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STABILIZED 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, a 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 nozzles.

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 Shiff'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:

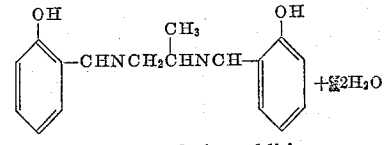
HO—A—CH=N—R—N=CH—A—OH

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 1-olefin-maleic anhydride heteropolymers 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 Shiff'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. 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 is the full, neutral alkyl esters of certain olefin-maleic anhydride heteropolymers. The heteropolymer is produced by copolymerizing equimolar amounts of a 1-olefin and maleic acid anhydride. The 1-olefin reactant should contain between about 2 carbon atoms and about 18 carbon atoms per molecule. The reactants are heated together, either in bulk, or in the presence of a suitable solvent, such as, benzene, toluene, xylene, dioxane, or carbon tetrachloride, at temperatures varying between about 100° C. and about 175° C. Preferably, the copolymerization is carried out in the presence of a peroxide catalyst, such as benzoyl peroxide. The amount of peroxide used is between about one percent and about 5 percent, by weight of the rectants. The time required to complete the copolymerization varies between about one hour and about 10 hours.

The ester component is made by fully esterifying the heteropolymer with an aliphatic alcohol containing between about 4 carbon atoms and about 20 carbon atoms per molecule. The branched-chain alkyl alcohols are particularly preferred. Non-limiting examples of the esterifying alcohols are butanol; 2-methyl-propanol; 2,2-dimethyl-propanol; amyl alcohol; isoamyl alcohol; hexanol; 3-methyl-pentanol; 2-ethylhexanol; isodecanol; decanol; dodecanol; iso-tridecanol; hexadecanol; hexadecenol; octadecanol; octadecenol; and eicosanol. 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 two moles of the alcohol with the acid anhydride, with or without the use of catalysts. For example, the esters of 1-olefin-maleic anhydride copolymers can be prepared by heating at 100–200° C. from 1 to 6 hours one mole of 1-olefin-maleic anhydride copolymer with 2 moles of alcohol with the elimination of one mole of water. The esterification is carried out in the presence of a catalyst such as p-toluene sulfonic acid monohydrate or sulfuric acid. The amount of p-toluene sulfonic acid monohydrate or sulfuric acid used is from 0.1 percent to 5 percent by weight of the reactants. Likewise, there can be used 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 little importance to the additive compositions of this invention or to the 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 component, 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 boling 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 0.02 percent. In terms of weight per unit volume of fuel, the concentration of additive composition will vary between about 2.0 pounds per thousand barrels of fuel and about 2000 pounds per thousand barrels of fuel. Preferably, the concentration will vary between about 25 pounds per thousand barrels of fuel and about 50 pounds per thousand barrels of fuel.

The following examples are for the purpose of illustrating the additive compositions of this invention and demonstrating the effectiveness thereof in rendering jet fuels thermally stable. It must be strictly understood that the invention is not to be limited to the particular compositions shown or to the operations or manipulations involved. A variety of other additive compositions as described hereinbefore can be used as those skilled in the art will readily appreciate.

In the examples, "Olefin A" is a mixture containing 8.2 weight percent 1-hexene, 7 weight percent 1-decene, 48 weight percent 1-dodecene, 17.5 weight percent 1-tetradecene, 8.8 weight percent 1-hexadecene, and 10.5 weight percent 1-octadecene.

"Olefin B" is a mixture containing 3 weight percent 1-decene, 66 weight percent 1-dodecene, 20 weight percent 1-tetradecene, 10.5 weight percent 1-hexadecene, and 0.5 weight percent 1-octadecene.

"Olefin C" is a mixture containing 6 weight percent 1-dodecene, 14 weight percent 1-tetradecene, 42 weight percent 1-hexadecene, 33 weight percent 1-octadecene, and 5 weight percent 1-eicosene.

