3,115,483
Patented Dec. 24, 1963

3,115,483

STABILIZED JET COMBUSTION FUELS

Paul Y. C. Gee, Woodbury, and Harry J. Andress, Jr., Pitman, N.J., assignors to Socony Mobil Oil Company, Inc., a corporation of New York

No Drawing. Original application Jan. 20, 1960, Ser. No. 3,484. Divided and this application Dec. 7, 1961, Ser. No. 157,822
13 Claims. (Cl. 260—78.5)

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.

The present application is a division of our copending application, Serial Number 3,484, filed January 20, 1960, and now Patent No. 3,051,562.

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 reaction product of certain partial esters with polyamines and a hydroxyaromatic aldehyde 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 esters and certain metal deactivating compounds. A more specific object is to provide jet combustion fuels containing the reaction product of certain partial esters with polyamines and hydroxyaromatic aldehyde. 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 the reaction product obtained by (1) esterifying a 1:1 molar copolymer of a 1-olefin, having between about 2 carbon atoms and about 20 carbon atoms per molecule, and maleic acid anhydride with between about 1.5 moles and about 1.75 moles, per mole of said copolymer, of a primary or secondary aliphatic alcohol containing between about 4 carbon atoms and about 20 carbon atoms per molecule to produce a mixed mono- and di-ester product; (2) reacting said ester product with between about 0.25 mole and about 0.50 mole of a polyamine of the formula $H_2N(—R—NH)_n—H$, wherein R is ethylene or propylene and n is 1 or 2, and between about 0.25 mole and about 0.50 mole salicylaldehyde, per mole of said ester product; and a jet combustion fuel containing between about 0.001 percent and about one percent, by weight, of the said additive composition.

The mixed mono- and di-ester product used in the reaction products of this invention is the mixed mono- and di-aliphatic ester 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 20 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 75° 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 reactants. The time required to complete the copolymerization varies between about one hour and about 10 hours.

The mixed mono- and di-aliphatic ester is made by esterifying the heteropolymer with a primary or secondary 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; hexenol; 3-methylpentanol; 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 a mixed mono- and di-aliphatic ester. Accordingly, the alcohol reactant is reacted with the olefin-maleic anhydride in amounts of between about 1.5 moles and about 1.75 moles per mole of olefin-maleic anhydride copolymer.

As will readily be appreciated by those familiar with the art the ester can be made by any of the known methods for preparing esters of carboxylic acids. For example, the mixed esters of 1-olefin-maleic anhydride copolymers can be prepared by heating at 100–200° C., from 1 to 10 hours, one mole of 1-olefin-maleic anhydride copolymer with 1.5–1.75 moles of alcohol with the elimination of 0.5–0.75 mole of water. The esterification is suitably 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, or removal of water by the use of applied vacuum. It is to be understood that the particular method used to prepare the mixed ester component is of little importance to the additive compositions of this invention or to the jet combustion fuels containing them.

The mixed mono- and di-aliphatic ester component is then further reacted with, per mole of mixed ester, between about 0.25 mole and about 0.5 mole of a polyamine reactant as hereinafter defined and between about 0.25 mole and about 0.5 mole of salicylaldehyde. The polyamine reactant has the formula $H_2N(—RNH)_n—H$, wherein R is ethylene or propylene and n is 1 or 2. Examples of the polyamine reactant are ethylenediamine, propylenediamine, diethylenetriamine and dipropylenetriamine. The reaction between the copolymer ester, polyamine reactant, and salicylaldehyde is a condensation reaction accompanied by the formation of water of reaction. The reaction is suitably carried out at temperatures varying between about 90° C. and about 175° C. and for a period of time varying between about one hour and about 5 hours, or until water of condensation ceases to form. As was described in the case of the esterification step, various techniques of esterification (or condensation in general) are equally applicable to the reaction with amine and salicylaldehyde. Thus, for example, water can be removed by azeotropic distillation. Following both the esterification step and the step of reacting with amine and salicylaldehyde, it is desirable to water-wash. This ensures removal of any water-soluble matter that may remain following each step.

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, i.e., reaction product aforedescribed, that is added to the jet combustion fuels will vary between about 0.001 percent and about one 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 5.0 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 about 8.2 weight percent 1-hexene, about 7 weight percent 1-decene, about 48 weight percent 1-dodecene, about 17.5 weight percent 1-tetradecene, about 8.8 weight percent 1-hexadecene, and about 10.5 weight percent 1-octadecene.

