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STABILIZED HYDROCARBON FUELS

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This application is a continuation-in-part of our prior and copending application Serial Number 178,251, now Patent Number 3,155,463, filed March 8, 1962.

This invention relates to hydrocarbon fuels that are stable at relatively high temperatures. In one of its aspects, the invention relates to petroleum hydrocarbon distillate fuels, and more particularly, in this aspect, to petroleum hydrocarbon distillate jet combustion fuels, adapted for use in jet engines, and which do not undergo thermal degradation at relatively high temperatures.

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 effect heat removal and also to preheat the incoming fuels, 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 relatively high temperature conditions. In this respect, many jet fuels have been found to be relatively unstable when subjected to such high temperatures. This results in decomposition products being formed, which tend to foul the heat exchange tubes and to cause plugging of the injection nozzles. It will thus be realized that the use of such fuels results in shortened operational life of the engine, and can constitute a source of hazard in the operation of the jet aircraft. Accordingly, a means of stabilizing such fuels against degradation is highly desirable.

It is, therefore, an object of the present invention to provide new and improved hydrocarbon fuels that are stable at relatively high temperatures.

Another object of the invention is to provide new and improved petroleum hydrocarbon distillate fuels, adapted for use in jet engines and which do not undergo thermal degradation at relatively high temperatures.

Still another object of the invention is to provide new and improved jet combustion fuels having a greatly reduced tendency to foul heat exchange tubes and to plug injection nozzles.

Other objects and advantages inherent in the invention will become apparent to those skilled in the art from the following detailed disclosure.

It has now been found, as more fully hereinafter described, that thermally unstable hydrocarbon fuels, and petroleum hydrocarbon distillate jet combustion fuels in particular, can be stabilized against degradation in a simple, effective and economical manner. In this respect, it has been found that the addition of a straight-chain alkylated catechol having at least 6 carbon atoms per alkyl group will stabilize the aforementioned fuels, and jet combustion fuels, particularly, against thermal degradation at relatively high temperatures, and thereby minimize the fouling of heat exchange tubes and plugging of nozzles. The use of the aforementioned straight-chain alkylated catechol may also include the presence of polymeric acids which function as rust inhibitors and lubricity improving agents.

As indicated above, the catechols employed in the fuel compositions of the present invention are straight-chain alkylated catechols having at least 6 carbon atoms per alkyl group. Straight-chain alkylated catechols having from 6 to about 30 carbon atoms per alkyl group, and, more particularly, straight-chain alkylated catechols having

from about 9 to about 30 carbon atoms per alkyl group, or straight-chain wax alkylated catechols, are preferred. In this respect, it was found that the relatively long straight-chain alkylated catechols of the present invention are effective jet fuel stabilizers at temperatures as high as from about 500° F. to about 750° F. In contrast, it was found that relatively short-chain and branched chain alkylated catechols, such as tertiary butyl catechols, diisopropyl catechols and tritetrapropyl catechols did not show any efficacy as jet fuel stabilizers but actually degraded the base jet fuel. The preparation of the straight-chain alkylated catechols having 6 or more carbon atoms per alkyl group employed in the improved hydrocarbon fuel compositions, is more fully hereinafter discussed. In general, however, they may be readily synthesized from catechol and a 1-olefin in the presence of various catalysts, e.g., a boron fluoride catalyst, or from an alkyl halide and catechol in the presence of, e.g., a zinc chloride catalyst.

Relatively small amounts of the aforementioned catechols are added to the hydrocarbon fuels to obtain the desired protection against thermal degradation at relatively high temperatures. This beneficial effect is realized by incorporating into the fuel the catechol in an amount from about 0.0001 to about 1.0 percent by weight of the fuel. In instances where the use of the straight-chain alkylated catechol also includes the presence of polymeric acids, prepared as more fully hereinafter disclosed, to function as rust inhibitors and lubricity improving agents, there is incorporated into the fuel a mixture of the aforementioned straight-chain alkylated catechol having at least 6 carbon atoms per alkyl group and the polymeric acid, in an amount from about 0.01 to about 1.0 percent by weight of the fuel, in which the weight ratio of catechol to polymeric acid can vary from about 1:1 to about 1:100.

