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FUEL FOR AND METHOD OF OPERATING A JET ENGINE

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This invention relates to a novel composition having excellent high temperature stability and a method for cooling heated materials utilizing said composition.

The composition of the present invention has particular application in the operation of jet aircraft. The advanced high speed engines employed in jet aircraft have extremely high combustion temperatures and many of the materials which necessarily are exposed to such temperatures are decomposed to the extent that they cannot perform their assigned tasks. Compositions used to lubricate the moving parts of jet engines, for instance, may break down with a loss of viscosity and the formation of sludge and deposits which tend to prevent proper lubrication. It is therefore most important that some means or method be utilized to keep these materials at temperatures in which they may function properly.

The use of the jet fuel as a heat sink for cooling vital aircraft components such as the lubricating oil provides one solution to the problem of high temperatures. This technique is exemplified by passing the fuel in heat exchange relationship with the lubricating oil prior to fuel consumption. This use has imposed a new and serious requirement of extremely high thermal stability on jet fuel. Heat stability is of the utmost importance because thermal degradation of the fuel will result in carbon build-up and clogging of the fuel lines and will in time prevent operation of the jet aircraft. Thermal stability has been imparted to jet fuel in two main ways, namely, by refining techniques such as hydrogenation and by the use of additives. This invention provides a thermally stable jet fuel by the use of a particular type of additive.

In accordance with the present invention, an excellent heat stable composition is formed by the addition of from 0.001 to 0.03 percent by weight of at least one compound selected from the group consisting of alkyl primary and alkyl secondary amines, having a total of from 16 to 32 carbon atoms in the alkyl radicals, to a major portion of a hydrocarbon stock boiling within the range of from 250 to 700° F. The preferred addition range of said alkyl amines is from 0.005 to 0.02 percent by weight. The preferred alkyl primary amines in accordance with this invention are those having from 18 to 24 carbon atoms in a tertiary alkyl radical. The preferred alkyl secondary amines are those substituted with a tertiary C₁₂ to C₁₅ alkyl radical and with an alkyl-substituted aralkyl radical having 10 to 14 carbon atoms in the substituted alkyl group. Some examples of other primary amines which may be used either individually or in mixtures with other amines in accordance with this invention are as follows: cetyl amine, 2-ethylpentadecyl amine, stearyl amine, neostearyl amine, behenyl amine, cerotyl amine, montanyl amine, myricyl amine, melissyl amine, lacceryl amine, and ceromelissyl amine. Examples of some useful secondary amines are as follows: 2-isobutylhexyl-2-ethylhexyl benzyl amine, 2,2,5-trimethylhexyl-2,2-dimethyldecylbenzyl amine, 2-ethyl-2-butylonyl-2-hexyldecylbenzyl amine, neostearyl myristyl

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phenylethyl amine, and 2,2-dimethyldecyl-2,2-diethylnonyl phenylethyl amine. Further, the invention includes a method of cooling material in a jet propelled aircraft comprising passing the above composition in heat exchange relationship with said material and thereafter passing said composition to the combustion chamber of said jet engine for utilization as a fuel.

In order to demonstrate the superior heat stability of the composition in accordance with the present invention, the base fuel alone and together with various types of amines have been tested in an Erdco Fuel Coker Test Unit. When testing fuels with this unit, the fuel under consideration is pumped through a preheater in the form of an annular heat exchanger. The heated fuel is then passed through a heated sintered steel filter. Sludge and sediment formed by the heating of the fuel deposit on the filter. Test conditions on all the runs, the results of which are published in the following tables, were as follows: preheater temperature, 400° F.; filter temperature, 500° F.; fuel flow, 4 lbs./hr.; fuel pressure, 150 p.s.i.g. The thermal stability of a fuel is indicated by the time for a filter to partially plug. In order to determine this, the test is run until the drop in pressure (ΔP) across the filter reaches either 25 inches of mercury or a test duration of 5 hours. A good fuel in this test is one which obtains a filter ΔP below 20 inches of mercury in five hours or more.