EXAMPLE 1

A mixture of 70 grams (0.5 mole) of 1-decene, 49 grams (0.5 mole) of maleic anhydride, 1.19 grams (1%) of benzoyl peroxide and 25 cc. xylene as a diluent was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic and the temperature rose rapidly to 150° C., then dropped. The mixture was stirred at 150° C. for 10 hours to complete copolymerization. The copolymer was diluted with 100 cc. of xylene. To the copolymer was added at room temperature 150 grams (1 mole) of primary isodecyl alcohol and 0.55 gram (0.2%) of p-toluene sulfonic acid monohydrate with stirring. The mixture was refluxed at 145–175° C. until water stopped coming over (about 4 hours). The amount of water collected during the reaction was 7 cc., theory 9 cc. The reaction product was filtered through Hiflo clay. The final product, the di-isodecyl ester of 1-decene-maleic anhydride copolymer, which contained 8% xylene was blended with N,N′ disalicylaldimine of propylene diamine (4% by wt. of ester) to form an additive composition.

EXAMPLE 2

A mixture of 70 grams (0.5 mole) of 1-decene, 49 grams (0.5 mole) of maleic anhydride, 1.19 grams (1%) of benzoyl peroxide, and 25 cc. of xylene as a diluent was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic and the temperature rose rapidly to 155° C., then dropped. The mixture was stirred at 150° C. for 8 hours to complete copolymerization. The copolymer was diluted with 100 cc. of xylene. To the copolymer was added at room temperature 210 grams (1 mole + 10 grams excess) of primary isotridecyl alcohol and 2.75 grams (1%) of p-toluene sulfonic acid monohydrate with stirring. The mixture was refluxed at 145° C. for 4 hours. The temperature was then gradually raised to 200° C. and was held there until water stopped coming over (about 3 hours). The amount of water collected during the reaction was 8 cc., theory 9 cc. The reaction product was diluted with 200 cc. of benzene, water-washed until neutral, filtered and topped to 150° C. to remove the benzene. The final product, the di-isotridecyl ester of 1-decene-maleic anhydride copolymer, was blended with N,N′ disalicylaldimine of propylene diamine (4% by weight of ester) to form an additive composition.

EXAMPLE 3

A mixture of 84 grams (0.5 mole) of 1-dodecene, 49 grams (0.5 mole) of maleic anhydride, 2 grams (1.5%) of benzoyl peroxide and 66 cc. of xylene as a diluent was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic and the temperature rose rapidly to 150° C., then dropped. The mixture was stirred at 150° C. for 4 hours to complete copolymerization. The copolymer was diluted with 50 cc. of xylene and 50 cc. of benzene. To the copolymer was added 158 grams (1 mole) of primary isodecyl alcohol and 4.3 grams (1.5%) of p-toluene sulfonic acid monohydrate. The mixture was refluxed at 132° C. for 4 hours. The temperature was then gradually raised to 185° C. and was held there until water stopped coming over (about 3 hours). The amount of water collected during the reaction was 9 cc., theory 9 cc. The final product, the di-isodecyl ester of 1-dodecene-maleic anhydride copolymer, was blended with N,N′ disalicylaldimine of propylene diamine (4% by weight of ester) to form an additive composition.

EXAMPLE 4

A mixture of 84 grams (0.5 mole) of 1-dodecene, 49 grams (0.5 mole) of maleic anhydride, 1.33 grams (1%) of benzoyl peroxide and 33 cc. of xylene as a diluent was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic and the temperature rose rapidly to 150° C., then dropped. The mixture was stirred at 150° C. for 10 hours to complete copolymerization. The copolymer was diluted with 100 cc. of xylene. To the copolymer was added 220 grams (1 mole + 20 grams excess) of primary isotridecyl alcohol and 3.33 grams (1%) of p-toluene sulfonic acid monohydrate. The mixture was refluxed at 145° C. for 4 hours and then at 200° C. for 3 hours. The amount of water collected during the reaction was 9 cc., theory 9 cc. The reaction product was diluted with approximately 300 cc. of benzene, water-washed until neutral and was topped to 150° C. under 1.5 mm. The final product, the

di-isotridecyl ester of 1-dodecene-maleic anhydride copolymer, was blended with N,N' disalicylaldimine of propylene diamine (4% by weight of ester) to form an additive composition.

