United States Patent

Sweeney et al.

[15] **3,652,239**

[45] **Mar. 28, 1972**

[54] THERMALLY STABLE JET FUEL COMPOSITION

[72] Inventors: **William M. Sweeney**, Wappingers Falls; **Jerzy J. Bialy**, Lagrangeville; **Kenneth L. Dille**, Wappingers Falls, all of N.Y.

[73] Assignee: **Texaco Inc.**, New York, N.Y.

[22] Filed: **Nov. 17, 1969**

[21] Appl. No.: **877,487**

[52] **U.S. Cl.** **44/63**, 44/62, 44/71, 44/73

[51] **Int. Cl.** **C10l 1/18**, C10l 1/22

[58] **Field of Search** 44/62, 63, 71, 73

[56] **References Cited**

UNITED STATES PATENTS

3,010,810	11/1961	Stayner et al.	44/63 X
3,034,876	5/1962	Gee et al.	44/62

Primary Examiner—Daniel E. Wyman
Assistant Examiner—W. J. Shine
Attorney—Thomas H. Whaley and Carl G. Ries

[57] **ABSTRACT**

Thermally stable turbine or jet fuel composition containing in combination an ethylene C_3 to C_4 olefin-diene terpolymer/maleic anhydride-alkylamine reaction product and an aldehyde-amine condensation product and a method of operating a turbine engine on said fuel composition.

9 Claims, No Drawings

THERMALLY STABLE JET FUEL COMPOSITION

BACKGROUND OF THE INVENTION

1. Field of Invention

Turbine or jet engines are powdered by light hydrocarbon distillate fuel compositions. It is recognized that petroleum hydrocarbon turbine or jet fuels are susceptible to thermal degradation and oxidation and can produce a suspension of finely divided insoluble bodies in the fuel and cause the formation of deposits on the heat exchanging surfaces in the engine. The degree that these undesirable changes take place is dependent on the amount of unstable constituents present in the oil and on the temperature stress and oxidation conditions to which the oil is subjected. The thermal stability rating of a fuel composition of the type in question is determined in Fuel Coker Tests more fully described hereinbelow.

The problem of thermal stability is particularly serious for light hydrocarbon oils which must be maintained at a relatively high temperature for extended periods of time in intimate contact with an oxygen-containing atmosphere. Jet fuels carried in the wing tanks of aircraft are maintained in such an environment. This problem becomes more acute for jet fuel compositions designed to fuel aircraft having speeds in the Mach 2 and 3 speed ranges or above, such as the forthcoming supersonic transports, because of the substantially higher wing tank temperatures which will be generated.

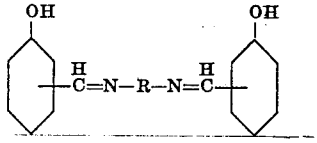
The finely divided insoluble bodies formed in a jet fuel having insufficient thermal stability are separated from the fuel in the fuel filters of the engine. When excessive amounts of insoluble bodies are present in the fuel, the fuel line filters become partially or completely blocked resulting in seriously curtained or lost engine power due to fuel starvation.

The tendency toward deposit formation in a thermally unstable fuel also causes a deposits build-up on the fuel oil heat exchanger in an airplane known as heater tube deposits. It is recognized that the buildup of heater tube deposits cuts down on the heat exchanging efficiency and causes lubricating oil overheat and engine failure. In supersonic aircraft, the heat exchanger requirements or load are further increased because of the need to cool the passenger and crew compartments.

2. Description of the Prior Art and Related Copending Application

U.S. Pat. No. 3,403,011 discloses a middle distillate fuel composition having a reduced pour point containing a minor amount of a reaction product of an ethylene-propylene-terpolymer and maleic anhydride.

