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THERMALLY-STABLE JET COMBUSTION FUELS

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This invention relates to jet combustion fuels that are stable at relatively high temperatures. It is more particularly concerned with jet combustion fuels adapted for use in high temperature jet engines and with novel additive compositions therefor.

As is well known to those familiar with the art, aviation turbine engines, or jet engines, are operated at extremely high temperatures, particularly in the case of supersonic jet aircraft engines. In order to remove some of the heat and also preheat the incoming fuel, the fuel is subjected to indirect heat exchange with the combustion chamber. Then, when passing through the injection nozzles the incoming fuel is further subjected to high temperature conditions. Many jet fuels have been found to be relatively unstable when subjected to high temperatures. Decomposition products are formed which tend to foul the heat exchange tubes and to cause plugging of the injection nozzles. As will readily be appreciated, the use of such fuels results in shortened operational life of the engine and can be a source of hazard in the operation of the jet aircraft. Accordingly, the means of stabilizing such fuels against degradation is highly desirable.

It has now been found that thermally unstable jet combustion fuels can be stabilized against degradation simply and economically. It has been discovered that the addition of a small amount of a mixture of certain full esters and certain metal deactivating compounds will stabilize jet combustion fuels against thermal degradation, thereby minimizing the fouling of heat exchange tubes and the plugging of the filters.

Accordingly, it is an object of this invention to provide stable jet combustion fuels. Another object is to provide a means for stabilizing jet combustion fuels against thermal degradation. A further object is to provide jet combustion fuels having a greatly reduced tendency to foul heat exchange tubes and to plug injection nozzles. A specific object is to provide jet combustion fuels containing an additive composition of certain fuel esters and certain metal deactivating compounds. A more specific object is to provide jet combustion fuels containing certain full esters and aldehyde-amine condensation products of the type of arylidene amines or Schiff's bases. Other objects and advantages of this invention will become apparent to those skilled in the art from the following detailed description.

In general, the present invention provides an additive composition comprising between about 1 percent and about 10 percent, by weight of the additive mixture, of a deactivator having the formula:

HO—A—CH=N—R—N=CH—A—OH

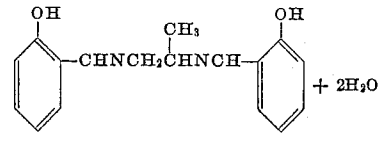
wherein A represents a benzene ring, the OH radical being attached directly to a ring carbon atom ortho to the —CH=N— group and R represents an aliphatic radical having the two N atoms attached directly to different carbon atoms of the same open chain of R, and between about 99 percent and about 90 percent, by weight of the additive mixture, of the full neutral aliphatic esters of a polycarboxylic acid selected from the group consisting of citric acid, phthalic acid, oxalic acid, and azelaic acid, wherein the esterifying alcohol contains between about 4 carbon and about 20 carbon atoms; and a jet combustion fuel containing between about 0.001 percent and about 1 percent, by weight, of the said additive composition.

The metal deactivator component of the additive compositions of this invention are aldehyde-amine condensation products of the type of arylidene amines or Schiff's bases having the formula:

HO—A—CH=N—R—N=CH—A—OH

wherein A represents a benzene ring, the OH radical being attached directly to a ring carbon atom ortho to the —CH=N— group and R represents an aliphatic radical having the two N atoms attached directly to different carbon atoms of the same open chain of R, and between about 99 percent and about 90 percent, by weight, of the additive mixture, of the full neutral aliphatic esters of a polycarboxylic acid selected from the group consisting of citric acid, phthalic acid, oxalic acid, and azelaic acid, wherein the esterifying alcohol contains between about 4 carbon and about 20 carbon atoms.

These materials have been fully described in U.S. Letters Patents Numbers 2,181,121 and 2,284,267. Generally, they are produced by reacting two moles of salicylaldehyde with one mole of a diamine such as ethylene diamine or propylene diamine with the elimination of two moles of water of condensation. The preferred metal deactivator is the N,N'-disalicylaldimine of propylene diamine having the structure:



The ester component of the additive compositions of this invention are the full neutral esters of citric acid, phthalic acid, oxalic acid or azelaic acid. The esterifying alcohols can contain between about 4 carbon and about 20 carbon atoms. Nonlimiting examples of the ester component are tri-n-butyl citrate, di-amyl phthalate, di-hexyl oxalate, di-2-ethyl-hexyl azelate, tri-2-ethyl-hexyl citrate, tri-n-decyl citrate, tri-isodecyl citrate, di-azelate decyl phthalate, tri(isotridecyl) citrate, di(tridecyl) phthalate, di(isodecyl) oxalate, di(isotridecyl) azelate, di-hexyl decenyl phthalate, tri-octadecenyl citrate, and di-octadecenyl azelate. It is to be noted that the esters utilizable herein must be, the full neutral esters. It has been found that the partial esters are ineffective and many have a tendency to develop undesirable, heavy emulsions with water in the fuels.

