United States Patent

Bialy et al.

[15] **3,658,496**

[45] ***Apr. 25, 1972**

[54] THERMALLY STABLE FUEL COMPOSITION

[72] Inventors: **Jerzy J. Bialy**, Lagrangeville; **George W. Eckert**, Wappingers Falls, both of N.Y.

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

[*] Notice: The portion of the term of this patent subsequent to Dec. 17, 1985, has been disclaimed.

[22] Filed: **Apr. 3, 1968**

[21] Appl. No.: **718,345**

[52] **U.S. Cl.** **44/66**, 44/73

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

[58] **Field of Search** 44/66, 73

[56] **References Cited**

UNITED STATES PATENTS

3,034,876	5/1962	Gee et al.	44/73 X
3,304,162	2/1967	Marvel	44/66
3,416,903	12/1968	Eckert et al.	44/73

Primary Examiner—Daniel E. Wyman
Assistant Examiner—W. J. Shine
Attorney—K. E. Kavanagh and Thomas H. Whaley

[57] **ABSTRACT**

Thermally stable middle distillate or jet fuel composition containing in combination a Mannich base (alkyl-phenol-sulfide-formaldehyde-alkylene diamine reaction product) polymeric acid and metal deactivator.

6 Claims, No Drawings

THERMALLY STABLE FUEL COMPOSITION

This invention relates to a mineral oil composition and, more particularly, to a petroleum hydrocarbon middle distillate or jet fuel composition having improved thermal stability. This invention is an improvement over a commonly assigned application Ser. No. 693,141 filed on Dec. 26, 1967 now U.S. Pat. No. 3,416,903.

It is recognized that petroleum hydrocarbon middle distillates and jet fuels are susceptible to thermal degradation and oxidation resulting in the formation of a suspension of finely divided insoluble bodies in the fuel and the formation of deposits. The degree that these undesirable changes take place is dependent on the amount of the unstable constituents present in the oil and on the temperature stress and oxidation conditions to which the oil is subjected. The thermal stability ratings of the fuel compositions are determined in a Fuel Coker Test more fully described hereinbelow.

The problem of thermal stability is particularly serious for hydrocarbon oils which must be maintained at a relatively high temperature for extended periods of time in intimate contact with an oxygen-containing atmosphere. Light middle distillates and jet fuels are maintained in such an environment in the wing tanks of supersonic aircraft. 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 skin and wing tank temperatures generated.

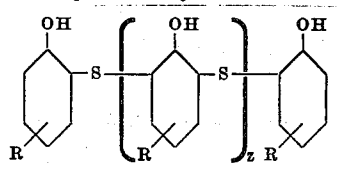
When a middle distillate or jet fuel has insufficient thermal stability, degradation will take place resulting in the formation of a suspension of finely divided insoluble bodies. These insoluble bodies are separated from the fuel in the fuel filters of the engine. With excessive amounts of insoluble bodies in the fuel, fuel line filters can become partially or completely blocked resulting in seriously curtailed or lost engine power due to fuel starvation.

The tendency toward deposit formation in a thermally unstable fuel causes a deposit build-up referred to as heater tube deposits. This deposit formation simulates the deposit formation on the fuel-oil heat exchanger in a plane where the build-up of deposits will cut down on heat exchanging efficiency thus resulting in lubricating oil overheat and engine failure. In supersonic aircraft, additional fuel-air heat exchangers are present for cooling the passenger and crew space.

A middle distillate fuel oil composition has now been discovered having substantially improved thermal stability. More particularly, a jet fuel composition has been discovered which exhibits improved thermal stability even after extended high temperature stress while under constant agitation in the presence of air.

