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STABILIZATION OF THERMALLY UNSTABLE LIQUID HYDROCARBON FUELS

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This invention relates to improving the thermal stability of combustion gas turbine fuels. More particularly, the invention relates to reducing the tendency of combustion gas turbine fuels to form solid deposits at very high service temperatures by incorporating therein small amounts of a monoester of a higher fatty acid and diethylene glycol.

Combustion gas turbine fuel is presently employed as a cooling medium, or "heat sink," in combustion gas turbine powered aircraft to remove heat by indirect heat exchange from lubricating oil that has absorbed heat developed in the engine by the compression of combustion air, by fuel combustion, and by friction of moving parts. As a result, the fuel is subjected to heat transfer surface temperatures during service of the order of 300 to 400° F. for relatively substantial time intervals. In addition, the fuel is subjected to even higher temperatures, of the order of 500° F., for short periods of time in the area of the nozzles or orifices from which the fuel is introduced into the combustion chamber of the engine. As a result, certain components of the fuel tend to undergo decomposition due to polymerization, oxidation, and thermal decomposition, and to form solid or semi-solid degradation products that clog the fuel orifices and thereby interfere with proper combustion of the fuel. Ordinary stabilizing agents, antioxidants and the like, of the kind that are employed to stabilize the fuels during storage have been found inadequate to inhibit deterioration of the fuels at the high service temperatures encountered in aviation turbine engines.

The present invention relates to improving the thermal stability of liquid hydrocarbon combustion gas turbine fuels, such as aviation turbine fuels, and more particularly to reducing the tendencies of such fuels to form deposits on heat transfer surfaces at temperatures in excess of 300° F. and in the fuel inlet regions of the combustion zones of the engines in which the fuels are consumed, whereby such fuels are rendered more suitable for use in combustion gas turbine engines. It has been found that the thermal stability characteristics of the above-indicated fuels, as well as other characteristics of these and other hydrocarbon oils, can be improved by incorporating therein a small amount of a monoester of a fatty acid that contains 8 to 18 carbon atoms and diethylene glycol. In a preferred embodiment the monoester is the ester of lauric acid, but monoesters of other fatty acids including saturated acids such as Oxo-octanoic, palmitic, stearic, oleic, linoleic, and linolenic acids can be used. When protection also is desired against clogging of fuel orifices due to thermal degradation of thermally unstable fuel contacted by the hot fuel orifices under high temperature service conditions, without sacrificing the exceptional protection against fouling of heat transfer surfaces provided by the diethylene glycol monoesters alone, there can also be included in the fuel compositions of this invention a supplemental anticlogging agent such as (I) an oil-soluble, nitrogenous, anticlogging copolymer containing as its essential monomeric components in a weight ratio of about 0.03 to 1:1, preferably 0.05 to 0.75:1 (a) a copolymerizable alkyl ester of an acid such as acrylic and lower alkacrylic acids whose alkyl ester substituent contains 8 to 18 carbon atoms, and (b) a copolymerizable unsaturated compound containing one ethylenic linkage copolymerizable with the aforesaid alkyl ester and a nitrogen-containing substituent group that is not polymerizable with said alkyl ester, such as amine salts, quaternary ammonium salts or aminoesters of acrylic or lower alkacrylic acids, or (II) an oil-soluble phosphosulfurized hydrocarbon anticlogging agent obtained by reacting a phosphorus sulfide with an aliphatic hydrocarbon. A specific example of a preferred copolymer is the 1:9 weight ratio copolymer of di-Oxo-octyl)aminoethyl methacrylate and lauryl methacrylate, but other copolymers having their extralinear nitrogen substituents linked to the polymer chain through a linkage other than an ester linkage, for example, a quaternary ammonium salt linkage or an amine addition salt linkage, including the dehydrated or amido form of such amine salt linkage, can be used. Specific examples of such other copolymers include the 1:9 weight ratio copolymer of soyaalkyltrimethylammonium methacrylate and lauryl methacrylate and the 1:9 weight ratio copolymer of di(Oxo-octyl)ammonium methacrylate and lauryl methacrylate. A specific example of an oil-soluble phosphosulfurized aliphatic hydrocarbon is the phosphosulfurized product obtained by reacting P_2S_5 with pentapropylene, but the phosphosulfurized products obtained by reacting other phosphorus sulfides and other aliphatic hydrocarbons, including other olefin polymers, can be used. The diethylene glycol monoesters are effective as such to reduce heat transfer surface deposits, and, in combination with the supplemental anticlogging agents disclosed herein they are effective to reduce fuel nozzle deposits when employed in small amounts. Proportions in the range of 10 to 20 pounds of each material per 1,000 barrels of fuel are preferred but other proportions, for example, as little as about 2.5 pounds or more per thousand barrels of fuel, can be used. When the supplemental anticlogging agents are employed in conjunction with the diethylene glycol monoesters disclosed herein, the respective materials can be used in varying proportions with respect to each other. The respective materials are preferably added to the fuels in about equal proportions by weight, but other proportions can be used provided the compound present in the smaller amount is present in an amount corresponding to at least about 2.5 pounds per thousand barrels of fuel. Ordinarily, the respective materials will be employed in weight ratios of about 1:4 to 4:1, but other weight ratios, for example, 1:8 to 8:1 can be used.