As will readily be appreciated by those familiar with the art, the ester component can be made by any of the known methods for preparing esters of carboxylic acids. Thus, for example, the esters can be prepared by reacting the alcohol in proper proportions with the acid or with the acid anhydride, with or without the use of catalysts such as a p-toluene sulfonic acid monohydrate. Likewise, it can be used for various techniques of esterification such as azeotropic distillation, removal of water or the use of applied vacuum. It is to be understood that the particular method used to prepare the ester component is of no importance to the preparation of the additive compositions of this invention or of jet combustion fuels containing them.

The amount of metal deactivator component in the additive composition of this invention can vary between about 1 percent and about 10 percent, by weight, of the additive composition, the balance being the full neutral ester aforedescribed. In preferred practice the additive composition will contain between about 2 percent and about 5 percent by weight, of the metal deactivator com-

ponent, and an especially preferred composition contains about 4 weight percent of the metal deactivator component.

The hydrocarbon jet fuels that are improved in accordance with this invention are hydrocarbon fractions having an initial boiling point of at least about 100° F. and an end boiling point as high as about 750° F. These fuels can be made up of straight-run distillate fractions, catalytically or thermally cracked (including hydrocracked) distillate fractions, or mixtures of straight-run fuel oil, naphtha, etc. with cracked distillate stocks, alkylate, and the like. The principal properties that characterize the jet fuels is their boiling range. Each fuel will have a boiling range which falls within the aforespecified range. Specifications that define typical specific fuels are MIL–F–5616, MIL–J–5624D, MIL–F–25656, MIL–F–2524A, MIL–F–25576A, MIL–F–25558B, and MIL–J–5161E.

The amount of additive composition that is added to the jet combustion fuels will vary between about 0.001 percent and about 1 percent, by weight of the fuel, and preferably between about 0.01 percent and about 0.1. In terms of weight per unit volume of fuel the concentration of additive composition will vary between about 2 pounds per thousand barrels of fuel and about 2000 pounds per thousand barrels of fuel, and preferably the concentration will vary between about 25 pounds per thousand barrels of fuel and about 250 pounds per thousand barrels of fuel.

The test method used for determining the thermal stability characteristics of aviation turbine fuels is a method developed by the Coordinating Research Council which has published in CRC Report "Investigation of Thermal Stability of Aviation Turbine Fuels With CFR Fuel Coker" (CRC Project CFA–2–54), July 1957. The method is set forth in detail in Appendix XV of the "ASTM Standards on Petroleum Products and Lubricants," November 1957, commencing at page 1059. This method provides a means for measuring the high temperature stability of aviation turbine fuels, using an apparatus known as the "CFR Fuel Coker," which subjects the test fuel to temperatures and conditions similar to those occurring in some aviation turbine engines. Fuel is pumped at a rate of about 6 pounds per hour through a preheater section which simulates the hot fuel line sections of the engine as typified by an engine fuel-oil cooler. It then passes through a heated filter section which represents the nozzle area or small fuel passages of the hot section of the engine where fuel degradation products may become trapped. A precision sintered stainless steel filter in the heated filter section traps fuel degradation products formed during the test. The extent of the build-up is noted as an increased pressure drop across the test filter, and in combination with the deposit condition of the preheater, is used as an assessment of the fuel's high-temperature stability. In the testing described herein the filter temperature was 500° F. and the preheater tube temperature was 400° F. In each run the test was continued until there was a pressure drop of 25 inches of mercury across the filter or until a time of 300 minutes had elapsed, whichever occurred first. In order to be satisfactory in the test a fuel should show little or no pressure drop across the filter at the end of 300 minutes. The preheater deposits in the tests are evaluated according to a code rating varying from 0 to 4 wherein code 0 means no visible deposits; code 1, haze or dulling, no color; code 2, barely visible discolorization; code 3, light tan; and code 4, heavier than code 3. It will be readily appreciated that a rating lower than code 3 is desirable for an effective stable aviation turbine fuel.