A copending U.S. Pat. application, Ser. No. 808,942 filed on Mar. 17, 1969 discloses a turbine or jet fuel composition comprising an ethylene-propylene-diene terpolymer and maleic anhydride reaction product and a metal deactivator. More particularly, a light hydrocarbon or jet fuel composition is provided containing from about 0.0005 to 0.1 weight percent of the reaction product of a relatively low molecular weight ethylene-propylene-diene terpolymer and maleic anhydride reaction product and from about 0.0003 to 0.005 weight percent of a metal deactivator represented by the formula:

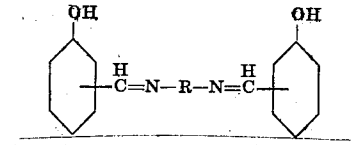


in which R is a divalent hydrocarbyl radical having from two to four carbon atoms.

SUMMARY OF THE INVENTION

The fuel composition of the invention comprises a mixture of hydrocarbons in the light distillate boiling range and minor amounts of (1) an aldehyde-amine condensation product and (2) of an ethylene C_3–C_4 olefin-diene terpolymer-alkylamine reaction product. More specifically, the fuel composition of the invention comprises a light distillate mineral oil, from

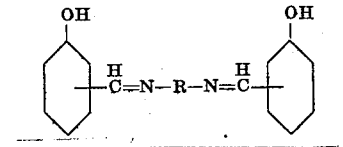
about 0.0003 to 0.01 weight percent of an aldehyde-amine condensation product represented by the formula:



in which R is a divalent hydrocarbyl radical having from two to four carbon atoms, and from about 0.0005 to 1.0 weight percent of an ethylene C_3 to C_4 olefin-diene terpolymer-maleic anhydride-alkylamine reaction product prepared by forming a mixture of from 1 to 50 percent maleic anhydride and the balance said ethylene C_3 to C_4 olefin-diene terpolymer and heating said mixture above about 200° C. until the reaction has been substantially completed to form a first reaction product and then reacting this with an alkylamine at an elevated temperature to form a second reaction product, said ethylene C_3 to C_4 olefin-diene terpolymer component being the amorphous polymerization reaction product of ethylene, a C_3 to C_4 olefin and a C_5 to C_{30} non-conjugated diene in the proportions of 10 to 90 mole percent ethylene, 5 to 70 mole percent C_3 to C_4 olefin and 0.1 to 20 mole percent of said diene, said amorphous reaction product having an Inherent Viscosity in the range from 0.2 to 0.9. The method of this invention involves the operation of a jet engine in such a way that the formation of insoluble bodies in the fuel and of heater tube deposits is avoided or minimized.

The turbine or jet fuel composition of the invention exhibits outstanding thermal stability even when the fuel is maintained under extended high temperature stress and constant agitation in the presence of air.

The metal deactivator component, as earlier noted, is an aldehyde-amine condensation product represented by the formula:



in which R is a divalent hydrocarbyl radical having from two to four carbon atoms. Examples of typical deactivators are N,N′-disalicylidene-1, 2-propanediamine and N,N′-disalicylidene-1,2-ethanediamine. The metal deactivator is employed in the fuel at a concentration ranging from about 0.0003 to 0.01 weight percent, which corresponds to about 0.8 and 14 PTB respectively, with the preferred concentration being from 0.001 to 0.005 weight percent. Metal deactivators of this general type are commercially available.

The ethylene C_3 to C_4 olefin-diene terpolymer-maleic anhydride-alkylamine reaction product component of the invention is prepared in a series of reaction steps. The starting material is an amorphous ethylene C_3 to C_4 olefin-diene terpolymer having an Inherent Viscosity in the range of 0.2 to 0.9. The Inherent Viscosity equals the natural log of the specific viscosity divided by the concentration in grams per 100 ml.

Methods for preparing the terpolymer are well known. In general, a mixture of ethylene, a C_3 to C_4 olefin and a C_5 to C_{30} non-conjugated diene in the proportions of 10 to 90 mole percent ethylene, 5 to 70 mole percent C_3 to C_4 olefin and 0.1 to 20 mole percent diene are polymerized followed by cracking to produce the terpolymer having the prescribed Inherent Viscosity. A mixture of ethylene, C_3 to C_4 olefin and an unconjugated diene in a suitable solvent is polymerized under atmospheric pressure in the presence of a Ziegler-Natta catalyst to produce an amorphous terpolymer product. Suitable C_3 to C_4 olefins are propylene, butene-1, butene-2, and isobutylene. Suitable unconjugated dienes for the reaction include bi-cyclo (2,2,1) hepta-2,5-diene, 1,4-cyclohexadiene, 1,5-cyclooctadiene, dicyclopentadiene, diisopropenyl benzene, dipentene, 2,2-dimethyl-1,5-hexadiene, 1,5-heptadiene, 1,5-hex-