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

Alcohol "C" is a mixture of normal aliphatic, monohydric alcohols containing about 2.8 weight percent decanol, about 61 weight percent dodecanol, about 21 weight percent tetradecanol, about 11 weight percent hexadecanol, an dabout 2.2 weight percent octadecanol.

Example 1

A mixture of 115 grams (0.5 mole) of olefin B, 49 grams (0.5 mole) of maleic anhydride, 2.5 grams (1.5%) of benzoyl peroxide and 25 cc. of xylene as diluent was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic, and the temperature rose rapidly to 161° C., then dropped. The mixture was stirred at 150–155° C. for 4 hours to complete copolymerization. To the copolymer was added, at room temperature with stirring, 65 grams (0.875 mole) of n-butyl alcohol, 6 grams (2.6%) of p-toluene sulfonic acid monhydrate and 200 cc. of benzene. The mixture was refluxed at 105° C. for 8 hours and 150° C. for 2 hours to form a mixture of mono-ester and di-ester. The amount of water collected during the esterification was 7 cc., theory 6.75 cc. The ester mixture was diluted with 200 cc. of benzene and water-washed until the water layer was neutral. To the water-washed ester mixture was added at room temperature with stirring 15.25 grams (0.125 mole) of salicylaldehyde and 7.5 grams (0.125 mole) of ethylenediamine. The mixture was refluxed at 95° C. for 2 hours and 150–155° C. for 2 hours. The amount of water collected during the reflux was 4.5 cc., theory 4.5 cc. The reaction product was diluted with 200 cc. of benzene, water-washed and topped to 165° C. under a pressure of 1 mm. of mercury.

Example 2

A mixture of 115 grams (0.5 mole) of olefin B, 49 grams (0.5 mole) of maleic anhydride, 2.5 grams (1.5%) of benzoyl peroxide and 25 cc. of xylene as diluent was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic, and the temperature rose rapidly to 178° C., then dropped. The mixture was stirred at 150° C. for 4 hours to complete copolymerization. The copolymer was diluted with 200 cc. of toluene. To the copolymer was added at room temperature with stirring 114 grams (0.875 mole) of 2-ethyl-hexyl alcohol and 5.56 grams (2%) of p-toluene sulfonic acid monohydrate. The mixture was refluxed at 132° C. for 3 hours, 150° C. for 4 hours and 175° C. for one hour to form a mixture of mono-ester and di-ester. The amount of water collected during the reflux was 7.5 cc., theory 6.75 cc. The ester mixture was diluted with 150 cc. of benzene and water-washed until the water layer was neutral. To the water-washed ester mixture was added at room temperature with stirring 15.25 grams (0.125 mole) of salicylaldehyde and 7.5 grams (0.125 mole) of ethylenediamine. The mixture was refluxed at 95–105° C. for 2 hours and 150–165° C. for 2 hours. The amount of water collected during the reflux was 4.5 cc., theory 4.5 cc. The reaction product was diluted with 200 cc. of benzene, water-washed and topped to 175° C. under a pressure of 1.5 mm. of mercury.

Example 3

A mixture of 115 grams (0.5 mole) of olefin B, 49 grams (0.5 mole) of maleic anhydride, 2.5 grams (1.5%) of benzoyl peroxide and 25 cc. of xylene as diluent was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic, and the temperature rose rapidly to 178° C., then dropped. The mixture was stirred at 150–155° C. for 4 hours to complete copolymerization. The copolymer was diluted with 250 cc. of xylene. To the copolymer was added at room temperature 138 grams (0.875 mole) of isodecyl alcohol and 6.04 grams (2%) of p-toluene sulfonic acid monohydrate. The mixture was refluxed at 150° C. for 4 hours and 175° C. for 2 hours to form a mixture of mono-ester and di-ester. The amount of water collected during the esterification was 7 cc., theory 6.75 cc. The ester mixture was diluted with 150 cc. of benzene and water-washed until the water layer was neutral. To the water-washed ester mixture was added at room temperature with stirring 15.25 grams (0.125 mole) of salicylaldehyde and 7.5 grams (0.125 mole) of ethylenediamine. The mixture was refluxed at 95° C. for 3 hours and 150–155° C. for 2 hours. The amount of water collected during the reaction was 5 cc., theory 4.5 cc. The reaction product was diluted with 300 cc. of benzene, water-washed and topped to 150° C. under a pressure of 1.5 mm. of mercury.