EXAMPLE 5

A mixture of 126 grams (0.5 mole) of 1-octadecene, 49 grams (0.5 mole) of maleic anhydride, 2.63 grams (1.5%) of benzoyl peroxide and 35 cc. of xylene as a diluent was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic and the temperature rose rapidly to 156° C., then dropped. The mixture was stirred at 150° C. for 10 hours to complete copolymerization. The copolymer was diluted with 100 cc. of xylene. To the copolymer was added 210 grams (1 mole + 10 grams excess) of primary isotridecyl alcohol and 5.5 grams (1.5%) of p-toluene sulfonic acid monohydrate. The mixture was refluxed at 145° C. for 2 hours and then at 175–200° C. for 4 hours. The amount of water collected during the reaction was 9 cc., theory 9 cc. The reaction product was water-washed until neutral and topped to 175° C. under house vacuum. The final product, the di-isotridecyl ester of 1-octadecene-maleic anhydride copolymer, was blended with N,N' disalicylaldimine of propylene diamine (4% by weight of ester) to form an additive composition.

EXAMPLE 6

A mixture of 115 grams (0.5 mole) of Olefin C, 49 grams (0.5 mole) of maleic anhydride, 2.5 grams (1.5%) of benzoyl peroxide and 16 grams of xylene as a diluent was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic and the temperature rose rapidly to 142° C., then dropped. The mixture was stirred at 150° C. for 5 hours to complete copolymerization. The copolymer was diluted with 100 cc. of xylene. To the copolymer was added 158 grams (1 mole) of primary isodecyl alcohol and 6.5 grams (2%) of p-toluene sulfonic acid monohydrate. The mixture was gradually heated to 185° C., and was held at 185° C. until water stopped coming over (about 5 hours). The amount of water collected during the reaction was 9 cc., theory 9 cc. The final product, the di-isodecyl ester of Olefin C-maleic anhydride copolymer, was blended with N,N' disalicylaldimine of propylene diamine (4% by weight of ester) to form an additive composition.

EXAMPLE 7

A mixture of 115 grams (0.5 mole) of Olefin C, 49 grams (0.5 mole) of maleic anhydride, 2.5 grams (1.5%) of benzoyl peroxide and 16 grams of xylene was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic and the temperature rose rapidly to 162° C., then dropped. The mixture was stirred at 150° C. to complete copolymerization (5 hours). The copolymer was diluted with 100 cc. of xylene. To the copolymer was added, at room temperature, 200 grams (1 mole) of primary isotridecyl alcohol and 5.5 grams (1.5%) of p-toluene sulfonic acid monohydrate with stirring. The mixture was gradually heated to 185° C. and was held at 185° C. until water stopped coming over (about 5 hours). The amount of water collected during the reaction was 9 cc., theory 9 cc. The final product, the di-isotridecyl ester of Olefin C-maleic anhydride copolymer, was blended with N,N' disalicylaldimine of propylene diamine (4% by weight of ester) to form an additive composition.

EXAMPLE 8

A mixture of 105 grams (0.5 mole + 9 grams excess) of Olefin B, 49 grams (0.5 mole) of maleic anhydride, 1.5 grams (1%) of benzoyl peroxide and 50 cc. of xylene as a diluent was stirred at 75–80° C. for 3 hours. The temperature was gradually raised to 150° C. and was held at 150° C. for 3 hours to complete copolymerization. The copolymer was diluted with 100 cc. of xylene. To the copolymer was added at room temperature 158 grams (1 mole) of primary isodecyl alcohol and 4.6 grams (1.5%) of p-toluene sulfonic acid monohydrate with stirring. The mixture was gradually heated to 175° C. and was held there until water stopped coming over (about 6 hours). The amount of water collected during the reaction was 9 cc., theory 9 cc. The reaction product was water-washed until neutral and topped to 175° C. under house vacuum. The final product, the di-isodecyl ester of Olefin B-maleic anhydride copolymer, was blended with N,N' disalicylaldimine of propylene diamine (4% by weight of ester) to form an additive composition.