EXAMPLE 1

A hydrocarbon jet combustion fuel boiling between about 370° F. and about 520° F. was subjected to the Fuel Coker test. Then another portion of the fuel containing 1.2 pounds per thousand barrels of fuel of N,N'-disalicylaldimine of propylene diamine was tested. Pertinent test results are set forth in Table I.

EXAMPLE 2

Another test was run in the Fuel Coker test using the base fuel defined in Example 1 which contained 28.8 pounds per thousand barrels of fuel of tri(isotridecyl) citrate. Pertinent test results are also set forth in Table I.

EXAMPLE 3

The base fuel described in Example 1 containing 1.2 pounds per thousand barrels of fuel of N,N'-disalicylaldimine of propylene diamine and 28.8 pounds per thousand barrels of fuel of tri(tridecyl) citrate was subjected to the Fuel Coker test. It will be noted that the additive content of this fuel is a combination of the additives tested in Examples 1 and 2. Pertinent test results are set forth in Table I.

Table I

Example	Inhibitor	Conc. lbs./1,000 bbls.	Filter Plugging		Preheater Deposits at 300 min. Rating
			Press. Drop Inches, Hg	Time, Min.	
1	Fuel+N,N' - disalicyl - aldimine of propylene diamine.	1.2	25.0	263	Code 3.
2	Fuel+tri(tridecyl) citrate.	28.8	25.0	224	Code 4.
3	Fuel+N ,N' - disalicyl - aldimine of propylene diamine and tri (tridecyl) citrate.	1.2, 28.8	1.0	300	Code 0.

It is to be noted that neither the neutral ester nor the metal deactivator was appreciably effective in preventing filter plugging and preheater deposits. On the other hand, the combination of the two additives was completely effective in both respects.

As has been mentioned hereinbefore combinations of other esters with the metal deactivator are also effective in stabilizing jet combustion fuels. Using the base fuel described in Example 1, a series of blends were prepared in accordance with the present invention and each blend was subjected to the Fuel Coker test. Pertinent data and results of these tests are set forth in Table II.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

What is claimed is:

1. An additive composition that consists essentially of between about 1 percent and about 10 percent, by weight of the additive composition, of a deactivator having the formula:

$$HO—A—CH=N—R—N=CH—A—OH$$

wherein A represents a benzene ring, the OH radical being attached directly to a ring carbon atom ortho to the —CH=N— group and R represents an alkylene hydrocarbon radical having the two N atoms attached directly to different carbon atoms of the same open chain of R; and between about 99 percent and about 90 percent, by weight of the additive composition, of the full neutral aliphatic hydrocarbon esters of a polycarboxylic acid selected from the group consisting of citric acid, phthalic acid, oxalic acid, and azelaic acid, wherein the esterifying alcohol contains between about 4 carbon atoms and about 20 carbon atoms.

2. An additive coposition that consists essentially of between about 2 percent and about 5 percent, by weight

Table II

Example	Additive Combination				Additive Combination, Conc. lb./1,000 bbls. fuel	Filter Plugging		Preheater Deposits at 300 Min. Rating
	Ester	Wt. Percent	Metal Deactivator	Wt. Percent		Press. Drop Inches, Hg	Time Min.	
2	Tri-isodecyl citrate	96	N,N'-disalicylaldimine of propylene diamine.	4	30	0.0	300	Code 1.
3	Tri-(2-ethylhexyl) citrate	96	do	4	30	0.2	300	Code 0.
4	Tri-(n-decyl) citrate	96	do	4	30	0.8	300	Do.
5	Tri-(n-butyl) citrate	96	do	4	30	2.0	300	Do.
6	Tri-octadecenyl citrate	96	do	4	30	0.0	300	Do.
7	Di-(isotridecyl) phthalate	96	do	4	30	0.7	300	Do.
8	Di-isodecyl phthalate	96	do	4	30	0.3	300	Do.
9	Di-(isotridecyl) oxalate	96	do	4	30	0.2	300	Code 1.
10	Di-(isotridecyl) azelate	96	do	4	30	0.6	300	Code 2.
	Uninhibited fuel				0	25.0	100	Code 4.

of the additive composition, of a deactivator having the formula:

HO—A—CH=N—R—N=CH—A—OH

wherein A represents a benzene ring, the OH radical being attached directly to a ring carbon atom ortho to the —CH=N— group and R represents an alkylene hydrocarbon radical having the two N atoms attached directly to different carbon atoms of the same open chain of R; and between about 98 percent and about 95 percent, by weight of the additive composition, of the full neutral aliphatic hydrocarbon esters of a polycarboxylic acid selected from the group consisting of citric acid, phthalic acid, oxalic acid, and azelaic acid, wherein the esterifying alcohol contains between about 4 carbon atoms and about 20 carbon atoms.

