./100 ml. ----- 0.5
Potential gum, mg./100 ml. ----- 3.4
Aromatics, vol. percent ----- 16.2
Olefins, vol. percent ----- 1.5
Thermal value, B.t.u./lb. ----- 18,576
Aniline gravity constant ----- 6,343
Distillation:

Over point, ° F. ----- 335
End point, ° F. ----- 532
10% evap. at ° F. ----- 368
50% evap. at ° F. ----- 418
90% evap. at ° F. ----- 486
95% evap. at ° F. ----- 518

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Table

	I	II	III	IV
Make-Up, Percent by Vol.: Aviation Turbine Fuel A.....	100	100	100	100
Stabilizer Added, Lb./1,000 Bbls.—				
1 - Phenyl - 2 - Hexadecyl - 1,3-Eicosanedione.....		20		20
N,N' - Disalicylidene - 1,2 - Propylenediamine.....			20	20
Inspections—Thermal Stability, CFR Fuel Coker:				
Time to Reach a Pressure Drop of 10 In. Hg, Minutes.....	127	>300	10	>300
Time to Reach a Pressure Drop of 25 In. Hg, Minutes.....	163	>300	15	>300
ΔP at 300 Minutes, In. Hg.....	>25.0	0.20	>25	0.10
Maximum Preheater Deposit Rating.....	3	4	0	0
Average Preheater Deposit Rat- ing.....	0.9	1.8	0	0

From the results set forth in the preceding table, it is apparent that neither beta - diketones nor N,N' - di(orthohydroxyarylmethylidene)alkylenepolyamines of the classes disclosed herein are capable of inhibiting deposit formation in both the hot fuel line section and the fuel nozzles of an aviation turbine engine. In fact, as shown by the foregoing data, although the beta-diketones are excellent inhibitors of filter deposits (fuel nozzle deposits), they tend to promote preheater deposits (hot fuel line deposits). Similarly, although the N,N' - di(orthohydroxyarylmethylidene)alkylenepolyamines are excellent inhibitors of preheater deposits, they tend to promote filter deposits. As also shown by the foregoing data, when a combination of the materials is employed, each material modifies the undesirable characteristics of the other without diminishment of its own desirable characteristics.

It will be understood that the invention is not limited to the particular beta - diketone and N,N' - di(orthohydroxyarylmethylidene)alkylenepolyamine set forth in the specific preceding embodiment, and that other materials disclosed herein can also be employed with good results. For example, there can be substituted for the beta-diketone in the foregoing specific embodiment, in proportions of, for example, 10 or 20 pounds per thousand barrels of fuel,

1-tolyl-2-octyl-1,3-hexadecanedione,
1-xylyl-2-decyl-1,3-tetradecanedione,
1-tolyl-2-decyl-1,3-hexadecanedione, and
1-tolyl-2-hexadecadienyl-1,3-tetradecanedione.

Similarly for the N,N' - di(orthohydroxyarylmethylidene)alkylenepolyamine of the foregoing specific embodiment, there can be substituted in proportions of 10 to 20 pounds per thousand barrels of fuel any of

N,N' - di(2-hydroxy-6-methylbenzylidene) - 2,3-butylenediamine,
N,N' - di(orthohydroxynaphthylidene) - 1,3-propylenediamine,
N,N' - di(2-hydroxy-3-methoxybenzylidene) - 3,4-diaminohexane,
N,N' - di(2-hydroxy-5-chlorobenzylidene) - 1,2-propylenediamine,
N,N' - di(2-hydroxy-3-cyanobenzylidene) ethylenediamine,
N,N' - di(2-hydroxy-3-carboxybenzylidene) ethylenediamine, and
N,N' - disalicylidenediethylenetriamine.

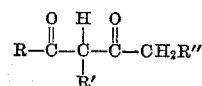
The aviation turbine fuel compositions of this invention can contain various other addition agents adapted to improve one or more properties of the fuel. For example, the fuel compositions of this invention can contain in addition to the addition agents disclosed herein, corrosion inhibitors, freezing point depressants, antioxidants, other metal deactivators and the like.

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Many modifications and variations of the invention as herein described will suggest themselves to those skilled in the art, and resort may be had to such modifications and variations without departing from the spirit and scope of the invention. Accordingly, only such limitations should be imposed as are indicated in the claims appended hereto.

I claim:

1. A combustion gas turbine fuel composition comprising a major amount of a normally thermally unstable, liquid hydrocarbon aviation turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel of a combination of (a) an N,N' - di(orthohydroxyarylmethylidene)alkylenepolyamine containing 2 to 3 amino nitrogen atoms and whose alkylene groups contain 2 to 6 carbon atoms each, and (b) a beta-diketone having the general formula:

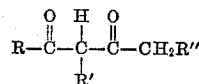


where R is an aromatic hydrocarbon group having a nuclear carbon atom thereof connected directly to the adjacent carbonyl carbon atom and containing 6 to 22 carbon atoms, and R' and R'' are acyclic aliphatic hydrocarbon radicals that contain 8 to 22 carbon atoms, said small amount comprising at least about five pounds of each member of said combination per thousand barrels of fuel.

2. The fuel composition of claim 1 where said small amount comprises about 5 to 250 pounds of each member of said combination per thousand barrels of fuel, and the members are present in the composition in a weight ratio with respect to each other of about 10:1 to about 1:10.

3. The fuel composition of claim 1 where said small amount comprises about 10 to 20 pounds of each member of said combination per thousand barrels of fuel, and the members are present in the composition in a weight ratio with respect to each other of about 4:1 to 1:4.

4. A combustion gas turbine fuel composition comprising a major amount of normally thermally unstable, liquid hydrocarbon aviation turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel of a combination of (a) an N,N' - di(orthohydroxyarylmethylidene)alkylenepolyamine containing 2 to 3 amino nitrogen atoms and whose alkylene groups contain 2 to 6 carbon atoms each, and whose orthohydroxyaryl substituent is selected from the group consisting of unsubstituted orthohydroxyaryl radicals and orthohydroxyaryl radicals whose only substituents contain carbon and hydrogen atoms, and (b) a beta-diketone having the general formula:



where R is a mononuclear hydrocarbon radical containing 6 to 20 carbon atoms and R' and R'' are alkyl groups containing 12 to 18 carbon atoms, said small amount comprising at least about five pounds of each member of said combination per thousand barrels of fuel.

5. A combustion gas turbine fuel composition comprising a major amount of a normally thermally unstable, liquid hydrocarbon aviation turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel, of a combination of 1-phenyl-2-hexadecyl-1,3-eicosanedione, and N,N' - disalicylidene-1,2-propylenediamine, said small amount comprising 5 to 250 pounds of each member of said combination per thousand barrels of fuel.

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