In accordance with this invention, there is provided a middle distillate fuel composition of enhanced thermal stability containing a minor amount of an additive combination of a Mannich base defined below, a polymeric acid and a metal deactivator. More particularly, a middle distillate fuel or jet fuel composition is provided containing from about 0.001 to 0.1 weight percent of a Mannich base reaction product formed from an alkylphenol sulfide, formaldehyde and an alkylene diamine, from about 0.001 to 0.05 weight percent of a polymeric acid and from about 0.003 to 0.005 weight percent of a metal deactivator. Still more particularly, the Mannich base reaction product comprises an alkylphenol sulfide, defined below, formaldehyde and an alkylene diamine, defined below, reacted in mole ratios of a:b:1 respectively where *a* and *b* each can have a value of from 1 to 8 but *a* is never greater than *b* or greater than $x+4$.

The alkylphenol sulfide component of the Mannich base reaction product is represented by the formula:



in which R is an alkyl radical having from four to 60 carbon atoms and z is 1 or 0. The preferred alkylphenol sulfides are those in which R is an alkyl radical having from 10 to 18 carbon atoms and z has a value of 1. When z is 0, the alkylphenol sulfide contains 2 moles of an alkylphenol and 1 mole of sulfur (2:1) and when z is 1 the alkylphenol sulfide contains three moles of an alkylphenol and 2 moles of sulfur (3:2). Alkylphenol sulfides are prepared by reacting suitable proportions of an alkylphenol with sulfur dichloride. These materials are reacted in a solvent, such as isooctane, at a moderate temperature generally from about 15° to 25° C. The reaction mixture is heated to reflux temperature to effect solvent removal and recovery of the alkylphenol sulfide.

The alkylene diamine component of the reaction product is represented by the formula:

$$H_2N-CH_2-CH_2\left(\begin{matrix}N-CH_2-CH_2\\ H\end{matrix}\right)_x NH_2$$

in which x has a value of 0 to 4. The preferred alkylene diamine for the reaction product is ethylenediamine.

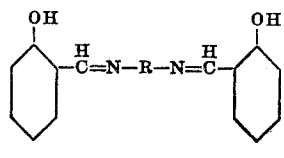
The alkylphenol sulfide, formaldehyde and alkylene diamine components of the reaction product are reacted in mole ratios of *a:b:*1 respectively where *a* and *b* each can have a value from 1 to 8 but *a* is never greater than *b* or greater than $x+4$. In general, preparation of the reaction product involves mixing the alkylphenol sulfide with alkylene diamine and then adding the formaldehyde solution. The reactants are heated with stirring to a temperature of about 80° C. (176° F.) to effect the reaction. Water is then stripped out of the reaction mixture and the temperature raised to about 143° C. (290° F.) to insure completion of the reaction. Upon completion of the reaction, a hydrocarbon oil is added to the reaction mixture to make an oil blend of the reaction product. This blend is filtered to remove any insoluble materials.

In general, the Mannich base component is employed in the jet fuel composition in a concentration ranging from about 0.001 to 0.1 weight percent. A preferred concentration of the Mannich base is an amount from about 0.002 to 0.01 which corresponds to about 5 and 25 PTB (pounds of additive material per thousand barrels of fuel) respectively. It is convenient to employ the Mannich base in an oil blend in which case allowance must be made for that portion of the additive representing the inert oil carrier.

The polymer acid component of the additive of the invention comprises a dimer or trimer of a dienoic or trienoic acid containing from about 16 to 18 carbon atoms. Specific olefinic acids which can be employed are linoleic, linolenic, 9,11-octadecadienoic and eleostearic acids. Effective polymeric acids can be prepared from naturally occurring materials, such as linseed fatty acids, soya bean fatty acids and other natural unsaturated fatty acids. The preparation of polymeric acids is disclosed in U.S. Pat. No. 2,632,659. Suitable polymeric acids are available commercially, such as Empol 1022 "Dimer Acid," a dimer of linoleic acid.

The polymeric acid is employed in the jet fuel composition in a concentration ranging from about 0.001 to 0.05 weight percent. Preferred concentrations are from about 0.0015 to 0.006 weight percent which correspond to about 4 and 16 PTB.