With respect to the alkylated catechols of the present invention, they can be prepared by conventional procedures, as previously indicated, by reacting, in the presence of various catalysts catechol with a 1-olefin or an alkyl halide. This reaction between catechol and olefin or alkyl halide is, in general, carried out at a temperature between about 75° C. and about 220° C. to alkylate the catechol. In this repect, as previously indicated, the alkylated catechols of the present invention have at least 6 carbon atoms per alkyl group. Representative examples include such alkylated catechols as trihexadecyl catechol, tetrahexyl catechol, and various straight-chain wax alkylated catechols.

As previously indicated, the straight-chain alkylated catechols of the present invention may also include the presence of polymeric acids as rust inhibitors and lubricity improving agents. These polymeric acids may be present in the form of dimer, trimer or higher polymeric acids. A dimer, as defined in Hackh's Chemical Dictionary, is a condensation product or polymer of two molecules. This, when two molecules of a polyethenoid mono-carboxylic fatty acid condense to form a di-carboxylic acid, the product, by definition, is a dimer, or the mono-carboxylic acid is said to be dimerized. Similarly, the condensation of a molecule of one polyethenoid mono-carboxylic acid with a molecule of a second polyethenoid mono-carboxylic acid forms a dimer which is a di-carboxylic acid. On a parallel basis, a trimer can be formed, and mono-carboxylic acids can similarly be said to be trimerized. Higher polymeric acids are, accordingly, formed in a similar manner with proper corresponding higher molecular weight substitution being employed. It should be noted that many of the dimeric acids that are commercially available contain, e.g., approximately 85% dimeric acids and about 12% trimeric and higher polymeric acids, and the second still residue

of the dry distillation of castor oil in the presence of sodium hydroxide contains from about 45 to 50% of the dimeric acids and about 50% of the trimeric and higher polymeric acids. Inasmuch as neither or these industrially available products can be said to constitute 100% dimeric acids, it will be apparent that materials containing more highly polymerized acids than the dimeric acids can be used. However, it should be noted that these materials contain only small amounts, viz., less than about 10%, of the mono-carboxylic or unpolymerized fatty acids and saturated acids. Preferred materials are those containing not more than about 15% of unpolymerized unsaturated fatty acids and saturated fatty acids. In general, the contents of dimer acids and trimer and higher polymeric acids is preferably of the order of at least about 85%, with the dimeric acids representing at least about 50% of the dimeric and higher polymeric acids. A more detailed description of the polymeric acids suitable for use in the formulations of the present invention, and the method for their preparation, is disclosed in U.S. Patent No. 2,632,695. Thus, the polymeric acids contemplated for use in the present formulation as disclosed in the aforementioned Patent No. 2,632,695, are selected from the group consisting of (1) dimeric acids produced by the condensation of unsaturated, aliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, (2) dimeric acids produced by the condensation of hydroxyaliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, (3) trimeric acids produced by the condensation of unsaturated, aliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, and (4) trimeric acids produced by the condensation of hydroxyaliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule.