adiene, 2-methyl-1,4-cyclohexadiene, methylcyclopentadiene dimer, 5-methylene-2-norbornene, 3-methyl-1,5-heptadiene, 2-methyl-1,5-hexadiene, 3-methyl-1,5hexadiene 1,7-octadiene, 1,4-pentadiene, 4-vinyl-1-cyclohexene, and 2-methyl-1,4-pentadiene.

The initial polymerization product is a terpolymer consisting of 10 to 90 mole percent ethylene, 5 to 70 mole percent C_3 to C_4 olefin and 0.1 to 20 mole percent diene and having an Inherent Viscosity of at least 1.1 and generally in the range from 1.1 to 5. This polymer component must be cracked to a polymer of reduced and prescribed Inherent Viscosity. This cracking step can be effected by any conventional cracking process but thermal cracking is preferred. It is desirably accomplished by heating the terpolymer to a temperature in the range of 250° to 450° C. and holding the terpolymer in this temperature range until the polymer has been cracked, generally in a period of time ranging from about 15 seconds to 10 hours. The cracked polymer, which is a starting component in the present invention, is characterized by consisting of 10 to 90 percent ethylene, 5 to 70 percent C_3 to C_4 olefin and 0.1 to 20 percent of a non-conjugated diene having from five to 30 carbon atoms and having an Inherent Viscosity in the range of 0.2 to 0.9.

Examples of suitable terpolymers include

a. a terpolymer consisting of 50 to 90 mole percent ethylene, 5 to 45 mole percent butene-1 and 1 to 5 mole percent of a non-conjugated diene, and

b. a terpolymer consisting of 60 mole percent ethylene, about 38 mole percent butene-1 and about 2 mole percent of dicyclopentadiene.

Alternatively, a suitable low-Inherent Viscosity ethylene C_3 to C_4 olefin-terpolymer can be prepared by polymerizing ethylene, a C_3 to C_4 olefin and a non-conjugated diene in the presence of hydrogen and a polymerization catalyst to produce a terpolmyer of low Inherent Viscosity.

Maleic anhydride is reacted with the low Inherent Viscosity terpolymer described above in the second step of preparing this addive component. This reaction is effected by preparing a mixture consisting of about 1 to 50, preferably from 2 to 15, percent by weight of maleic anhydride and the balance consisting of the described terpolymer followed by heating the mixture at a temperature preferably above about 200° C. until the components have reacted. The reaction will generally be completed at a temperature from 200°–300° C. in a period of time ranging from about 30 minutes to 12 hours although shorter and longer reaction periods can be employed. The ethylene C_3 to C_4 olefin-diene terpolymer and maleic anhydride are conveniently reacted in a mineral oil carrier to produce an oil solution of the reaction product followed by vacuum stripping of any unreacted material from the oil solution.

The above ethylene C_3 to C_4 olefin-diene terpolymer-maleic anhydride reaction product is reacted with an alkyl monoamine to complete the preparation of this component of the fuel composition. The alkyl monoamines which can be employed are the primary, secondary and tertiary alkylamines having from one to 18 carbon atoms. The secondary alkyl primary amines having from about eight to 16 carbon atoms are preferred. These alkylamines are commercially available as mixtures such as a mixture of C_{10} to C_{14} secondary alkyl primary amines.

The reaction product obtained above is mixed with about 0.5 to 15.0 percent of an alkylamine and the mixture reacted at a temperature of about 100° C. or above up to the decomposition temperature. After a suitable reaction period for completion, the reaction product is vacuum stripped at 250° C. followed by recovery of the reaction product.