The metal deactivator component of this invention is an aldehyde-amine condensation product represented by the formula:



in which R is a divalent hydrocarbyl radical having from 2 to 4 carbon atoms. Examples of typical deactivator are N,N'-disalicylidene-1,2-propanediamine and N,N'-disalicylidene-1,2-ethane diamine. The metal deactivator is employed in the fuel

at a concentration ranging from about 0.0003 to 0.005 weight percent which corresponds to about 0.8 and 14 PTB respectively.

The following examples illustrate the preparation of the additive Mannich base component of the invention.

EXAMPLE 1

618 grams (6.0 moles) of sulfur dichloride was added to a mixture of 3,660 grams (12.0 moles) of tetrapropenyl phenol and about 2,000 ml. of isooctane while the mixture was maintained at a temperature ranging from 15° to 25° C. The reaction mixture was maintained in this temperature range for about 60 minutes after which the solution was heated to reflux and the isooctane distilled off to effect recovery of the tetrapropenyl phenol sulfide.

40.5 grams (0.50 moles) of 37 (w) % aqueous formaldehyde was added to a mixture of 16.5 grams (0.25 moles) of 85 (w) % aqueous ethylenediamine and 321 grams (0.50 moles) of tetrapropenyl phenol sulfide. The mixture was then heated to 80° C. (175° F.) and stirred there for 6 hours. The water was then stripped off and the temperature of the reaction mixture raised to about 143° C. (290° F.) to complete the formation of the reaction product. The reaction product was taken up in approximately 343 grams of oil to form about a 50 percent by weight blend of the tetrapropenylphenol sulfide-formaldehyde-ethylene diamine reaction product in oil. The reaction product (active material) of this example was called "Additive A."

EXAMPLE 2

3,660 grams (12.0 moles) of tetrapropenyl phenol and 824 grams (8.0 moles) of sulfur dichloride were reacted in isooctane as in Example 1 to form a tetrapropenylphenol sulfide in the mole proportions of 3 moles of alkylphenol and 2 moles sulfur.

328 grams (0.34 moles) of the above tetrapropenylphenol sulfide, 55 grams (0.68 moles) 37 (w) % aqueous formaldehyde and 22.4 grams (0.34 moles) 85 (w) % aqueous ethylenediamine were reacted as in Example 1. Approximately equal weight amount of oil was added to the reaction product to form approximately a 50 percent by weight blend of the active material in the oil solution. The reaction product (active material) of this Example was called "Additive B."

The preparation of the jet fuel composition of the invention simply involves the addition of the three component additive to the fuel in the indicated quantities. In general, the thermal stability additive will be effective in middle distillates and jet fuels boiling in the range from about 300° to 600° F.

The effectiveness of the additive combination of the invention is determined by preparing a typical jet fuel with the additive combination and testing for thermal stability in a Fuel Coker Test. The Fuel Coker Test employed to test the thermal stability of the fuels of this invention was much more severe than the conventional CFR Fuel Coker Test (ASTM-D-1660-61-T). The reason for a more severe test is that the fuels now 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 test 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 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. 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 test is conducted follow the procedure set forth in the CFR Fuel Coke 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 was at a rate of 6 lbs. per hour for 5 hours (300 minutes). If the back pressure caused by filter plugging reaches 25.0 inches of mercury before the 300 minutes, the fuel fails this test but the run is continued 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 (see MIL-J-5624F). The deposits formed on the tube are rated as from 0 to 8 (where 0 = best; 8 = worst) depending on the extent of the deposit formation on the tube. A tube rating of 2 or less is satisfactory and a rating greater than 2 fails.