The base fuels with which the additives were tested included a JP-4 fuel which is used by the military and commercial air lines and comprises a mixture of about 65 percent gasoline and 35 percent light distillate. This product also adheres to the following characteristics:

Gravity ° API	45-57
Reid vapor pressure, lbs.	2-3
Freezing point	max -76
Smoke pt. volatility index	min 54
Water reaction	max -1
Sulfur, percent	max 0.4
Mercaptan sulfur, percent (1)	max 0.005
Aromatics percent by vol.	max 25
Olefins percent by vol.	max 5.0
Bromine No.	max 5.0
Potential gum, mg./100 ml.	max 14
Existent gum, mg./100 ml.	max 7
Heating value, B.t.u./lb.	min 18,400
Distillation:	
20% ° F.	max 270
50% ° F.	max 370
90% ° F.	max 470

Another fuel used was a so-called JP-4 Referee fuel which can be described as a special grade of JP-4 fuel. The fuel is designed to be typical of lower quality JP-4 fuel which would be available in wartime. It is used almost exclusively in the developing and testing of military jet engines. It may be further distinguished from the ordinary JP-4 fuel by reference to the following characteristics:

Gravity ° API	45-50
Smoke point volatility index	50-54
Sulfur, percent	0.15-0.40
Heating value, B.t.u./lb.	18,400-18,750
Distillation:	
20%	250-290
50%	350-390
90%	450-490

The remaining characteristics are essentially the same as those listed for the ordinary JP-4 fuel.

Still another fuel used for the investigation of these compounds was an experimental fuel comprising a kero-

sine having a high aromatic and a low sulfur content. Inspection tests on this fuel are as follows:

ASTM distillation:

IBP, ° F.	350
10% -----	394
50% -----	448
90% -----	504
FBP -----	534
API gravity -----	37.9
Existent gum -----mg./100 ml.	0.6
Accelerated gum -----mg./100 ml.	0.6
Sulfur, total wt. percent -----	0.027
Mercaptan sulfur, wt. percent -----	0.0009
Freezing point, ° F. -----	-40
Heating value -----B.t.u./lb.	18,473
Aniline gravity constant -----	4991
Viscosity at -30° F. -----cs.	13.4
Volume percent aromatics -----	21.8
Volume percent olefins -----	9.5
Smoke point, mm. -----	15
Water tolerance -----	Pass
Flash point (P.M.), ° F. -----	150

The Erdco Fuel Coker Unit Test results with respect to heat stability of jet fuels are set forth in the following tables. A mixture of C₁₈-C₂₄ tertiary alkyl primary amines sold as Primene JM-R and a secondary amine of the general formula:



wherein R is a mixture of C₁₂ to C₁₅ tertiary alkyl groups and R' is a C₁₂ alkyl substituted benzyl radical which was supplied as EB-974, an experimental amine, were the amines used in Table I.

Table I

Fuel	Additive wt., percent	Filter ΔP, in. Hg	Time (Min.)
Experimental Fuel -----	None	25	56
Primene JM-R -----	0.018	-1.1	1 262
EB-974 -----	0.018	0.05	300

¹ Fuel shortage prevented completion.

The foregoing table demonstrates that alkyl primary and alkyl secondary amines at concentrations of 0.018 weight percent (50 lbs./1000 bbl.) will greatly improve the heat stability of an unstable jet fuel. Although the run in which the additive Primene JM-R was tested was not completed due to fuel shortage, the negative ΔP indicates that the ΔP in 300 minutes would still remain below zero.

The following table is set forth to compare the effectiveness of other amines as heat stabilizing additives for jet fuels.

The product Armeen DM-18D is a tertiary amine which contains 92 percent of distilled dimethyl stearyl amine.

Table II

Fuel	Additive wt., percent	Filter ΔP, in. Hg	Time (Min.)
JP-4 Referee -----	None	25	1 43
JP-4 Referee + Armeen DM-18D -----	0.018	25	19
JP-4 Referee + 1-naphthylamine -----	0.018	25	35
JP-4 Referee + diphenylamine -----	0.018	25	33
JP-4 Referee + N,N'-di-sec-butyl-p-phenylene diamine -----	0.018	25	30

¹ Ck. 44.

The foregoing table shows that a tertiary amine (Armeen DM-18D) is of no value as a heat stabilizing additive. Further, the table shows that aromatic amines,

represented by 1-naphthylamine, diphenylamine and N,N'-di-sec-butyl-p-phenylene diamine at additive percentages of 0.018 by weight have no value as additives for heat stabilizing jet fuels.

These results further emphasize the unexpectedness of the fact that the alkyl primary and secondary amines of this invention are excellent additives for high temperature fuel stability at surprisingly low concentrations.

Table III

Fuel	Additive wt., percent	Filter ΔP, in. Hg	Time (Min.)
JP-4 -----	None	25	1 58
JP-4 + Primene JM-R -----	0.009	-0.0	300
JP-4 + Primene JM-R -----	0.0036	0.0	300
JP-4 + Primene JM-R -----	0.0018	0.0	2 240

¹ Ck. 50.

² Fuel shortage prevented completion.