The above reaction product is generally employed in the fuel composition in a concentration ranging from about 0.0005 to 1.0 weight percent with the preferred concentration of this additive being in the range of 0.001 to 0.005 weight percent, the latter amounts corresponding to about 3 and 15 ptb (pounds per thousand barrels).

The preparation of the foregoing reaction product is shown in the following example.

EXAMPLE I

About 2 liters of purified n-heptane were saturated at 60° F. with a gas mixture from a tank filled with 25 p.s.i.g. butene-1, 25 p.s.i.g. ethylene and 5 p.s.i.g. hydrogen. With this same gas mixture bubbling through the saturated mixture, 2 ml. dicyclopentadiene, 4 ml. of 20 percent solution of diethylaluminum chloride in heptane (A) and 1 ml. of 20 percent solution of tri-n-butyl vanadate in heptane (B) were added. The mixture was stirred rapidly and the gas mixture was added continuously through the reaction. During the reaction an additional 4 ml. of (A) and 1 ml. of (B) was added. After 20 min., the reaction was halted by adding 250 ml. of 15 percent aqueous HCl to the stirring mixture. The HCl was separated and the volume of the hydrocarbon layer was reduced in half by evaporation on a steamplate. Then 50 g. of cetane and 0.1 g. of an antioxidant 2,6-di-t-butyl-4-methyl phenol were added and the remaining n-heptane removed by heating this mixture to 500° F. The weight of the stripped product was 77.2 g.

To the above 77.2 g. of terpolymer-cetane mixture, 1.355 g. of maleic anhydride was added and the mixture heated at 250° C. for 7 hours with stirring. Unreacted maleic anhydride was removed by vacuum stripping the reaction 1 hour at 250° C.

To the above reaction product, about 2 g. of a mixture of C_{10}–C_{14} secondary alkyl primary amines were added at 100° C. and the mixture stirred at this temperature for 4 hours. The product was vacuum stripped 1 hr. at 250° C. Final weight 75.4 g. which assayed 33 percent polymer products.

The base fuel of the invention is a light distillate hydrocarbon or a mixture of hydrocarbons in the kerosene and/or gasoline boiling ranges. These base fuels boil in a temperature range from about 90° to 550° F., the preferred turbine fuels for supersonic aircraft are those boiling from about 300° to 550° F. Typical fuels for turbine engines include JP-1 through JP-5. JP-4 consists of about 65 percent gasoline and 35 percent light distillate and JP-5 is an especially fractionated kerosene having a high flash point and a low freezing point.

The preparation of the turbine or jet fuel composition of the invention simply involves the addition of the two component additive to the fuel in the indicated amounts.

The effectiveness of the fuel compositions of the invention is determined by preparing typical jet fuel compositions and testing for thermal stability in Fuel Coker Tests. The standard Fuel Coker Test employed to test the thermal stability of jet fuels is the CFR Fuel Coker Test (ASTM–D–1160–61–T).

The fuels being formulated for use in supersonic flight are so thermally stable that the conditions of the standard CFR Fuel Coker Test do not approach or stress the thermal stability limits of these fuels. Because of this, a much more severe test has been developed called the CFR Research Fuel Coker Test. This test is patterned after the standard CFR Fuel Coker Test and uses similar equipment manufactured by the Erdco Engineering Corporation who make all of the industry adopted Fuel Coker Test equipment. The principal difference in the Research Fuel Coker Test is that the fuel is maintained at an elevated temperature, usually 200° F. for an extended period of time, generally 5 hours, all the while being agitated or stirred in the presence of air. This treatment markedly increases the thermal stress placed on the fuel composition. Because of the greater severity of this test, the heater tube deposits are rated from 1 to 8 (worst) for each 1 inch section of the tube and the total deposits ratings for all tube sections is given. The balance of the test is similar to the standard CFR Fuel Coker Test in that the fuel is passed over a heated tube for the determination of tube deposits (tube rating) and through a heated filter to measure filter plugging. The Research Fuel Coker Test is described in "Technical Documentary Report No. ASD–TDR–62–852, Sept. 1962" of the U.S. Air Force under the subject "An Investigation of the Thermal Stability of Potential Supersonic Jet Fuels."