The exact manner in which the diethylene glycol monoesters disclosed herein function to improve the thermal stability of combustion gas turbine fuels has not been definitely determined. Inasmuch as the diethylene glycol monoesters disclosed herein effect a substantially greater reduction in the heat transfer surface deposits than in fuel nozzle deposits, it is clear that the inhibitive mechanism involved is highly selective. In view of the distinct nature of the heat exchanger surface deposits and the fuel orifice deposits, as evidenced by the failure of the diethylene glycol monoesters greatly to reduce both deposits, it might be supposed that the diethylene glycol monoesters disclosed herein and the anticlogging agents, when the latter are employed, function independently of one another. However, this is contradicted by the fact that some materials that are effective as such to inhibit fuel nozzle deposits in combustion gas turbine fuels, have been found ineffective to inhibit such deposits in the presence of diethylene glycol monoesters. The fact that normally effective anticlogging agents are not necessarily effective to inhibit fuel nozzle deposits in the presence of the diethylene glycol monoesters suggests strongly an interaction between the monoesters and the anticlogging agents disclosed herein.

Although it is clear that heat transfer surface deposits and fuel nozzle deposits differ markedly from each other, it should be noted in passing that each of these types of deposits also differs, respectively, from deposits formed from fuels at low temperatures, that is, below 300° F. The distinction between low- or moderate-temperature deposits and the high temperature deposits with which the present invention is concerned is emphasized by the fact that many of the distillate fuels that are benefited by the use of the improvement agents disclosed herein form no deposits whatsoever at temperatures significantly below 300° F. and also by the fact that many improvement agents that are effective to reduce deposits formed in hydrocarbon oils that are unstable at temperatures below about 300° F. have no effect whatsoever in reducing deposits formed in combustion gas turbine fuels at higher temperatures.

The diethylene glycol monoesters disclosed herein can be prepared in any convenient manner, for example, by transesterification of the glyceride of a selected fatty acid or mixture thereof containing 8 to 18 carbon atoms with diethylene glycol in a 1:1 mol ratio in the presence of a sodium hydroxide catalyst. An example of a preferred diethylene glycol monoester is diethylene glycol monolaurate. Examples of other diethylene glycol monoesters whose use is included by this invention are diethylene glycol mono-Oxo-octanoate, mono-Oxotridecanoate, monopalmitate, monostearate, monooleate, monolinoleate, and monolinolenate.

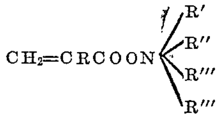
Any suitable anticlogging agent can be used to supplement the heat transfer surface deposit inhibiting properties of the diethylene glycol monoesters disclosed herein. That is, any nozzle-clogging inhibitor can be used that will reduce deposition of thermal degradation fuel deposits in the fuel inlet area of a combustion gas turbine engine in the presence of the diethylene glycol monoesters disclosed herein, without significantly detracting from the advantageous properties of such monoesters. As indicated, good results are obtainable with various chemical types of nozzle clogging inhibitor agents, including oil-soluble, nitrogen-containing copolymers and oil-soluble phosphosulfurized hydrocarbons.