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

Gravity, °API	43.5
Sulfur, %	0.02
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

The effectiveness of the additives of the invention in the above jet fuel is shown by the CFR Research Fuel Coker Test results set forth in Table I below:

TABLE I.—RESEARCH COKER TEST

Run No.	Additive in jet fuel	Concentration, lbs./1,000 bbls.	Temperature conditions	Maximum preheater rating	Pressure drop inches, Hg	Time/min.
1	Base fuel (no additive)		200[a]/375[b]/475[c]	[1] 2	3.4	300
2	Base fuel (no additive)		200/400/500	[2] 4	10	300
3	Commercial thermal stability additive	30	200/425/525	[2] 3	0	300
4	N,N'-disalicylidene-1,2-propanediamine	1.5	200/425/525	[2] 3	25	[2] 295
5	Additive B	8	200/425/525	[2] 3	0.2	300
5a	Dimer acid	6	200/425/525	[2] 6	25	[2] 180
6	Additive B	8	200/425/525	[2] 3	0.1	300
	N,N'-disalicylidene-1,2-propanediamine	1.5				
7	Dimer acid[d]	6	200/450/550	[2] 3	1.1	300
	N,N'-disalicylidene-1,2-propanediamine	1.5				
8	Additive B	8	200/425/525	[2] 3	0.2	300
	Dimer acid	6				
9	Additive B	8	200/450/550	[1] 2	0	300
	Dimer acid	6				
	N,N'-disalicylidene-1,2-propanediamine	1.5				

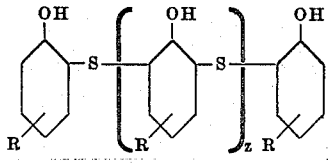
[1] Pass.
[2] Fail.
[a] Soak temperature during test, 5 hours at 200° F. with constant agitation in the presence of air.
[b] Temperature of preheater.
[c] Temperature of filter.
[d] Dimer acid, dimer of linoleic acid, Empol 1022.

It is evident from the above results that a jet fuel composition of outstanding thermal stability has been provided by the invention as exemplified in Run 9 above. This improvement greatly extends the ability of a jet fuel composition to meet the stringent heat stress requirements of fuels for advanced turbine powered aircraft.

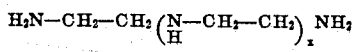
Obviously, many modifications and variations of the invention, as hereinabove set forth, may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be imposed as are indicated in the appended claims.

WE CLAIM:

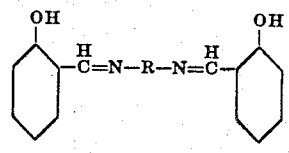
1. A middle distillate fuel composition consisting of petroleum hydrocarbons boiling in the range from about 300° to 600° F. containing in combination from about 0.001 to 0.1 weight percent of the reaction product of an alkylphenol sulfide, formaldehyde and an alkylene diamine in mole proportions of *a*:*b*:1 respectively, where *a* and *b* each can have a value from 1 to 8 but *a* is never greater than *b* or greater than $x + 4$, said alkylphenol sulfide having the formula



in which R is an alkyl radical having from 4 to 60 carbon atoms and *z* is 1 or 0, and said alkylene diamine has the formula



in which *x* has the value of 0 to 4, from about 0.001 to 0.05 weight percent of a polymeric acid comprising a dimer or trimer of a dienoic or trienoic acid containing from 16 to 18 carbon atoms, and from about 0.0003 to 0.005 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.

2. A middle distillate fuel composition according to claim 1 in which the alkyl radical R in said alkylphenol sulfide has from 10 to 18 carbon atoms.

3. A middle distillate fuel composition according to claim 1 in which said alkylphenol sulfide is tetrapropenylphenol sulfide (3:2 mole ratio) and said alkylene diamine is ethylenediamine.

4. A middle distillate fuel composition according to claim 1 in which *a* and *b* each have the value of 2.

5. A middle distillate fuel composition according to claim 1 in which said polymeric acid is the dimer of linoleic acid.

6. A middle distillate fuel composition according to claim 1 in which said aldehyde-amine condensation product is N,N'-disalicylidene-1,2-propane diamine

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,658,496 Dated April 25, 1972

Inventor(s) Jerzy J. Bialy, et. al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 61, "0.003" should read -- 0.0003 -- .
Column 2, line 54, "U. S. 2,632,659" should read -- U. S. 2,632,695 -- .

Signed and sealed this 2nd day of January 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.