As previously indicated, hydrocarbon fuels, and particularly petroleum hydrocarbon distillate jet combustion fuels, when used with the additive compositions of the present invention, can be stabilized against thermal degradation. The hydrocarbon distillate jet combustion fuels that are improved in accordance with the present invention, include 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 may comprise straight-run distillate fractions, catalytic 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 above-specified 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 most useful jet combustion fuels, employed in combintion with the additives of the present invention comprise liquid compositions, which boil within the range of from about 350° F. or 375° F. to about 550° F., and consist essentially of (1) a mixture of paraffins within the range of C_{10} or C_{11} and higher and (2) naphthenes. These compositions are further characterized by having a net heat of combustion of at least about 18,850 B.t.u./lb., and containing not more than about 5 volume percent aromatics, substantially devoid of C_9 and lower paraffins, and containing these paraffins in a concentration substantially in excess of the naphthene concentration, with the predominant amount of the paraffins being in the C_{11} to C_{16} range. Compositions having a luminometer number of at least about 100, and maximum freeze points of —30° F. are preferred. With respect to the aforementioned liquid fuels, compositions are preferred which contain a maximum of about 35 volume percent naphthenes when the aromatic content is about 5 volume percent and, for each one volume percent decrease in aromatics to below 5 volume percent, the maximum naphthene content is decreased by about 3 volume percent. Particularly desirable liquid compositions, adapted for use as jet fuels, in combination with the additives of the present invention, are those boiling within the range of from about 350° F. to about 550° F. and consisting essentially of (1) a mixture of paraffins within the range of C_{10} and higher and (2) naphthenes, in which these compositions are further characterized by (a) having a net heat of combustion of at least about 18,900 B.t.u./lb., a flash point of 150° F. (minimum) and a vapor pressure at 500° F. of 50 p.s.i. (maximum), (b) containing not more than about 5 volume percent aromatics and substantially devoid of C_9 and lower paraffins, and (c) containing paraffins within the range of C_{10}+ in a concentration substantially in excess of the naphthene concentration with the predominant amount of the paraffins being in the C_{11} to C_{16} range.

The following examples will serve to illustrate the preparation of the additive compositions of the present invention and to demonstrate the effectiveness thereof in rendering hydrocarbon fuels, and particularly petroleum hydrocarbon distillate jet combustion fuels thermally stable. It will be understood that it is not intended that the invention be limited to the particular compositions shown or to the operations or manipulations involved. Various modifications of these additives, as previously described, can be employed and will be readily apparent to those skilled in the art.

It will also be understood that a wax-catechol, produced in accordance with the following examples, in which a quantity of chlorowax containing 2 atomic proportions of chlorine and having a chlorine content of 10%, by weight, is reacted with 1 mol of catechol is designated "wax catechol 2–10." Similarly, "wax-catechol 3–12" and "wax-catechol 4–12" are also produced by the reaction of sufficient amounts of chlorinated wax, containing 12%, by weight, of chlorine, to provide 3 atomic proportions and 4 atomic proportions of chlorine per mol of catechol, respectively.

EXAMPLE 1

A mixture of 92 grams (0.836 mol) catechol, 422 grams (2.51 mols) propylene tetramer, and 25 grams boron trifluoride ethyl etherate was stirred for a period of about 10 to 12 hours at a temperature between about 90° C. and about 95° C. About 100 grams of water was introduced at this point to destroy the boron fluoride catalyst. The reaction mixture was then washed with hot water until the washings were neutral to pH paper. The final product, a tritetrapropyl catechol, was obtained by topping under reduced pressure at 240° C.

EXAMPLE 2

A mixture of 355 grams (1 mol) 10% chlorowax, 55 grams (0.5 mol) catechol, and 41 grams anhydrous zinc chloride was slowly heated to about 210° C. over a period of about 12 hours. The reaction mixture was filtered and washed with hot water until the washings were neutral to pH paper. The final product, a wax catechol (2–10), was obtained by topping under reduced pressure at 230° C.

EXAMPLE 3

A mixture of 400 grams (1.36 mols) 12% chlorowax, 50 grams (0.454 mol) catechol, and 45 grams anhydrous zinc chloride was slowly heated to about 210° C. over a period of about 12 hours. The reaction mixture was filtered and topped at 240° C. under reduced pressure to produce a wax catechol (3–12).