The conditions under which the coking tests are conducted follow the procedure set forth in the CFR Fuel Coker Test wherein the severity of the temperature of the heater tube and fuel filter are increased in 25° F. increments until the fuel fails to pass the test. These temperatures are important indicators of the severity of the test and are shown in the test results. The fuel flow employed is a rate of 6 lbs. per hour for 5 hours (300 minutes). When and if the back pressure caused by filter plugging reaches 25.0 inches of mercury before 300 minutes, the fuel fails this test but the run is contained with the filter bypassed until the 300 minutes elapse. For military purposes, a filter pressure of less than 12.0 inches of mercury in 300 minutes is satisfactory according to MIL-J-5624F. The deposits formed on the tube are rated as from 0=best to 4=worst in the CFR Fuel Coker Test and from 0=best to 8=worst in the Research Coker Test. In either test, a tube rating of 2 or less passes and a rating of 3 or more fails the tube rating test.

The base fuel employed in these tests was a typical jet fuel having the following properties:

Gravity, °API	43.5
ASTM Distillation, °F.	
IBP	327
10	361
20	374
30	389
40	404
50	419
60	435
70	450
80	467
90	487
95	502
EP	517
Flash Point, °F.	125
Freezing Point, °F.	−56
FIA Analysis	
Aromatics %	13.5
Olefins	2.0
Saturates	84.5
Net Heat of Combustion	
BTU/lb.	18,483
Luminometer Number	51.4

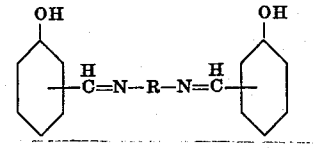
The effectiveness of the additives of the invention in the above jet fuel is shown by the Fuel Coker Test results set forth in the tables below. The concentration of the additive components in the fuels is shown in ptb (pounds per thousand barrels)of the fuel composition. The concentration of the polymer is shown on the active material basis (minus the diluent oil).

Runs 8 and 9 illustrate the outstanding thermal stability of the fuel composition of the invention in the Research Coker thermal stability test. Run 10 shows that there is no filter plugging at an even higher temperature level. The present invention represents a remarkable improvement in the development of turbine and jet fuels which exhibit a high level of thermal stability under conditions of high temperature stress.

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

We claim:

1. A turbine fuel composition comprising a mixture of hydrocarbons boiling in the range from about 90° to 550° F. containing from about 0.0003 to 0.01 weight percent of (1) an aldehydeamine condensation product represented by the formula:



in which R is a divalent hydrocarbyl radical having from two to four carbon atoms and from about 0.0005 to 1.0 weight percent of (2) an ethylene C_3 to C_4 olefin-non-conjugated-diene terpolymer-maleic anhydride C_1 to C_{18} alkyl monoamine reaction product prepared by forming a mixture of from 1 to 50 percent maleic anhydride and the balance said ethylene C_3 to C_4 olefin-non-conjugated-diene terpolymer and heating said mixture above about 200° C. until the reaction has been substantially completed to form a first reaction product and then reacting this with from about 0.5 to 15.0 percent of C_1 to C_{18}alkyl monoamine at a temperature about 100° C. until substantially completed to form the final reaction product, said ethylene C_3 to C_4 olefin-non-conjugated-diene terpolymer consisting of ethylene, a C_3 to C_4 olefin and a non-conjugated diene having from five to 30 carbon atoms, in the mole ratios of from 10 to 90 mole percent ethylene, 5 to 70 mole percent C_3 or C_4 olefin and 0.1 to 20 mole percent of said diene, said ethylene C_3 to C_4 olefin-non-conjugated-diene terpolymer being amorphous and having an Inherent Viscosity in the range of 0.2 to 0.9.

2. A turbine fuel composition according to claim 1 in which said condensation product is N,N'-disalicylidene-1,2-propanediamine and said terpolymer consists of ethylene, butene-1 and dicyclopentadiene.