EXAMPLE 9

A mixture of 95.5 grams (0.5 mole) of Olefin B, 49 grams (0.5 mole) of maleic anhydride, 1.44 grams (1%) of benzoyl peroxide and 30 cc. of xylene as a diluent was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic and the temperature rose rapidly to 148° C., then dropped. The mixture was stirred at 150° C. for 10 hours to complete copolymerization. The copolymer was diluted with 100 cc. of xylene. To the copolymer was added 220 grams (1 mole + 20 grams excess) of primary isotridecyl alcohol and 3.5 grams (1%) of p-toluene sulfonic acid monohydrate at room temperature with stirring. The mixture was gradually heated to 200° C. and was held at 200° C. until water stopped coming over (about 6 hours). The amount of water collected during the reaction was 9 cc., theory 9 cc. The reaction product was water-washed until neutral, filtered and topped to 175° C. under a pressure of 1.75 mm. of mercury. The final product, the di-isotridecyl ester of Olefin B-maleic anhydride copolymer, was blended with N,N' disalicylaldimine of propylene diamine (4% by weight of ester) to form an additive composition.

EXAMPLE 10

A mixture of 99 grams (0.5 mole + 9 grams excess) of Olefin A, 49 grams (0.5 mole) of maleic anhydride, 1.39 grams (1%) of benzoyl peroxide and 50 cc. of xylene as a diluent was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic and the temperature rose rapidly to 153° C., then dropped. The mixture was stirred at 150° C. for 4 hours to complete copolymerization. The copolymer was diluted with 100 cc. of xylene. To the copolymer was added 158 grams (1 mole) of primary isodecyl alcohol and 4.44 grams (1.5%) of p-toluene sulfonic acid monohydrate. The mixture was refluxed at 142° C. for 3 hours. The temperature was then gradually raised to 175° C. and held there until water stopped coming over (about 3 hours). The amount of water collected during the reaction was 9 cc., theory 9 cc. The reaction product was water-washed until neutral. The final product, the di-isodecyl ester of Olefin A-maleic anhydride copolymer, was blended with N,N' di-salicylaldimine of propylene diamine (4% by weight of ester) to form an additive composition.

EXAMPLE 11

A mixture of 90 grams (0.5 mole) of Olefin A, 49 grams (0.5 mole) of maleic anhydride, 1.39 grams (1%) of benzoyl peroxide and 45 cc. of xylene as a diluent was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic and the temperature rose rapidly to 164° C., then dropped. The mixture was stirred at 150° C. for 10 hours to complete copolymerization. The copolymer was diluted with 100 cc. of xylene. To the copolymer was added 220 grams (1 mole + 20 grams excess) of primary isotridecyl alcohol and 3.4 grams (1%) of p-toluene sulfonic and monohydrate at room temperature with stirring. The

mixture was refluxed at 150° C. for 3 hours. The temperature was then gradually raised to 200° C. and was held there until water stopped coming over (about 6 hours). The amount of water collected during the reaction was 9 cc., theory 9 cc. The reaction product was water-washed until neutral and topped to 150° C. under a pressure of 2.5 mm. of mercury. The final product, the di-isotridecyl ester of Olefin A-maleic anhydride copolymer, was blended with N,N' disalicylaldimine of propylene diamine (4% by weight of ester) to form an additive composition.

EXAMPLE 12

An ethylene-maleic anhydride copolymer was produced using the method of United States Letters Patent No. 2,854,357, particularly Example 4. This copolymer anhydride had a specific viscosity of 0.65 in one percent solution in dimethyl formamide. A mixture of 50.4 grams (0.4 mole) of this copolymer anhydride, 126.4 grams (0.8 mole) of isodecanol, and 2 grams p-toluene sulfonic acid monohydrate was refluxed at 150° C. in xylene solution until about 9 cc. water evolved. The mixture was water-washed until neutral and topped to remove xylene. The product, di-isodecyl ester of ethylene-maleic anhydride copolymer was blended with N,N'-disalicylaldimine of propylene diamine (4% by weight of ester) to form an additive composition.

EXAMPLE 13

An ethylene-maleic anhydride copolymer was produced using the method of United States Letters Patent No. 2,854,357, particularly Example 4. This copolymer anhydride had a specific viscosity of 0.65 in one percent solution in dimethyl formamide. A mixture of 50.4 grams (0.4 mole) of this copolymer anhydride, 160 grams (0.8 mole) of isotridecanol, and 2 grams p-toluene sulfonic acid monohydrate was refluxed at 150° C. in xylene solution until about 9 cc. of water evolved. The mixture was water-washed until neutral and topped free of xylene. The product, a di-isotridecyl ester of ethylene-maleic anhydride copolymer was blended with N,N'-disalicylaldimine of propylene diamine (4% by weight of ester) to form an additive composition.

