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3,019,097

JET FUEL COMPOSITIONS

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This invention relates to new jet fuel compositions characterized by high thermal stability.

Fuel temperatures in modern jet aircraft power plants are becoming so high that harmful deposits are formed in the precombustion phase of the fuel system. Contributing to this has been the use of the fuel as a heat sink to aid in lubricating oil cooling, which has increased fuel temperatures to the point where deposits are so severe that they interfere with normal fuel combustion as well as lubricating oil temperature control. The jet fuel thermal stability problem is so serious that it can eventually lead to engine failure of the turbine section due to uneven temperature patterns. In fact, it is considered the outstanding problem in jet fuels at the present time.

Prior investigators have found that conventional gasoline antioxidants are incapable of overcoming this oppressive problem. The art is replete with reports by eminent investigators which are universally to the effect that conventional antioxidants do not overcome the jet fuel thermal stability problem. For example, it has been stated that neither 4-methyl-2,6-di-tert-butyl phenol nor N,N'-di-sec-butyl-p-phenylenediamine improves the high temperature stability of jet fuels. In fact, some gasoline anti-oxidants have been shown to be deleterious in that they increase the severity of the problem. Consequently, the experts in the field have turned their attention to other types of additives—i.e., materials which are not antioxidants. One approach has been the use of dispersants in an attempt to keep the deposits suspended in the fuel and thereby prevent them from adhering to critical engine surfaces. However, this approach has not proved satisfactory because the deterioration of the fuel does occur under jet engine operating conditions and little, if any, improvement in engine performance has as yet been attained. Another approach has been the use of various jet fuel treating procedures. However, these are unsatisfactory because they are expensive and complicated, and, in most cases, little improvement is achieved. Special fuel blending procedures have also been suggested but found totally impractical. Thus, in general, all approaches to the solution of this substantial problem have thus far been unsuccessful.

An object of this invention is to alleviate the thermal stability problems in jet fuels. Another object is to provide new jet fuel compositions which are characterized by a high degree of thermal stability problems in jet fuels in a simple and inexpensive manner. A still further object is to provide processes of inhibiting deterioration of jet fuel normally tending to occur at elevated temperatures below the cracking temperatures of the fuel. Other objects will be apparent from the ensuing description.

It has now been found that the above and other objects of this invention are accomplished by providing jet fuel containing from about 0.01 to about 0.2 percent by weight of a 2,6-di-alkyl phenol. The thermal stabilizers of this

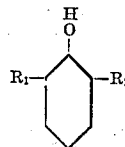
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invention exhibit the unique property of greatly improving the thermal stability of jet fuels and this effectiveness is independent of the hydrocarbon types from which the jet fuel has been prepared. Thus, the present invention affords extreme protection against thermal instability of all present-day jet fuels.

The jet fuel additives of this invention attack and overcome the jet fuel thermal instability problem at its source by conferring greatly improved thermal stability characteristics upon the fuels. Thus, a direct benefit accruing from the practice of this invention is the considerable reduction in the amount of insoluble products formed when the jet fuels of this invention are subjected to elevated temperatures. Hence, markedly reduced is the amount of insoluble thermal decomposition products which heretofore deposited to plug orifices in the fuel system, to distort fuel flow and thus impair flame pattern, and to foul surfaces. This is a particularly unexpected result in view of the fact that 2,4,6-tri-alkyl phenols have been shown to be ineffective in overcoming this jet fuel thermal instability problem. It is thus clear that the unsubstituted para position in the jet fuel additives of this invention is tied in, in some currently unexplainable manner, with the unexpected effectiveness they exhibit. Furthermore, the additives of this invention do not introduce secondary problems in use, such as jet fuel foaming at high altitudes, emulsification difficulties, interference with low-temperature flows, and the like. At the same time, all of these highly important and unique advantages are achieved in a simple manner and at very low cost. Hence, the present invention represents a substantial contribution to the jet fuel art.

It is known that conventional jet fuel normally tends to deteriorate when subjected to the condition of elevated temperatures below the cracking temperature of the fuel, i.e., temperatures in the range of about 300 to about 500° F. Hence, another part of this invention is the process of inhibiting such deterioration which comprises subjecting a jet fuel containing from about 0.01 to about 0.2 percent by weight of a 2,6-dialkyl phenol to said condition. Thus, greatly enhanced thermal stability of jet fuel is achieved by blending with a jet fuel from about 0.01 to about 0.2 percent by weight of a 2,6-dialkyl phenol and subjecting the resulting fuel to the above condition.

The 2,6-dialkyl phenol jet fuel additives have the formula:



wherein R₁ and R₂ are alkyl groups which preferably contain up to about 12 carbon atoms.