Example 4

A mixture of 115 grams (0.5 mole) of olefin B, 49 grams (0.5 mole) of maleic anhydride, 2.5 grams (1.5%) of benzoyl peroxide and 25 cc. of xylene as diluent was gradually heated with stirring. Heat was turned off at

100° C. The reaction was exothermic, and the temperature rose rapidly to 154° 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 at room temperature 175 grams (0.875 mole) of primary isotridecyl alcohol and 3.4 grams (1%) of p-toluene sulfonic acid monohydrate. The mixture was heated under reflux at 150° C. for 5 hours and 185° C. for 2 hours to form a mixture of mono-ester and di-ester. The amount of water collected during the reflux was 6.75 cc., theory 6.75 cc. The ester mixture was diluted with 200 cc. of benzene. To the ester mixture was added at room temperature with stirring 15.25 grams (0.125 mole) of salicylaldehyde and 7.5 grams (0.125 mole) of ethylenediamine. The mixture was refluxed at 90° C. for 3 hours and at 175° C. for 30 minutes. The amount of water collected during the reaction was 4.5 cc., theory 4.5 cc. The product was topped to 175° C. under the house vacuum to remove the xylene.

Example 5

A mixture of 115 grams (0.5 mole) of olefin B, 49 grams (0.5 mole) of maleic anhydride, 1.65 grams (1%) of benzoyl peroxide and 30 cc. of xylene as 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 4 hours to complete copolymerization. The copolymer was diluted with 150 cc. of toluene. To the copolymer was added at room temperature 175 grams (0.875 mole) of alcohol C and 5.5 grams (1.5%) of p-toluene sulfonic acid monohydrate. The mixture was refluxed at 130–150° C. for 3 hours to form a mixture of mono-ester and di-ester. The amount of water collected during the reflux was 7 cc., theory 6.75 cc. The ester mixture was diluted with 100 cc. of benzene. To the ester mixture was added gradually at room temperature with stirring 7.5 grams (0.125 mole) of ethylenediamine and 15.25 grams (0.125 mole) of salicylaldehyde. The mixture was refluxed at 102° C. for 2 hours and 150° C. for 3 hours. The reaction product was diluted with 500 cc. of benzene, water-washed and topped to 160° C. under a pressure of 1.5 mm. of mercury.

Example 6

A mixture of 115 grams (0.5 mole) of olefin B, 49 grams (0.5 mole) of maleic anhydride, 2.5 grams (1.5%) of benzoyl peroxide and 25 cc. of xylene as 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 100 cc. of xylene. To the copolymer was added at room temperature with stirring 216 grams (0.875 mole) of octadecenyl alcohol and 7.6 grams (2%) of p-toluene sulfonic acid monohydrate. The mixture was refluxed at 150° C. for 3 hours and 175° C. for 2 hours to form a mixture of mono-ester and di-ester. The amount of water collected during the esterification was 7 cc., theory 6.75 cc. The ester mixture was diluted with 200 cc. of benzene and water-washed until the water layer was neutral. To the water-washed ester mixture was added at room temperature with stirring 15.25 grams (0.125 mole) of salicylaldehyde and 7.5 grams (0.125 mole) of ethylenediamine. The mixture was refluxed at 95–105° C. for 3 hours and 155° C. for 2 hours. The amount of water collected during the reaction was 4.5 cc., theory 4.5 cc. The reaction product was water-washed and topped to 175° C. under a pressure of 0.5 mm. of mercury.

Example 7

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 was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic, and the temperature rose rapidly to 152° C., then dropped. The mixture was stirred 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 with stirring 175 grams (0.875 mole) of isotridecyl alcohol and 2.94 grams (1%) of p-toluene sulfonic acid monohydrate. The mixture was gradually heated to 175° C., and held at 175° C. for 3 hours to complete the formation of a mixture of mono-ester and di-ester. The amount of water collected during the esterification was 6 cc., theory 6.75 cc. The ester mixture was diluted with 100 cc. of benzene. To the ester mixture was added at room temperature with stirring 15.25 grams (0.125 mole) of salicylaldehyde and 7.5 grams (0.125 mole) of ethylenediamine. The mixture was gradually heated to 150 C., and the temperature was held at 150° C. until water stopped coming over (about 2 hours). The amount of water collected during the reaction was 4.5 cc., theory 4.5 cc. The reaction product was diluted with 100 grams of xylene and was filtered through Hiflo clay.