The above Table III demonstrates the effectiveness of a tertiary C₁₈-C₂₄ alkyl primary amine as a heat stabilizing additive at extremely low concentrations. Even at the extremely low concentration of 0.0018 percent by weight in a jet fuel (5 lbs./1000 bbls.) its effectiveness is surprisingly evident. Although a fuel shortage prevented the completion of this run, it is quite apparent that the fuel was effectively stabilized by this small amount of additive.

In the development of an effective jet fuel additive it is also necessary to reject those additives which although effective in promoting heat stability in the fuels, also lend to the fuel an affinity for water. In order to determine a limiting value for the solubility of water in jet turbine fuels, the fuels must pass a water tolerance test. The following is a description of the ASTM-D1094-50T Water Tolerance Test of aircraft fuels which was used on the fuel compositions of this invention.

An 80 ml. sample of the fuel to be tested is shaken vigorously at room temperature with 20 ml. of distilled water in a 100 ml. glass stopper graduated cylinder for at least 2 minutes and thereafter allowed to settle. The change in volume of the aqueous layer after 5 minutes of settling is reported to the nearest 0.5 ml. A pass rating denotes an increase of 1 ml. or less in either layer. This change in volume is taken as the water tolerance of the fuel. The following table sets forth the results of water tolerance tests on various effective heat stabilizing additives.

Table IV

Fuel	Additive wt., percent	Water Tolerance
JP-4 + Primene JM-R -----	0.009	Pass.
JP-4 + Primene JM-R -----	0.0036	Do.
JP-4 + Primene JM-R -----	0.0018	Do.
F-105 + Primene JM-R -----	0.018	Do.
F-105 + alkyl-sec-amine -----	0.018	Do.
F-105 + polyoxyethylene sorbitol hexa-laureate -----	0.018	Fail.
F-105 + basic metal sulfonate -----	0.018	Do.
F-105 + Nitrogen substituted methacrylate polymer -----	0.018	Do.
F-105 + Nitrogen substituted methacrylate polymer -----	0.0061	Do.
JP-4 Referee + normal barium sulfonate -----	0.018	Do.

It is evident from the above table that many additives although imparting effective heat stability to fuels will fail to provide good water tolerance characteristics to the fuel composition and, therefore, be undesirable as jet turbine propellant additives.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and, therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A method of operating a jet aircraft comprising cooling the lubricant employed in the lubrication of jet engines by indirect heat exchange with a composition consisting essentially of a hydrocarbon stock boiling within the range of from 250 to 700° F. containing 0.001 to 0.03 percent by weight of at least one amine selected from the group consisting of alkyl primary and alkyl, aralkyl secondary amines containing a total of 16 to 32 carbon atoms in the alkyl radicals and subsequently using said hydrocarbon for fuel for operation of said jet engine.

2. A heat stable jet fuel composition consisting essentially of a major proportion of a hydrocarbon stock boiling within the range of from 250 to 700° F. and from 0.005 to 0.02 percent by weight of a compound having the general formula:



wherein R is selected from the group consisting of C₁₂ to C₁₅ alkyl groups and mixtures thereof and R' is a C₁₂ to C₁₅ alkyl substituted benzyl radical.

3. A method of cooling a jet aircraft component comprising passing the jet fuel composition, consisting essentially of a hydrocarbon stock boiling within the range of from 250 to 700° F. containing from 0.001 to 0.03 percent by weight of at least one compound selected from the group consisting of alkyl primary amines having from 16 to 32 carbon atoms in the alkyl group and a compound having a general formula:



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wherein R is selected from the group consisting of C₁₂ to C₁₅ alkyl groups and R' is an alkyl substituted benzyl radical in which said alkyl group contains 10-14 carbon atoms, in indirect heat exchange relationship with said material.

4. A method of cooling a material in a jet aircraft as described in claim 3 wherein the jet fuel composition contains from 0.005 to 0.02 percent of the alkyl primary amine.

5. A method of cooling the engine lubricant in a jet aircraft comprising passing the jet fuel composition consisting essentially of a hydrocarbon stock boiling within the range of from 250 to 700° F. containing from 0.005 to 0.02 percent by weight of a tertiary alkyl primary amine having from 18 to 24 carbon atoms in the alkyl group, in indirect heat exchange relationship with said lubricant.

References Cited in the file of this patent

UNITED STATES PATENTS

2,474,183	King	June 21, 1949
2,573,471	Malina et al.	Oct. 30, 1951
2,607,665	Duncan	Aug. 19, 1952
2,675,671	Malgieri	Apr. 20, 1954

FOREIGN PATENTS

627,386	Great Britain	Aug. 8, 1949
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