3. A turbine fuel composition according to claim 1 contain-

TABLE I.—ASTM COKER THERMAL STABILITY TEST

Run	Fuels	Polymer conc. (PTB)	Metal deactivator (PTB) *	Temperature of preheater/filter	Rating: Preheater	Rating: Filter ΔP, Hg	Rating: Filter Time, Min.
1	Base fuel			450° F./550° F.	4	25	105
2	Base fuel			450° F./550° F.	4	25	166
3	Base fuel		3	450° F./550° F.	3	25	105
4	Base fuel +	7 PTB Ex. I	3	450° F./550° F.	0	0.4	300

* N,N'-disalicylidene-1,2-propanediamine.

Run 4 in the above table illustrates the outstanding heat stability of the fuel composition of the invention in the CFR Coker Test.

TABLE II.—RESEARCH COKER THERMAL STABILITY TEST

Run	Fuels	Polymer conc. (PTB)	Metal deactivator (PTB)*	Temperature of reservoir/preheater/filter	Rating: Preheater Max.	Rating: Preheater Total	Rating: Filter ΔP, Hg	Rating: Filter Time, min.
5	Base fuel			200/375/475	2	14	91.3	300
6	Base fuel			200/400/500	4	30	25	185
7	Base fuel		3	200/425/525	3	30	25	265
8	Base fuel +	7 PTB Ex. I	3	200/400/500	1	7	0	300
9	Base fuel +	7 PTB Ex. I	3	200/450/550	2	17	0.6	300
10	Base fuel +	7 PTB Ex. I	3	200/475/575	3	30	0	300

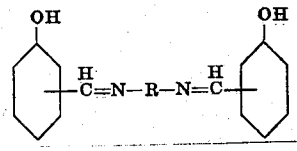
* N,N'disalicylidene-1,2-propanediamine

ing from about 0.0003 to 0.01 weight percent of said aldehyde-amine condensation product and from about 0.0005 to 1.0 weight percent of said reaction product.

4. A turbine fuel composition according to claim 1 in which said terpolymer consists of 50 to 90 mole percent ethylene, 5 to 45 mole percent butene-1 and 1 to 5 mole percent of a non-conjugated diene.

5. A turbine fuel composition according to claim 1 in which said terpolymer consists of about 60 mole percent ethylene, about 38 mole percent butene-1 and about 2 mole percent of dicyclopentadiene.

6. A method for operating a turbine engine which comprises supplying to and burning in said engine a turbine fuel composition comprising a a mixture of hydrocarbons boiling in the range from about 90° to 550° F. containing from about (1) 0.0003 to 0.01 weight percent of an aldehyde-amine condensation product represented by the formula:



in which R is a divalent hydrocarbyl radical having from two to four carbon atoms, and (2) 0.0005 to 0.1 weight percent of an ethylene C_3 to C_4 olefin-non-conjugated-diene terpolymer-maleic anhydride C_1 to C_{18} alkyl monoamine reaction product prepared by forming a mixture of from 1 to 50 percent maleic anhydride and the balance said ethylene C_3 to C_4 olefin-non-conjugated-diene terpolymer and heating said mixture above about 200° C. until the reaction has been substantially completed to form a first reaction product and then reacting this with from about 0.5 to 15.0 percent of a C_1 to C_{18} alkyl monoamine at a temperature above about 100° C. to form the final reaction product, said ethylene C_3 to C_4 olefin-non-conjugated-diene terpolymer consisting of ethylene, a C_3 or C_4 olefin and a non-conjugated diene having from five to 30 carbon atoms, in the mole ratios of from 10 to 90 mole percent ethylene, 5 to 70 mole percent C_3 or C_4 olefin and 0.1 to 20 mole percent of said diene, said terpolymer being amorphous and having an Inherent Viscosity in the range of 0.2 to 0.9.

7. A method according to claim 6 in which said condensation product is N,N'-disalicylidene-1,2-propanediene and said terpolymer consists of ethylene, butene-1 and dicyclopentadiene.

8. A method according to claim 6 in which said terpolymer consists of 50 to 90 mole percent ethylene, 5 to 45 mole percent butene-1 and 1 to 5 mole percent of a non-conjugated diene.

9. A method according to claim 8 in which said non-conjugated diene is dicyclopentadiene.

* * * * *