Example 8

A mixture of 84 grams (0.5 mole) of 1-dodecene, 49 grams (0.5 mole) of maleic anhydride, 2.66 grams (2%) of benzoyl peroxide and 25 cc. of xylene 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 150–155° C. for 3 hours to complete copolymerization. The copolymer was diluted with 250 cc. of xylene. To the copolymer was added at room temperature with stirring 175 grams (0.875 mole) of isotridecyl alcohol and 6.16 grams (2%) of p-toluene sulfonic acid monohydrate. The mixture was refluxed at 150° C. for 4 hours and 175° C. for 2 hours to form a mixture of mono-ester and di-ester. The amount of water collected during the reflux was 7 cc., theory 6.75 cc. The ester mixture was diluted with 200 cc. of benzene and water-washed until the water layer was neutral. To the water-washed ester mixture was added at room temperature with stirring 15.25 grams (0.125 mole) of salicylaldehyde and 7.5 grams (0.125 mole) of ethylenediamine. The mixture was refluxed at 95° C. for 2 hours and 150–155° C. for 2 hours. The amount of water collected during the reflux was 5 cc., theory 4.5 cc. The reaction product was diluted with 300 cc. of benzene, water-washed and topped to 158° C. under a pressure of 1.5 mm. of mercury.

Example 9

A mixture of 127 grams (0.5 mole+12 grams excess) of olefin B, 49 grams (0.5 mole) of maleic anhydride, 1.64 grams (1%) of benzoyl peroxide and 50 cc. of xylene as diluent was stirred at 75–80° C. for 6 hours to complete copolymerization. The copolymer was diluted with 100 cc. of xylene. To the copolymer was added at room temperature with stirring 150 grams (0.75 mole) of isotridecyl alcohol and 3.14 grams (1%) of p-toluene sulfonic acid monohydrate. The mixture was refluxed at 150° C. for 4 hours and 175° C. for 2 hours to form a mixture of mono-ester and di-ester. The amount of water collected during the esterification was 4.5 cc., theory 4.5 cc. The ester mixture was diluted with 100 cc. of xylene and 150 cc. of benzene. To the ester mixture was added at room temperature with stirring 16.75 grams (0.125 mole+1.5 grams excess) of salicylaldehyde and 7.5 grams (0.125 mole) of ethylenediamine. The mixture was refluxed at 85–95° C. for 2 hours and 148° C. for 2 hours. The amount of water collected during the reflux was 5 cc., theory 4.5 cc. The product contained 22% xylene and was fluid at room temperature.

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 was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic, and the temperature rose rapidly to 149° 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 and 50 cc. of benzene. To the copolymer was added at room temperature with stirring 118.5 grams (0.75 mole) of isodecanol and 2.57 grams (1%) of p-toluene sulfonic acid monohydrate. The mixture was refluxed at 135% C. for 3 hours and 175° C. for 3 hours to form a mixture of mono-ester and di-ester. The amount of water collected during the esterification was 4.5 cc., theory 4.5 cc. The ester mixture was diluted with 200 cc. of benzene and water-washed. To the water-washed ester mixture was added at room temperature 16.75 grams (0.125 mole+1.5 grams excess) of salicylaldehyde and 7.5 grams (0.125 mole) of ethylenediamine. The mixture was refluxed at 85° C. for one hour and 150° C. for 2 hours. The amount of water collected during the reaction was 4.5 cc., theory 4.5 cc. The product which contained 12% xylene was filtered through Hiflo clay.