Preferred jet fuel additives of this invention are 2,6-dialkyl phenols in which at least one of the alkyl groups is secondary or tertiary—i.e., is branched on the alpha carbon atom. These preferred additives are particularly effective in improving the high temperature stability characteristics of jet fuels.

Particularly preferred as jet fuel additives are 2,6-di-tert-butyl phenol and 2-methyl-6-tert-butyl phenol.

These compounds not only possess the excellent attributes of the preferred class of additives described above, but are easily made in high purity and at low cost.

The jet fuels whose thermal stability is greatly improved pursuant to this invention are principally hydrocarbon fuels which are heavier than gasoline, i.e., distilled liquid hydrocarbon fuels having a higher endpoint than gasoline. In general, the jet fuels can be comprised of distillate fuels and naphthas and blends of the above, including blends with lighter hydrocarbon fractions, so long as the endpoint of the final jet fuel is at least 435° F. and preferably greater than 480° F. It will be understood, however, that the jet fuels which are employed according to this invention can contain certain other ingredients such as alcohols or the like, provided the resulting fuel blend meets the specifications imposed upon jet fuels.

Typical jet fuels improved according to this invention include JP-3, a mixture of about 70 percent gasoline and 30 percent light distillate having a 90 percent evaporated point of 470° F.; JP-4, a mixture of about 65 percent gasoline and 35 percent light distillate, a fuel especially designed for high altitude performance; JP-5, an especially fractionated kerosene; high flash point-low freezing point kerosene, etc.

The following are specifications of typical liquid hydrocarbon jet fuels of this invention:

	Fuel A (JP-3)	Fuel B (JP-4)	Fuel C (JP-5)	Fuel D (JP-4)	Fuel E (JP-4 reference)	Fuel F (Kerosene)
10% Evaporated, F.	160	220	395	221		380
90% Evaporated, F.	470	470	480	379	460	480
Endpoint, ° F.	600	550	550	480	516	
Gravity, ° API	50	45	35	47.3	48.5	43
Existent Gum, mg./100 ml. max.	7	7	7	1.0	1.4	1.7
Potential Gum, mg./100 ml. max.	14	14	14	1.0	9.6	
Red Vapor Pressure, p.s.i.	7.0	3.0				
Aromatics, vol. percent	25.0	25.0	25.0	12.5	14.6	14.3
Olefins, vol. percent	5.0	5.0	5.0	0.3	1.2	

The following examples illustrate various specific embodiments of this invention.

Example I

To 100,000 parts of Fuel A is added with stirring 10 parts (0.01 percent) of 2,6-dimethyl phenol dissolved in 200 parts of ethanol. The resulting fuel is found to possess improved thermal stability characteristics.

Example II

To 100,000 parts of Fuel B is added 100 parts (0.1 percent) of 2-methyl-6-ethyl phenol dissolved in 500 parts of methanol. The resulting fuel possesses improved thermal stability properties.

Example III

With 100,000 parts of Fuel C is blended 50 parts (0.05 percent) of 2-methyl-6-isopropyl phenol. The resulting fuel blend possesses superior thermal stability characteristics.

Example IV

To 100,000 parts of Fuel D is added 120 parts (0.12 percent) of 2-methyl-6-tert-butyl phenol. The resulting fuel blend is found to possess vastly superior thermal stability characteristics.

Example V

With 100,000 parts of Fuel E is blended 80 parts (0.08 percent) of 2,6-di-tert-butyl phenol. The resulting fuel blend possesses enhanced thermal stability properties.

Example VI

To 100,000 parts of Fuel F is added 200 parts (0.2 percent) of 2,6-diisopropyl phenol dissolved in 1500 parts of isopropanol. After mixing, the resulting fuel blend is found to possess enhanced thermal stability properties.

Example VII

Fuel C is blended with a lighter hydrocarbon fraction to give a final jet fuel having an endpoint of 435° F. To 100,000 parts of the resultant fuel is added 90 parts (0.09 percent) of 2,6-di(2-dodecyl) phenol. The resulting fuel possesses improved thermal stability characteristics.

Example VIII

To 100,000 parts of a liquid hydrocarbon jet fuel having an endpoint of 550° F. is added 150 parts (0.15 percent) of 2-isopropyl-6-tert-butyl phenol dissolved in 1500 parts of mixed xylenes. The resulting jet fuel possesses superior thermal stability properties.

Example IX

With 100,000 parts of Fuel A is blended 60 parts (0.06 percent) of 2-methyl-6-tert-amyl phenol. This fuel after mixing possesses improved thermal stability characteristics.

Example X

170 parts of 2,6-di-(1,1,3,3-tetramethylbutyl) phenol is blended with 100,000 parts of Fuel B. The resulting jet fuel containing 0.17 percent of the phenol possesses improved thermal stability characteristics.