The anticlogging nitrogenous copolymers disclosed herein can be prepared in any convenient way. For example, such copolymers can be prepared by reacting the desired monomers in weight ratios of about 0.03 to 1 part by weight of the nitrogen-containing monomer for each part by weight of the nitrogen-free alkyl ester monomer, in the presence of a diluent, preferably a solvent, such as toluene, benzene, ethyl acetate, or other solvents having similar chain transfer activity, at a temperature in the range of −75° C. to 150° C., preferably 25° C. to 150° C., in the presence of a few hundredths percent to 2 percent, preferably 0.2 to 1.0 percent, of a free radical catalyst such as benzoyl peroxide, lauroyl peroxide, or alpha-alpha′-azodiisobutyronitrile, preferably in the substantial absence of oxygen, until the rate of formation of larger polymer molecules has declined substantially, usually after about 3 to 35 hours, as determined by periodic sampling of the reaction mixture and observing the same for the absence of further significant increases in viscosity.

The alkyl acrylate or alkyl alkacrylate ester monomers from which the nitrogenous anticlogging copolymers disclosed herein are prepared can be represented by the general formula: $CH_2{=}CRCOOR_1$, where R is hydrogen or a lower alkyl radical such as methyl, and R_1 is a straight or branched chain alkyl group containing 8 to 18 and preferably 12 to 18 carbon atoms, such as lauryl, Oxo-tridecyl, n-hexadecyl, or n-octadecyl.

The nitrogenous monomers from which the copolymers disclosed herein are derived are copolymerizable, unsaturated compounds containing an ethylenic linkage that is copolymerizable with the acrylate or alkacrylate monomers and a nitrogen-containing substituent group that is not copolymerizable with the acrylate or alkacrylate monomers. The nitrogen containing substituent group can be associated with the group containing the copolymerizable ethylenic linkage through an ester linkage, a salt linkage, including quaternary ammonium salts and amine addition salts, as well as the dehydrated form of the latter, that is, amides.

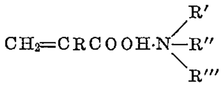
When the nitrogenous substituents are linked to the polymer chain through a quaternary ammonium salt linkage, the nitrogenous monomer will be a quaternary ammonium salt of acrylic acid or a lower acrylic acid such as methacrylic acid, one of whose four covalent N-bonds is attached to a monovalent aliphatic hydrocarbon radical containing 8 to 18 and preferably 12 to 18 carbon atoms, two other of whose covalent N-bonds are attached to monovalent aliphatic hydrocarbon radicals containing 1 to 18 carbon atoms, or aralkyl radicals containing 7 to 23 carbon atoms, and whose remaining covalent N-bond is attached to an alkyl group containing 1 to 4 carbon atoms. The preferred quaternary ammonium salt monomers from which the herein-described copolymers can be prepared can be represented by the general formula:



$$CH_2{=}CRCOON\left\langle\begin{array}{l}R'\\R''\\R'''\\R''''\end{array}\right.$$

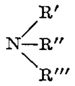
where R is as defined above, R′ is an alkyl, alkenyl, or alkadienyl radical containing 12 to 18 carbon atoms, such as lauryl, myristyl, n-hexadecyl, n-octadecyl, n-octadecenyl, or n-octadecadienyl, and R″ and R‴ are radicals of the same kind as R′ or alkyl radicals containing 1 to 4 carbon atoms such as methyl, ethyl, propyl, or butyl, or a mononuclear alkyl radical containing 7 to 23 carbon atoms such as benzyl, tolylethyl, or a polypropylated aralkyl radical such as p-tetrapropylbenzyl, and R⁗ is an alkyl radical containing 1 to 4 carbon atoms. A specific example of a preferred anticlogging quaternary ammonium salt copolymer is the 1:9 weight ratio copolymer of monomeric mixed octadecenyl- and octadecadienyltrimethylammonium methacrylate and monomeric lauryl methacrylate. Examples of other quaternary ammonium salt copolymers whose use is included by the invention are the 1:9 weight ratio copolymers of monomeric distearyldimethylammonium methacrylate and monomeric lauryl methacrylate and the 0.05:1, the 0.1:1, the 0.5:1, and 1:1 weight ratio copolymers of monomeric dioctadecenyldimethylammonium, octadecenyldimethylethylammonium, distearyldimethylammonium, laurylbenzyldimethylammonium, lauryldimethyl(ethylbenzyl)ammonium acrylates and methacrylates, and monomeric n-octyl, lauryl, Oxo-octyl, 2-ethylhexyl, Oxo-tridecyl, and n-hexadecyl acrylates and methacrylates. Quaternary ammonium salt copolymers of the kind disclosed herein are described and claimed as such in copending application Serial No. 862,056, filed December 28, 1959.