Example 11

A mixture of 115 grams (0.5 mole) of olefin B, 49 grams (0.5 mole) of maleic anhydride, 2.5 grams (1.5%) of benzoyl peroxide and 25 cc. of xylene as diluent was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic, and the temperature rose rapidly to 175° 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 and 50 cc. of benzene. To the copolymer was added at room temperature with stirring 175 grams (0.875 mole) of primary isotridecyl alcohol and 3.4 grams (1%) of p-toluene sulfonic acid monohydrate. The mixture was refluxed at 150° C. for 3 hours and 185° C. for 3 hours to form a mixture of mono-ester and di-ester. The amount of water collected during the esterification was 6.75 cc., theory 6.75 cc. The ester mixture was diluted with 200 cc. of benzene. To the ester mixture was added at room temperature with stirring 15.25 grams (0.125 mole) of salicylaldehyde and 9.25 grams (0.125 mole) of propylene diamine. The mixture was refluxed at 90° C. for one hour and 175° C. for 2 hours.

Example 12

A mixture of 115 grams (0.5 mole) of olefin B, 49 grams (0.5 mole) of maleic anhydride, 2.5 grams (1.5%) of benzoyl peroxide and 25 cc. of xylene as diluent was gradually heated with stirring. Heat was turned off at 100° C. The reaction was exothermic, and the temperature rose rapidly to 166° C., then dropped. The mixture was stirred at 150° C. for 4 hours to complete compolymerization. The copolymer was diluted with 100 cc. of xylene. To the copolymer was added at room temperature with stirring 175 grams (0.875 mole) of primary isotridecyl alcohol and 3.4 grams (1%) of p-toluene sulfonic acid monohydrate. The mixture was gradually heated to 175° C. and was refluxed at 175° C. for 4 hours to complete the formation of a mixture of mono-ester and di-ester. The amount of water collected during the esterification was 6.75 cc., theory 6.75 cc. The ester mixture was diluted with 150 cc. of benzene and 50 cc. of xylene. To the ester mixture was added at room temperature with stirring 15.25 grams (0.125 mole) of salicylaldehyde and 12.88 grams (0.125 mole) of diethylenetriamine. The mixture was gradually heated to 175° C. and was held at 175° C. until water stopped coming over (2 hours). The amount of water collected during the reaction was 4.5 cc., theory 4.5 cc. The product was filtered through Hiflo clay and was topped to 175° C. under house vacuum to remove the xylene.

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 the 300 minutes. The preheater deposits in the tests are evaluated according to a code rate varying from 0 to 4 wherein Code 0 means no visible deposits; Code 1, haze or dulling, no color; Code 2, barely visible discoloration; 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.

The base hydrocarbon jet combustion fuel used herein was a straight-run petroleum fraction boiling between about 325° F. and about 525° F. A portion of this base fuel, uninhibited was subjected to the Fuel Coker Test. Then, other portions of the base fuel were blended with the reaction products of the foregoing examples, and each blend so obtained was subjected to the Fuel Coker Test. Pertinent blend data and test results are set forth in the following table:

Inhibitor	Concn., lb./1,000 bbls.	Filter Plugging Press. Drop, Inches Hg	Time, Min.	Preheater Deposits at 300 Min. Rating
Uninhibited jet fuel	0	25.0	100	Code 4.
Fuel+Example 1	50	0.0	300	Code 0.
Fuel+Example 2	30	0.0	300	Code 1.
Fuel+Example 3	30	0.0	300	Code 0.
Fuel+Example 4	50	0.0	300	Code 0.
Fuel+Example 5	10	0.0	300	Code 0.
Fuel+Example 6	10	0.0	300	Code 0.
Fuel+Example 7	30	0.0	300	Code 0.
Fuel+Example 8	5	0.0	300	Code 0.
Fuel+Example 9	50	0.0	300	Code 0.
Fuel+Example 10	30	0.0	300	Code 1.
Fuel+Example 11	50	0.0	300	Code 3.
Fuel+Example 12	50	0.0	300	Code 3.

It will be noted that all the reaction products of this invention are effective jet fuel stabilizers. Some, however, are more effective than others, in that they are effective at lower concentrations.

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 comprising the reaction product obtained by (1) esterifying a 1:1 molar copolymer of a 1-olefin, having between about 2 carbon atoms and about 20 carbon atoms per molecule, and maleic acid anhydride with between about 1.5 moles and about 1.75 moles, per mole of said copolymer, of an aliphatic alcohol containing between about 4 carbon atoms and about 20 carbon atoms per molecule to produce a mixed mono- and di-ester product; (2) reacting said ester product with between about 0.25 mole and about 0.50 mole of a polyamine of the formula $H_2N(—R—NH)_n—H$, wherein R is selected from the group consisting of ethylene and propylene and n varies between 1 and 2, and between about 0.25 mole and about 0.50 mole salicylaldehyde, per mole of said ester product.