The test method used for determining the thermal stability characteristics of aviation turbine fuels is a method developed by the Coordinating Research Council which was 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 deposit; 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 14

A base 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 15

Another test was run in the fuel coker test, using the base fuel defined in Example 14, which contained 28.8 pounds per thousand barrels of fuel of the di-isodecyl ester of decene-maleic anhydride copolymer described in Example 1. Pertinent test results are also set forth in Table I.

EXAMPLE 16

The base fuel described in Example 14 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 the di-isodecyl ester of decene-maleic anhydride copolymer (i.e. 30 pounds per thousand barrels of fuel of the additive composition described in Example 1) 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 14 and 15. Pertinent test results are set forth in Table I.

Table I

Example	Fuel Tested	Conc., lbs./1000 bbls.	Filter Plugging		Preheater Deposits at 300 Min. Rating
			Press. Drop, Inches, Hg	Time, Min.	
14	Uninhibited jet fuel	0	25.0	100	Code 4.
	Fuel+N,N' disalicylaldimine of propylene diamine.	1.2	25.0	263	Code 3.
15	Fuel+Ester of Example 1.	28.8	0.35	300	Code 4.
16	Fuel+Composition of Example 1.	30	0.0	300	Code 0.

It is to be noted that the metal deactivator was not appreciably effective in preventing filter plugging and pre-

heater deposits. The neutral ester had effect to reduce filter plugging but no effect on 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 14, 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.

Table II

Inhibitor	Conc., lb./1000 bbls.	Filter Plugging		Preheater Deposits at 300 Min. Rating
		Press. Drop, Inches, Hg	Time, Min.	
Uninhibited jet fuel	0	25.0	100	Code 4.
Fuel+Ex. 2	30	0.0	300	Code 0.
Fuel+Ex. 3	30	0.0	300	Code 0.
Fuel+Ex. 4	30	0.0	300	Code 0.
Fuel+Ex. 5	30	0.0	300	Code 2.
Fuel+Ex. 6	50	0.0	300	Code 0.
Fuel+Ex. 7	50	0.0	300	Code 0.
Fuel+Ex. 8	30	0.0	300	Code 0.
Fuel+Ex. 9	15	0.1	300	Code 2.
Fuel+Ex. 10	30	0.0	300	Code 0.
Fuel+Ex. 11	30	0.0	300	Code 0.
Fuel+Ex. 12	30	0.0	300	Code 0.
Fuel+Ex. 13	30	0.1	300	Code 0.

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. A synergistic additive composition consisting essentially of between about one 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 alkyl radical having the 2 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 a full, neutral alkyl ester of a 1-olefin-maleic anhydride heteropolymer wherein the esterifying alcohol contains between about 4 carbon atoms and about 20 carbon atoms and the 1-olefin contains between about 2 carbon atoms and about 18 carbon atoms.

2. A synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N′-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of a full neutral, branched-chain alkyl ester of a 1-olefin-maleic anhydride heteropolymer, wherein the esterifying branched-chain alkanol contains between about 4 carbon atoms and about 20 carbon atoms and the 1-olefin contains between about 2 carbon atoms and about 18 carbon atoms.

3. A synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N′-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isodecyl ester of 1-decene-maleic anhydride heteropolymer.

4. A synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N′-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isotridecyl ester of 1-decene-maleic anhydride heteropolymer.

5. A synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N′-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isodecyl ester of 1-olefin-maleic anhydride heteropolymer, wherein the 1-olefin is a mixture, by weight, of about 8.2 percent 1-hexene, about 7 percent 1-decene, about 48 percent 1-dodecene, about 17.5 percent 1-tetradecene, about 8.8 percent 1-hexadecene, and about 10.5 percent 1-octadecene.