EXAMPLE 4

A mixture of 400 grams (1.36 mols) 12% chlorowax, 37.4 grams (0.34 mol) catechol, and 44 grams anhydrous zinc chloride was slowly heated to about 210° C.

over a period of about 12 hours. The reaction mixture was filtered and topped at 265° C. under reduced pressure to obtain a wax catechol (4–12).

EXAMPLE 5

A mixture of 110 grams (1 mol) catechol, 460 grams (2 mols) Adecene A51 (a mixture of straight-chain 1-olefins comprising 6% 1-dodecene, 14% 1-tetradecene, 42% 1 - hexadecene, 33% 1 - octadecene, 5% 1-eicosene, and having an average molecular weight of 230) and 28 grams boron trifluoride ethyl etherate was stirred for about 12 hours at 90° C. The reaction mixture was filtered and water washed with hot water until the washings were neutral to pH paper. The final product, a dialkyl catechol, was obtained by topping under reduced pressure at 182° C.

EXAMPLE 6

A mixture of 91 grams (0.827 mol) catechol, 344 grams (2.48 mols) of a mixed 1-olefin fraction (comprising 1% 1-octene, 25% 1-nonene, 53% 1-decene, 21% 1-undecene, and having an average molecular weight of about 139) and 25 grams boron trifluoride ethyl etherate was stirred at about 85° C. to about 90° C. for about 8 hours. About 100 grams of water was added to the reaction mixture, which was then water-washed with hot water until the washings were neutral to pH paper. The product, a trialkyl catechol, was obtained by topping at 255° C. under reduced pressure.

EXAMPLE 7

A mixture of 110 grams (1 mol) catechol, 556 grams (4 mols) of a mixed 1-olefin fraction (having a composition similar to that of the mixed 1-olefin fraction of Example 6) and 35 grams of boron trifluoride ethyl etherate was stirred at about 85° C. to about 90° C. for about 10 hours. About 200 grams of water was added to the reaction mixture, which was then water washed with hot water until the washings were neutral to pH paper. The product, a tetraalkyl catechol, was obtained by topping at 240° C. under reduced pressure.

EXAMPLE 8

A mixture was prepared comprising 9.1 grams wax catechol (4–12), prepared according to the procedure of Example 4, and 90.9 grams commercial dimer acid (comprising approximately 85% dimeric acids and about 14% trimeric and higher polymeric acids).

Each of the products of the foregoing examples was subjected to test under the conditions of a test method used for determining the thermal stability characteristics of aviation turbine fuels. The method was developed by the Coordinating Research Council as 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 600° F. to 650° F. and the preheater tube temperature was 500° F. to 550° 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 rating varying from 0 to 8, as shown in the following table, in which a rating lower than Code 3 is desirable for an effective stable aviation turbine fuel.

The base hydrocarbon jet combustion fuel, employed in connection with the data disclosed in the table, was a straight-run petroleum fraction comprising 100% isoparaffins, boiling within the range of approximately 330° F. to 400° F. Portions of this base fuel, uninhibited, were 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.

Table

Run No.	Inhibitor	Conc. lb./1,000 bbls.	Filter temp., ° F.	Preheater temp., ° F.	Filter plugging pressure drop (inches Hg)	Preheater deposits at 300 min. rating
1	Uninhibited jet fuel		600	500	0.0	55% Code 1, 30% Code 5, 15% Code 7.
2	do		650	550	0.0	39% Code 2, 8% Code 4, 15% Code 7. 15% Code 3, 8% Code 5, 15% Code 8.
3	Fuel plus 3,5-diisopropyl catechol	20	650	550	2.5	45% Code 1, 15% Code 3, 40% Code 8.
4	Fuel plus 4-tertiary butyl catechol	20	650	550	0.3	52% Code 2, 8% Code 3, 40% Code 8.
5	Fuel plus catechol of Example 1	20	600	500	0.0	67% Code 2, 8% Code 3, 25% Code 8.
6	Fuel plus catechol of Example 2	20	600	500	0.0	100% Code 2.
7	Fuel plus catechol of Example 3	20	650	550	0.0	92% Code 2, 2% Code 3.
8	Fuel plus catechol of Example 4	20	650	550	0.0	100% Code 2.
9	Fuel plus catechol of Example 5	20	650	550	0.0	70% Code 2, 30% Code 3.
10	Fuel plus catechol of Example 6	20	650	550	0.0	100% Code 2.
11	Fuel plus catechol of Example 7	20	650	550	0.0	Do.
12	Fuel plus catechol of Example 8	110	600	500	0.0	Do.