2. An additive composition comprising the reaction product obtained by (1) esterifying a 1:1 molar copolymer of a 1-olefin mixture, containing about 3 weight percent 1-decene, about 66 weight percent 1-dodecene, about 20 weight percent 1-tetradecene, about 10.5 weight percent 1-hexadecene, and about 0.5 weight percent 1-octadecene, and maleic acid anhydride with between about 1.5 moles and about 1.75 moles, per mole of said copolymer, of butanol to produce a mixed mono- and di-ester product; (2) reacting said ester product with between about 0.25 mole and about 0.50 mole of ethylenediamine and between about 0.25 mole and about 0.50 mole salicylaldehyde, per mole of said ester product.

3. An additive composition comprising the reaction product obtained by (1) esterifying a 1:1 molar copolymer of a 1-olefin mixture, containing about 3 weight percent 1-decene, about 66 weight percent 1-dodecene, about 20 weight percent 1-tetradecene, about 10.5 weight percent 1-hexadecene, and about 0.5 weight percent 1-octadecene, and maleic acid anhydride with between about 1.5 moles and about 1.75 moles, per mole of said copolymer of 2-ethylhexanol to produce a mixed mono- and di-ester product; (2) reacting said ester product with between about 0.25 mole and about 0.50 mole of ethylenediamine and between about 0.25 mole and about 0.50 mole salicylaldehyde, per mole of said ester product.

4. An additive composition comprising the reaction product obtained by (1) esterifying a 1:1 molar copolymer of a 1-olefin mixture, containing about 3 weight percent 1-decene, about 66 weight percent 1-dodecene, about 20 weight percent 1-tetradecene, about 10.5 weight percent 1-hexadecene, and about 0.5 weight percent 1-octadecene, and maleic acid anhydride with between about 1.5 moles and about 1.75 moles, per mole of said copolymer, isodecanol to produce a mixed mono- and di-ester product; (2) reacting said ester product with between about 0.25 mole and about 0.50 mole of ethylenediamine and between about 0.25 mole and about 0.50 mole salicylaldehyde, per mole of said ester product.

5. An additive composition comprising the reaction product obtained by (1) esterifying a 1:1 molar copolymer of a 1-olefin mixture, containing about 3 weight percent 1-decene, about 66 weight percent 1-dodecene, about 20 weight percent 1-tetradecene, about 10.5 weight percent 1-hexadecene, and about 0.5 weight percent 1-octadecene, and maleic acid anhydride with about 1.75 moles, per mole of said copolymer, of isotridecanol to produce a mixed mono- and di-ester product; (2) reacting said ester product with between about 0.25 mole and about 0.50 mole of ethylenediamine and between about 0.25 mole and about 0.50 mole salicylaldehyde, per mole of said ester product.

6. An additive composition comprising the reaction product obtained by (1) esterifying a 1:1 molar copolymer of a 1-olefin mixture, containing about 3 weight percent 1-decene, about 66 weight percent 1-dodecene, about 20 weight percent 1-tetradecene, about 10.5 weight percent 1-hexadecene, and about 0.5 weight percent 1-octadecene, and maleic acid anhydride with between about 1.5 moles and about 1.75 moles, per mole of said copolymer, of a mixture of normal aliphatic alcohols containing about 2.8 weight percent decanol, about 61 weight percent dodecanol, about 21 weight percent tetradecanol, about 11 weight percent hexadecanol, and about 2.2 weight percent octadecanol to produce a mixed mono- and di-ester product; (2) reacting said ester product with between about 0.25 mole and about 0.50 mole of ethylenediamine and between about 0.25 mole and about 0.50 mole salicylaldehyde, per mole of said ester product.

7. An additive composition comprising the reaction product obtained by (1) esterifying a 1:1 molar copolymer of a 1-olefin mixture, containing about 3 weight percent 1-decene, about 66 weight percent 1-dodecene, about 20 weight percent 1-tetradecene, about 10.5 weight percent 1-hexadecene, and about 0.5 weight percent 1-octadecene, and maleic acid anhydride with between about 1:5 moles and about 1.75 moles, per mole of said copolymer, of octadecenol to produce a mixed mono- and di-ester product; (2) reacting said ester product with between about 0.25 mole and about 0.50 mole of ethylenediamine and between about 0.25 mole and about 0.50 mole salicylaldehyde, per mole of said ester product.