6. A synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N′-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isotridecyl ester of 1-olefin-maleic anhydride heteropolymer, wherein the 1-olefin is a mixture, by weight, of about 8.2 percent 1-hexene, about 7 percent 1-decene, about 48 percent 1-dodecene, about 17.5 percent 1-tetradecene, about 8.8 percent 1-hexadecene, and about 10.5 percent 1-octadecene.

7. A synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N′-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isodecyl ester of 1-olefin-maleic anhydride heteropolymer, wherein the 1-olefin is a mixture, by weight, of about 3 percent 1-decene, about 66 percent 1-dodecene, about 20 percent 1-tetradecene, about 10.5 percent 1-hexadecene, and about 0.5 percent 1-octadecene.

8. A synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N′-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isodecyl ester of 1-olefin-maleic anhydride heteropolymer, wherein the 1-olefin is a mixture, by weight, of about 6 percent 1-dodecene, about 14 percent 1-tetradecene, about 42 percent 1-hexadecene, about 33 percent 1-octadecene, and about 5 percent 1-eicosene.

9. A synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N′-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isotridecyl ester of 1-olefin-maleic anhydride heteropolymer, wherein the 1-olefin is a mixture, by weight, of about 6 percent 1-dodecene, about 14 percent 1-tetradecene, about 42 percent 1-hexadecene, about 33 percent 1-octadecene, and about 5 percent 1-eicosene.

10. A synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N′-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isodecyl ester of 1-dodecene-maleic anhydride heteropolymer.

11. A synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N′-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isotridecyl ester of 1-dodecene-maleic anhydride heteropolymer.

12. A synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N'-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isotridecyl ester of ethylene-maleic anhydride heteropolymer.

13. A jet fuel composition consisting essentially of a liquid hydrocarbon jet combustion fuel, said jet combustion fuel having an initial boiling point of at least about 100° F. and an end boiling point as high as about 750° F., containing between about 2 pounds per thousand barrels of fuel and about 2000 pounds per thousand barrels of fuel of a synergistic additive composition consisting essentially of between about one 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 alkyl radical having the 2 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 a full, neutral alkyl ester of a 1-olefin-maleic anhydride heteropolymer wherein the esterifying alcohol contains between about 4 carbon atoms and about 20 carbon atoms and the 1-olefin contains between about 2 carbon atoms and about 18 carbon atoms.

14. A jet fuel composition consisting essentially of a liquid hydrocarbon jet combustion fuel, said jet combustion fuel having an initial boiling point of at least about 100° F. and an end boiling point as high as about 750° F., containing between about 25 pounds per thousand barrels of fuel and about 50 pounds per thousand barrels of fuel of a synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N'-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of a full neutral, branched-chain alkyl ester of a 1-olefin-maleic anhydride heteropolymer, wherein the esterifying branched-chain alkanol contains between about 4 carbon atoms and about 20 carbon atoms and the 1-olefin contains between about 2 carbon atoms and about 18 carbon atoms.

15. A jet fuel composition consisting essentially of a liquid hydrocarbon jet combustion fuel, said jet combustion fuel having an initial boiling point of at least about 100° F. and an end boiling point as high as about 750° F., containing between about 25 pounds per thousand barrels of fuel and about 50 pounds per thousand barrels of fuel of a synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N'-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isodecyl ester of 1-decene-maleic anhydride heteropolymer.

16. A jet fuel composition consisting essentially of a liquid hydrocarbon jet combustion fuel, said jet combustion fuel having an initial boiling point of at least about 100° F. and an end boiling point as high as about 750° F., containing between about 25 pounds per thousand barrels of fuel and about 50 pounds per thousand barrels of fuel of a synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N'-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isotridecyl ester of 1-decane-maleic anhydride heteropolymer.

17. A jet fuel composition consisting essentially of a liquid hydrocarbon jet combustion fuel, said jet combustion fuel having an initial boiling point of at least about 100° F. and an end boiling point as high as about 750° F., containing between about 25 pounds per thousand barrels of fuel and about 50 pounds per thousand barrels of fuel of a synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N'-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isodecyl ester of 1-olefin-maleic anhydride heteropolymer, wherein the 1-olefin is a mixture, by weight, of about 8.2 percent 1-hexene, about 7 percent 1-decene, about 48 percent 1-dodecene, about 17.5 percent 1-tetradecene, about 8.8 percent 1-hexadecene, and about 10.5 percent 1-octadecene.