When the nitrogen-containing substituent group is attached to the copolymerizable ethylenic linkage-containing portion of the monomers through an addition salt linkage or the like, the nitrogen-containing monomers from which the anticlogging copolymers disclosed herein can be derived will be monomeric nitrogen-containing salts formed from substantially equivalent proportions of an acrylic or lower alkyl acrylic acid such as methacrylic acid and an amine having as at least one N-substituent an aliphatic hydrocarbon radical containing 8 to 18 carbon atoms. The other N-substituents can be the same as or different from the first-mentioned N-substituent, for example, the other N-substituents can be hydrogen, aliphatic hydrocarbon radicals containing 1 to 18 carbon atoms, or alkylol groups containing 1 to 4 carbon atoms. The preferred amine salt monomers from which the nitrogenous addition salt-containing copolymers disclosed herein are prepared can be represented by the general formula:



$$CH_2{=}CRCOOH{\cdot}N\begin{array}{l}\diagup R' \\ - R'' \\ \diagdown R'''\end{array}$$

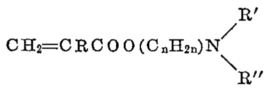
where R is hydrogen or a lower alkyl radical such as methyl



$$N\begin{array}{l}\diagup R' \\ - R'' \\ \diagdown R'''\end{array}$$

is a secondary or tertiary amine, R′ is an alkyl, alkenyl, or alkadienyl radical containing 8 to 18 carbon atoms, such as lauryl, myristyl, n-hexadecyl, n-octadecyl, n-octadecenyl, or n-octadecadienyl, and R″ is an alkylol group containing 1 to 4 carbon atoms such as ethylol or propylol or an aliphatic hydrocarbon radical containing 1 to 18 carbon atoms such as methyl, propyl, butyl, or any of those named in the description of R′, and R‴ is hydrogen or a radical of the same kind as R″. An example of a preferred anticlogging copolymer in which the nitrogen-containing substituent is linked to the polymer chain through an addition salt linkage is the 1:9 weight ratio copolymer of monomeric di(Oxo-octyl)ammonium methacrylate and monomeric lauryl methacrylate. Examples of other such copolymers are the 3:7 weight ratio copolymer of monomeric di(Oxo-octyl) ammonium methacrylate and monomeric lauryl methacrylate, the 1:9 weight ratio copolymer of monomeric di(Oxo-octyl)hydroxyethylammonium methacrylate and monomeric lauryl methacrylate, and the 0.05:1, 0.1:1, 0.5:1, and 1:1 weight ratio copolymers of monomeric octylammonium, dioctylammonium, trioctylammonium, laurylammonium, octadecylammonium, octadecenylammonium acrylates and methacrylates and monomeric n-octyl, lauryl, Oxo-octyl, 2-ethylhexyl, Oxo-tridecyl, and n-hexadecyl acrylates and methacrylates. Amine salt copolymers of the kind disclosed herein are described and claimed as such in combination with liquid hydrocarbon fuels in copending application Serial No. 33,934, filed June 6, 1960.