3. An additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of tri-(tridecyl) citrate.

4. An additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of tri-(isodecyl) citrate.

5. An additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of tri-(2-ethylhexyl) citrate.

6. An additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of tri-octadecenyl citrate.

7. An additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of di-(isotridecyl) phthalate.

8. An additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of di-(isodecyl) phthalate.

9. An additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of di-(isotridecyl) oxalate.

10. An additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of di-(isotridecyl) azelate.

11. A stable jet combustion fuel that consists essentially of a hydrocarbon jet fuel containing between about 2 pounds and about 2000 pounds per thousand barrels of fuel of an additive composition that consists essentially of between about 1 percent and about 10 percent, by weight of the additive composition, of a deactivator having the formula:

HO—A—CH=N—R—N=CH—A—OH

wherein A represents a benzene ring, the OH radical being attached directly to a ring carbon atom ortho to the —CH=N— group and R represents an alkylene hydrocarbon radical having the two N atoms attached directly to different carbon atoms of the same open chain of R; and between about 99 percent and about 90 percent, by weight of the additive composition, of the full neutral aliphatic hydrocarbon esters of a polycarboxylic acid selected from the group consisting of citric acid, phthalic acid, oxalic acid, and azelaic acid, wherein the esterifying alcohol contains between about 4 carbon atoms and about 20 carbon atoms.

12. A stable jet combustion fuel that consists essentially of a hydrocarbon jet fuel containing between about 25 pounds and about 250 pounds per thousand barrels of fuel of an additive composition that consists essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of a deactivator having the formula:

HO—A—CH=N—R—N=CH—A—OH

wherein A represents a benzene ring, the OH radical being attached directly to a ring carbon atom ortho to the —CH=N— group and R represents an alkylene hydrocarbon radical having the two N atoms attached directly to different carbon atoms of the same open chain of R; and between about 98 percent and about 95 percent, by weight of the additive composition, of the full neutral aliphatic hydrocarbon esters of a polycarboxylic acid selected from the group consisting of citric acid, phthalic acid, oxalic acid, and azelaic acid, wherein the esterifying alcohol contains between about 4 carbon atoms and about 20 carbon atoms.

13. A stable jet combustion fuel that consists of a hydrocarbon jet fuel containing between about 25 pounds and about 250 pounds per thousand barrels of fuel of an additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of tri-(tridecyl) citrate.

14. A stable jet combustion fuel that consists of a hydrocarbon jet fuel containing between about 25 pounds and about 250 pounds per thousand barrels of fuel of an additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of tri(isodecyl) citrate.

15. A stable jet combustion fuel that consists of a hydrocarbon jet fuel containing between about 25 pounds

and about 250 pounds per thousand barrels of fuel of an additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of tri(2-ethylhexyl) citrate.

16. A stable jet combustion fuel that consists of a hydrocarbon jet fuel containing between about 25 pounds and about 250 pounds per thousand barrels of fuel of an additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of tri-octadecenyl citrate.

17. A stable jet combustion fuel that consists of a hydrocarbon jet fuel containing between about 25 pounds and about 250 pounds per thousand barrels of fuel of an additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of di-(isotridecyl) phthalate.

18. A stable jet combustion fuel that consists of a hydrocarbon jet fuel containing between about 25 pounds and about 250 pounds per thousand barrels of fuel of an additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of di(isodecyl) phthalate.

19. A stable jet combustion fuel that consists of a hydrocarbon jet fuel containing between about 25 pounds and about 250 pounds per thousand barrels of fuel of an additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of di(isotridecyl) oxalate.

20. A stable jet combustion fuel that consists of a hydrocarbon jet fuel containing between about 25 pounds and about 250 pounds per thousand barrels of fuel of an additive composition that consists essentially of about 4 percent, by weight of the additive composition, of N,N'-disalicylaldimine of propylene diamine, and about 96 percent, by weight of the additive composition, of di(isotridecyl) azelate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,580,005	Cypers et al.	Dec. 25, 1951
2,747,979	Thompson	May 29, 1956
2,922,706	Durr et al.	Jan. 26, 1960
2,993,773	Stromberg	July 25, 1961