18. A jet fuel composition consisting essentially of a liquid hydrocarbon jet combustion fuel, said jet combustion fuel having an initial boiling point of at least about 100° F. and an end boiling point as high as about 750° F., containing between about 25 pounds per thousand barrels of fuel and about 50 pounds per thousand barrels of fuel of a synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N'-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isotridecyl ester of 1-olefin-maleic anhydride heteropolymer, wherein the 1-olefin is a mixture, by weight, of about 8.2 percent 1-hexene, about 7 percent 1-decene, about 48 percent 1-dodecene, about 17.5 percent 1-tetradecene, about 8.8 percent 1-hexadecene, and about 10.5 percent 1-octadecene.

19. A jet fuel composition consisting essentially of a liquid hydrocarbon jet combustion fuel, said jet combustion fuel having an initial boiling point of at least about 100° F. and an end boiling point as high as about 750° F., containing between about 25 pounds per thousand barrels of fuel and about 50 pounds per thousand barrels of fuel of a synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N'-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isodecyl ester of 1-olefin-maleic anhydride heteropolymer, wherein the 1-olefin is a mixture, by weight, of about 3 percent 1-decene, about 66 percent 1-dodecene, about 20 percent 1-tetradecene, about 10.5 percent 1-hexadecene, and about 0.5 percent 1-octadecene.

20. A jet fuel composition consisting essentially of a liquid hydrocarbon jet combustion fuel, said jet combustion fuel having an initial boiling point of at least about 100° F. and an end boiling point as high as about 750° F., containing between about 25 pounds per thousand barrels of fuel and about 50 pounds per thousand barrels of fuel of a synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N'-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isodecyl ester of 1-olefin-maleic anhydride heteropolymer, wherein the 1-olefin is a mixture, by weight, of about 6 percent 1-dodecene, about 14 percent 1-tetradecene, about 42 percent 1-hexadecene, about 33 percent 1-octadecene, and about 5 percent 1-eicosene.

21. A jet fuel composition consisting essentially of a liquid hydrocarbon jet combustion fuel, said jet combustion fuel having an initial boiling point of at least about 100° F. and an end boiling point as high as about 750° F., containing between about 25 pounds per thousand barrels of fuel and about 50 pounds per thousand barrels of fuel of a synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N'-di-

salicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isotridecyl ester of 1-olefin-maleic anhydride heteropolymer, wherein the 1-olefin is a mixture, by weight, of about 6 percent 1-dodecene, about 14 percent 1-tetradecene, about 42 percent 1-hexadecene, about 33 percent 1-octadecene, and about 5 percent 1-eicosene.

22. A jet fuel composition consisting essentially of a liquid hydrocarbon jet combustion fuel, said jet combustion fuel having an initial boiling point of at least about 100° F. and an end boiling point as high as about 750° F., containing between about 25 pounds per thousand barrels of fuel and about 50 pounds per thousand barrels of fuel of a synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N'-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isodecyl ester of 1-dodecene-maleic anhydride heteropolymer.

23. A jet fuel composition consisting essentially of a liquid hydrocarbon jet combustion fuel, said jet combustion fuel having an initial boiling point of at least about 100° F. and an end boiling point as high as about 750° F., containing between about 25 pounds per thousand barrels of fuel and about 50 pounds per thousand barrels of fuel of a synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N'-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isotridecyl ester of 1-dodecene-maleic anhydride heteropolymer.

24. A jet fuel composition consisting essentially of a liquid hydrocarbon jet combustion fuel, said jet combustion fuel having an initial boiling point of at least about 100° F. and an end boiling point as high as about 750° F., containing between about 25 pounds per thousand barrels of fuel and about 50 pounds per thousand barrels of fuel of a synergistic additive composition consisting essentially of between about 2 percent and about 5 percent, by weight of the additive composition, of the N,N'-disalicylaldimine of propylenediamine and between about 98 percent and about 95 percent, by weight of the additive composition, of the di-isotridecyl ester of ethylene-maleic anhydride heteropolymer.

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