

1

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BETA-DIKETONES IN AVIATION TURBINE FUELS

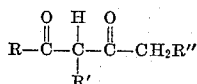
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5 Claims. (Cl. 44-77)

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

Aviation turbine fuels are 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 fuels are 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.

It has now been found that the tendency of aviation turbine fuels to form deposits in the fuel inlet area of the combustion zone of an aviation turbine engine, can be substantially improved by incorporation in the fuel of a small amount of 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, such as phenyl, tolyl, xylyl, isobutylphenyl, diisobutylphenyl, or dodecylphenyl groups, and R' and R'' are like or unlike open-chain, saturated or unsaturated aliphatic hydrocarbon radicals containing 8 to 22 carbon atoms, such as octyl, dodecyl, hexadecyl, octadecyl, hexadecenyl, hexadecadienyl, and the like. Beta-diketones where R is a mononuclear aromatic radical containing 6 to 12 carbon atoms, and R' and R'' are alkyl groups containing 12 to 18 carbon atoms are especially advantageous. An example of a beta-diketone that produces especially good results is 1-phenyl-2-hexadecyl-1,3-eicosanedione.

The beta-diketones disclosed herein are employed in the aviation turbine fuels in any proportion sufficient to improve the thermal stability of the fuels. Normally, an appreciable 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, but it is usually desirable to employ at least seven pounds per thousand barrels of fuel 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

2

barrels of fuel, 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, the beta-diketones disclosed herein can be employed in proportions of up to 50 pounds per thousand barrels of fuel.

The exact mechanism by which the beta-diketones disclosed herein function to improve the thermal stability of aviation turbine fuels has not been definitely established. It may be that the beta-diketones 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 beta-diketones of the class disclosed herein, that is, beta-diketones that contain high formula weight substituents in the 1, 2, and 3 positions, have been found to form exceptionally stable metallic complexes, apparently as a result of the shielding or hindering effect of the three bulky substituents.

The beta-diketones disclosed herein can be prepared in any convenient manner. For example, they can be prepared as described in copending application Serial No. 783,730 filed December 30, 1958, now U.S. Patent No. 3,004,070 directed to the beta-diketones as such, i.e., by condensation of a suitable disubstituted ketene dimer or codimer in the presence of a Friedel-Crafts catalyst, such as zinc chloride, aluminum chloride, or the like, with an equivalent proportion of a suitable aromatic hydrocarbon to provide a 1,2,3-substituted 1,3-dione, or beta-diketone.

The beta-diketones disclosed herein can be incorporated in aviation turbine fuels in any suitable manner. For example, they can be added as such or in diluted form to the fuels either promptly after distillation of the latter, or during or after storage of the fuels. Alternatively, the beta-diketones disclosed herein can be added to the fuels in admixture with other addition agents adapted to improve one or more characteristics of the fuels. For example, the beta-diketones can be added to the fuels in admixture with corrosion inhibitors such as amine salts of organic orthophosphates, antioxidants such as 2,6-di-tertiary-butyl-4-methylphenol, or 2,4-dimethyl-6-tertiary-butylphenol, and metal deactivators such as N,N'-disalicylidene-1,2-diaminopropane.

Aviation turbine fuels of the type whose use is included by this invention 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:

55	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
60	Freezing point, ° F. (max.) -----	-75 to -40
	Thermal value, B.t.u./lb. (min.) ---	18,300-18,500
	Aniline-gravity constant -----	¹ >4500
	Aromatics, vol. percent (max.) -----	5-25
	Olefins, vol. percent (max.) -----	1-5

65 ¹ Usually >5250.

It is emphasized that the position and character of the substituents of the beta-diketones disclosed herein are of utmost importance insofar as the ability of these compounds to improve the thermal stability of aviation turbine fuels. Thus, it has been found that 1,3-diones having relatively high formula weight substituents of the charac-

ter indicated herein in the 1, 2 and 3-positions exhibit a marked superiority in their ability to inhibit formation of deposits in aviation turbine fuels at high service temperatures as compared with other beta-diketones.

The ability of the beta-diketones 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. 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
Percent evap. at ° F.:	
10	368
50	418
90	486
95	518

The results of the test are set forth in the following table:

Table

	1	2
Make-Up, percent by Vol.:		
Aviation Turbine Fuel A	100	100
Stabilizer Added, Lb./1,000 Bbls. 1-Phenyl-2-Hexadecyl-1,3-Eicosanedione		20
Inspections:		
Thermal Stability, CFR Fuel Coker—		
Time to Reach a Pressure Drop of 10 In. Hg, Minutes	127	>300
Time to Reach a Pressure Drop of 25 In. Hg, Minutes	163	>300
ΔP at 300 Minutes, In. Hg	>25.0	0.20

From the results set forth in the preceding table, it is apparent that beta-diketones of the class disclosed herein impart substantially improved thermal stability characteristics to aviation turbine fuels at high service

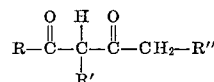
temperatures. It will be understood that the invention is not limited to the particular beta-diketone set forth in the preceding specific embodiment and that other beta-diketones disclosed herein can also be employed with good results. For example, there can be substituted for the beta-diketone in the foregoing specific embodiment, in proportions of 10 and 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-hexadecenedione, and 1-tolyl-2-hexadecadienyl-1,3-tetradecanedione.

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 beta-diketones disclosed herein, corrosion inhibitors, freezing point depressants, antioxidants, metal deactivators, and the like.

Obviously many modifications and variations of the invention as herein described may be resorted to without departing from the spirit or scope thereof. Accordingly, only such limitations should be imposed as are indicated in the appended claims.

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 beta-diketone having the general formula:

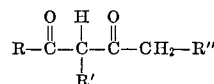


where R is an aromatic hydrocarbon group having a nuclear carbon atom thereof connected directly to the adjacent carbonyl carbon atom and containing 6 to 22 carbon atoms, and R' and R'' are open-chain aliphatic hydrocarbon radicals that contain 8 to 22 carbon atoms.

2. The turbine fuel composition of claim 1 where said small amount is of about 5 to 50 pounds per thousand barrels of fuel.

3. The turbine fuel composition of claim 1 where said small amount is in the range of about 10 to 20 pounds per thousand barrels of fuel.

4. 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 beta-diketone having the general formula:



where R is a mononuclear aromatic hydrocarbon radical containing 6 to 12 carbon atoms and R' and R'' are alkyl groups containing 12 to 18 carbon atoms.

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 1-phenyl-2-hexadecyl-1,3-eicosanedione.

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