8. An additive composition comprising the reaction product obtained by (1) esterifying a 1:1 molar copolymer of decene-1 and maleic acid anhydride with between about 1.5 moles and about 1.75 moles, per mole of said copolymer, of isotridecanol to produce a mixed mono- and di-ester product; (2) reacting said ester product with between about 0.25 mole and about 0.50 mole of ethylenediamine and between about 0.25 mole and about 0.50 mole salicylaldehyde, per mole of said ester product.

9. An additive composition comprising the reaction product obtained by (1) esterifying a 1:1 molar copolymer of dodecene-1 and maleic acid anhydride with between about 1.5 moles and about 1.75 moles, per mole of said copolymer, of isotridecanol to produce a mixed mono- and di-ester product; (2) reacting said ester product with between about 0.25 mole and about 0.50 mole of ethylenediamine and between about 0.25 mole and about 0.50 mole salicylaldehyde, per mole of said ester product.

10. An additive composition comprising the reaction product obtained by (1) esterifying a 1:1 molar copolymer of a 1-olefin mixture, containing about 3 weight percent 1-decene, about 66 weight percent 1-dodecene, about 20 weight percent 1-tetradecene, about 10.5 weight percent 1-hexadecene, and about 0.5 weight percent 1-octadecene, and maleic acid anhydride with about 1.5 moles, per mole of said copolymer, of isotridecanol to produce a mixed mono- and di-ester product; (2) reacting said ester product with between about 0.25 mole and about 0.50 mole of ethylenediamine and between about 0.25 mole and about 0.50 mole salicylaldehyde, per mole of said ester product.

11. An additive composition comprising the reaction product obtained by (1) esterifying a 1:1 molar copolymer of a 1-olefin mixture, containing about 8.2 weight percent 1-hexene, about 7 weight percent 1-decene, about 48 weight percent 1-dodecene, about 17.5 weight percent 1-tetradecene, about 8.8 weight percent 1-hexadecene, and about 10.5 weight percent 1-octadecene, and maleic acid anhydride with between about 1.5 moles and about 1.75 moles, per mole of said copolymer, of isodecanol to produce a mixed mono- and di-ester product; (2) reacting said ester product with between about 0.25 mole and about 0.50 mole of ethylenediamine and between about 0.25 mole and about 0.50 mole salicylaldehyde, per mole of said ester product.

12. An additive composition comprising the reaction product obtained by (1) esterifying a 1.1 molar copolymer of a 1-olefin mixture, containing about 3 weight percent 1-decene, about 66 weight percent 1-dodecene, about 20 weight percent 1-tetradecene, about 10.5 weight percent

1-hexadecene, and about 0.5 weight percent 1-octadecene, and maleic acid anhydride with between about 1.5 moles and about 1.75 moles, per mole of said copolymer, of isotridecanol to produce a mixed mono- and di-ester product; (2) reacting said ester product with between about 0.25 mole and about 0.50 mole of propylenediamine and between about 0.25 mole and about 0.50 mole salicylaldehyde, per mole of said ester proudct.

13. An additive composition comprising the reaction product obtained by (1) esterifying a 1:1 molar copolymer of a 1-olefin mixture, containing about 3 weight percent 1-decene, about 66 weight percent 1-dodecene, about 20 weight percent 1-tetradecene, about 10.5 weight percent 1-hexadecene, and about 0.5 weight percent 1-octadecene, and maleic acid anhydride with between about 1.5 moles and about 1.75 moles, per mole of said copolymer, isotridecanol to produce a mixed mono- and di-ester product; (2) reacting said ester product with between about 0.25 mole and about 0.50 mole of diethylenetriamine and between about 0.25 mole and about 0.50 mole salicylaldehyde, per mole of said ester product.

References Cited in the file of this patent

UNITED STATES PATENTS

2,938,775	Siegel	May 31, 1960
2,977,334	Zopf et al.	Mar. 16, 1961
2,984,654	Agus et al.	May 16, 1961