Example XI

With 100,000 parts of Fuel C is blended 70 parts (0.07 percent) of 2-ethyl-6-tert-butyl phenol. The resulting jet fuel blend possesses superior thermal stability characteristics.

Example XII

To 100,000 parts of Fuel B is added with stirring 180 parts (0.18 percent) of 2-octyl-6-isopropyl phenol. The resulting jet fuel is found to possess superior thermal stability characteristics.

Examples III and VI through XII illustrate preferred jet fuel compositions of this invention containing preferred 2,6-dialkyl phenols. Particularly preferred jet fuels of this invention are illustrated by Examples IV and V since the fuels in these examples contain the particularly preferred 2,6-dialkyl phenols.

The substantial improvements resulting from the practice of this invention are demonstrated by tests in an apparatus known as the Coordinating Fuel Research (CFR) Jet Fuel Coker, commonly called the "Erdco Rig." See Petroleum Processing, December, 1955, pages 1909-1911. In order to show the very good results of the compositions of this invention from the standpoint of reduced preheater deposits, this CFR fuel coker was operated without a filter and without heat on the filter furnace.

This permits all of the tests to be of equal and predetermined duration so that a direct comparison of deposits from a given quantity of fuel is provided. In this series of tests, the preheater temperature was 400° F., fuel flow was at a rate of six pounds per hour, and each individual run was carried out for a period of 150 minutes. The

fuel used in these tests was a commercially available JP-5 fuel having the following inspection data.

Gravity, ° API	39.0
Distillation, ASTM D-86, temp., ° F., at percent Recovered:	
Start	373
5	379
10	386
20	396
30	405
40	414
50	422
60	432
70	444
80	459
90	480
95	497
Endpoint	516
Recovered, percent	98
Residue, percent	1
Loss, percent	1
Flash, PM, ° F.	164
Aniline point	132
Aniline-gravity constant	5148
Hydrocarbon type analysis, FIAM:	
Aromatics, vol. percent	18
Olefins, vol. percent	2
Saturates, vol. percent	80
Viscosity, cs., at -30° F.	10.68
Freezing point, ° F.	-62
Existent gum (steam jet), mg./100 ml.	1
Potential gum, mg./100 ml.	1
Total sulfur, wt. percent	0.044
Mercaptan sulfur, wt. percent	0.001
Smoke point, mm.	18
Water reaction	1
Water tolerance OK, ml.	0

A jet fuel of this invention was prepared by blending 2-methyl-6-tert-butyl phenol with the above fuel at a concentration of 80 pounds per 100 barrels (approximately 0.025 percent by weight of additive). This fuel was then subjected to the above test and the extent and nature of deposits which formed on the preheater surfaces determined. The additive-free base fuel was also rated in manner. The extent of the deposit formation on the preheater surfaces is a direct measure of the thermal stability of the fuel subjected to the test. Hence, the greater the coverage of the preheater surfaces with deposits, the greater is the thermal instability of the fuel. An additional criterion of the thermal stability of the fuels is the coloration of these deposits. If a light-colored deposit is formed, only a small amount of high temperature deterioration of the fuel has occurred. Thus, the darker the deposits, the more thermally unstable is the fuel. It was found that as compared with the additive-free fuel, the fuel of this invention containing 2-methyl-6-tert-butyl phenol caused a 43 percent reduction in the extent of the preheater surfaces covered by deposits. Moreover, the deposits produced by the additive-free fuel were very dark brown to black in color, whereas the smaller amount of deposits produced from the jet fuel of this invention were of a brownish coloration. Similar effectiveness is achieved by using 2,6-di-tert-butyl phenol instead of 2-methyl-6-tert-butyl phenol. In fact, the jet fuels of this invention without exception possess superior thermal characteristics as compared with the corresponding additive-free fuels.

The test results discussed above are not only unexpected but represent a substantial improvement. This becomes even more apparent by noting that the above base fuel in the absence of an additive of this invention has very poor thermal stability properties. For example, when this clear base fuel was subjected to the Erdco Fuel Coker test using the heated, sintered steel filter (held at 500° F.) through

which the preheated fuel (preheater temperature 400° F.) was passed at a rate of six pounds per hour, a pressure drop across the filter of 25 inches of mercury occurred in only 45 minutes. A fuel that runs through this apparatus under these conditions for a full 300 minutes without causing any pressure drop is considered completely thermally stable. It is clear therefore that the above base fuel can be classified as highly unstable thermally.