Code 1—dulling of preheater. Code 2—slight discoloration. Code 3—light tan. Code 4—medium tan. Code 5—light brown. Code 6—medium brown. Code 7—dark brown. Code 8—black.

As is apparent from the foregoing data in the table, the uninhibited jet fuel (Runs 1 and 2) and the uninhibited fuels containing 3,5-diisopropyl catechol, 4-tertiary butyl catechol, and tritetrapropyl catechol, respectively (Runs 3, 4, and 5), had unsatisfactory readings (falling from Code 4 to Code 8) with respect to preheater deposits. The marked improvement that results from the practice of this invention by employing the aforementioned straight-chain alkylated catechols having at least 6 carbon atoms per alkyl group, as fuel additives, is evi-

denced from the data set forth for Runs 6 through 12. As shown, the fuel compositions containing the aforementioned catechol, passed the requirements of the test, i.e. principally Code 2 and with no pressure drop across the filter after about 300 minutes.

While preferred embodiments of the compositions of the present invention and the process for their preparation have been described, for the purpose of illustration, it should be understood that various modifications and adaptations thereof, which will be obvious to those skilled in the art may be made without departing from the spirit of the invention.

We claim:

1. A normally liquid hydrocarbon fuel containing a small amount, sufficient to inhibit said fuel against thermal degradation of a straight-chain polyalkylated catechol having at least 6 carbon atoms per alkyl group and a small amount of at least one polymeric acid selected from the group consisting of (1) dimeric acids produced by the condensation of unsaturated, aliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, (2) dimeric acids produced by the condensation of hydroxyaliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, (3) trimeric acids produced by the condensation of unsaturated, aliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, and (4) trimeric acids produced by the condensation of hydroxyaliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, the weight ratio of said catechol to polymeric acid varying from about 1:1 to about 1:100.

2. A fuel as defined by claim 1, wherein said fuel comprises a petroleum hydrocarbon distillate fuel having an initial boiling point of at least about 100° F. and an end boiling point as high as about 750° F.

3. A fuel as defined in claim 1, wherein said catechol and polymeric acid are present in a total amount of from about 0.0001 to about 1.0%, by weight, of said fuel.

4. A fuel as defined in claim 1, wherein said catechol and polymeric acid are present in a total amount of from about 0.01 to about 1.0%, by weight, of said fuel.

5. A fuel as defined in claim 1, wherein said fuel comprises a petroleum hydrocarbon distillate jet combustion fuel.

6. A fuel as defined in claim 1, wherein said straight-chain alkylated catechol has from about 6 to about 30 carbon atoms per alkyl group.

7. An additive composition, adapted for stabilizing a petroleum hydrocarbon distillate jet combustion fuel against thermal degradation comprising a straight-chain polyalkylated catechol having at least 6 carbon atoms per alkyl group and at least one polymeric acid selected from the group consisting of (1) dimeric acids produced by the condensation of unsaturated, aliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, (2) dimeric acids produced by the condensation of hydroxyaliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, (3) trimeric acids produced by the condensation of unsaturated, aliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, and (4) trimeric acids produced by the condensation of hydroxyaliphatic monocarboxylic acids having between about 16 and about 18 carbon atoms per molecule, the weight ratio of said catechol to polymeric acid varying from about 1:1 to about 1:100.

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