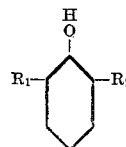
Typical additives which can be used in the practice of this invention include such compounds as 2,6-dimethyl phenol; 2,6-diethyl phenol; 2,6-dipropyl phenol; 2,6-di-butyl phenol; 2,6-dioctyl phenol; 2,6-didecyl phenol; 2,6-didodecyl phenol; 2-methyl-6-ethyl phenol; 2-methyl-6-propyl phenol; 2-methyl-6-octyl phenol; 2-ethyl-6-butyl phenol; 2,6-diisobutyl phenol, and the like. Preferred additives of this invention include 2-methyl-6-isopropyl phenol; 2-methyl-6-tert-amyl phenol; 2-ethyl-6-(2-dodecyl) phenol; 2-methyl-6-(1,1,3,3-tetramethylbutyl) phenol; 2-ethyl-6-(1,1,2,2-tetramethylpropyl) phenol; 2,6-diisopropyl phenol; 2-ethyl-6-tert-butyl phenol; 2,6-di-sec-butyl phenol; 2,6-di-(3-heptyl) phenol; 2,6-di-(3-nonyl) phenol; 2,6-di-(2-dodecyl) phenol, and the like. As pointed out above, the particularly preferred additives of this invention are 2-methyl-6-tert-butyl phenol and 2,6-di-tert-butyl phenol. The methods of preparing many of these 2,6-dialkyl phenols are well known to those skilled in the art and can be found in the literature. An especially elegant process for preparing 2,6-dialkyl phenols in which at least one of the alkyl groups is branched on the alpha carbon atom is described in co-pending application, Serial No. 426,556, filed April 29, 1954, now Patent No. 2,831,898.

The amount of the additive used in the jet fuels of this invention can range from about 0.01 to about 0.2 percent by weight. Ordinarily, amounts of 0.02 to about 0.15 percent are found to be satisfactory for present-day jet fuels. Variations from these concentration ranges are permissible. For example, in jet fuels initially possessing a fair degree of thermal stability, very small amounts of the additives are sufficient to improve the thermal stability characteristics of such fuels and, in some cases, provide improved storage stability properties. On the other hand, where the jet fuel initially has a very poor thermal stability, larger amounts (about 0.05 to 0.2 percent by weight or more) can be effectively used.

In preparing the improved jet fuels of this invention, the use of solvents for the 2,6-dialkyl phenols is frequently advantageous. While the solubility of these compounds in jet fuels is sufficiently high to provide the desired concentrations, blending procedures are simplified by pre-dissolving these thermal stabilizers in a suitable solvent. The resulting formulations can then be conveniently and readily blended with the jet fuels. Particularly suitable solvents for this purpose include benzene, toluene, xylene, acetone, methylethyl ketone, methanol, ethanol, isopropanol, methyl isobutyl carbinol, and the like. In general, ketones and alcohols containing up to about 6 carbon atoms and liquid aromatic hydrocarbons containing 6 to 18 carbon atoms are excellent solvents. Other materials that can be used in the jet fuels of this invention are anti-rust additives, dispersants, and, in general, additives which do not adversely affect the high temperature stability of the fuels.

We claim:

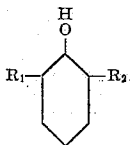
1. Distilled hydrocarbon jet fuel having an endpoint of at least about 480° F. containing from about 0.01 to about 0.2 percent by weight of a 2,6-dialkyl phenol having the formula:



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wherein R_1 and R_2 are alkyl groups containing up to about 12 carbon atoms each.

2. Distilled hydrocarbon jet fuel having an endpoint of at least about 480° F. containing from about 0.01 to about 0.2 percent by weight of a 2,6-dialkyl phenol in which at least one of the alkyl groups is branched on the alpha carbon, said phenol having the formula:



wherein R_1 and R_2 are alkyl groups containing up to about 12 carbon atoms each.

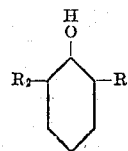
3. The composition of claim 2 wherein said phenol is 2-methyl-6-tert-butyl phenol.

4. The composition of claim 2 wherein said phenol is 2,6-di-tert-butyl phenol.

5. A process for cooling the lubricating oil in a jet engine comprising using as a coolant for heat transfer with the lubricating oil a thermally stabilized jet fuel consisting essentially of a distilled hydrocarbon fuel having an end point of at least about 480° F. and containing

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from about 0.01 to about 0.2 percent by weight of a 2,6-dialkyl phenol having the formula:



10 wherein R_1 and R_2 are alkyl groups containing up to about 12 carbon atoms each.

6. The process of claim 5 wherein at least one of the alkyl groups of said 2,6-dialkyl phenol is branched on the alpha carbon atom.

15 7. The process of claim 5 wherein said phenol is 2-methyl-6-tert-butyl phenol.

8. The process of claim 5 wherein said phenol is 2,6-di-tert-butyl phenol.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,019,097

January 30, 1962

George G. Ecke et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 41, for "100" read -- 1000 --.

Signed and sealed this 5th day of June 1962.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

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