When the nitrogen-containing substituent of the monomers from which the anticlogging copolymers disclosed herein are derived is associated with the polymer chain through an ester linkage, the nitrogen-containing monomer will be a monomeric ester of acrylic acid or a lower alkacrylic acid such as methacrylic acid and an amine having as at least one N-substituent an alkylol group, normally containing 2 to 4 carbon atoms, and as another N-substituent an aliphatic hydrocarbon radical containing 1 to 18 carbon atoms and as the third N-substituent hydrogen, an aliphatic hydrocarbon radical containing 1 to 18 carbon atoms or an alkylol radical containing 1 to 4 carbon atoms. The preferred nitrogen-containing ester monomers from which the copolymers disclosed herein are derived can be represented by the general formula:



$$CH_2{=}CRCOO(C_nH_{2n})N\begin{array}{l}\diagup R' \\ \diagdown R''\end{array}$$

where R is hydrogen or a lower alkyl radical such as methyl, where *n* is an integer of 2 to 4, preferably 2, R′ is an alkyl, alkenyl, or alkadienyl radical containing 8 to 18 carbon atoms, such as Oxo-octyl, lauryl, myristyl, n-hexadecyl, n-octadecyl, n-octadecenyl, or n-octadecadienyl and R″ is an aliphatic hydrocarbon radical containing 1 to 18 carbon atoms, such as methyl, ethyl or any of those comprising R′. A specific example of a preferred anticlogging copolymer in which the nitrogen containing substituent is linked to the copolymer chain through an ester linkage is the 1:9 copolymer of di(Oxo-octyl)aminoethyl methacrylate and lauryl methacrylate. Specific examples of other such copolymers are the 0.05:1, 0.1:1, 0.5:1, and 1:1 weight ratio copolymers of monomeric n-octylaminoethyl, laurylaminoethyl, octadecylaminoethyl, and octadecenylaminoethyl acrylates and methacrylates, and monomeric n-octyl, lauryl, Oxo-octyl, 2-ethylhexyl, Oxo-tridecyl, and n-hexadecyl acrylates and methacrylates.

The preferred supplemental, nitrogenous, anticlogging copolymers, disclosed herein are copolymers of the above-indicated monomers in weight ratios in the range of about 0.05 to 0.75 part by weight of nitrogen containing monomer to one part by weight of nitrogen-free ester monomer.

The average molecular weight of the anticlogging copolymers disclosed herein will normally be greater than about 2,000 and preferably greater than about 7,500, as determined by conventional methods. Usually the molecular weight of the copolymers will not exceed about 500,000 but the molecular weights can be greater, provided that the molecular weight is not so great as to render the copolymer insoluble in the liquid hydrocarbon fuel distillates disclosed herein.

The oil-soluble, supplemental, anticlogging phosphosulfurized hydrocarbon reaction products suitable for the purposes of this invention can be prepared in any convenient manner. For example, these materials can be prepared by reacting a sulfide of phosphorus with an aliphatic hydrocarbon in relative proportions and at reaction conditions sufficient to effect reaction of all of the phosphorus sulfide. Thus, good results are obtainable by effecting the reaction at a temperature of about 200° to 600° F., preferably about 300° to 500° F., using a mole ratio of about 1 to 10, preferably about 2 to 5, molecular proportions of hydrocarbon for each molecular proportion of the phosphorus sulfide, usually in an inert atmosphere, until substantially all of the phosphorus sulfide has reacted, usually about 2 to 10 hours. Although phosphorus pentasulfide is the preferred phosphorus sulfide, other phosphorus sulfides such as P_2S_3, P_4S_3, P_4S_7, or mixtures thereof can be used. The hydrocarbons starting materials include aliphatic hydrocarbons such as paraffins, olefins, olefin polymers, or petroleum fractions. Examples of such materials include diisobutylene, dodecene, and octadecene. Examples of suitable olefin polymers are those having molecular weights of about 50 to 10,000, examples of which are polymers of ethylene, propylene, butylene, isobutylene, and the like or copolymers of combinations of such monoolefins. An example of a preferred olefin polymer is pentapropylene. An example of a preferred phosphosulfurized hydrocarbon is the 0.82:3.28 mol ratio reaction product of P_2S_5 and pentapropylene obtained at a reaction temperature of 220° C. over a period of about 4.5 hours. An example of another such reaction product is the reaction product of a 150 SUS Mid-Continent bright stock and 10 percent by weight P_2S_5.

The diethylene glycol monoesters, as well as the supplemental anticlogging agents, when they are used, can be incorporated in combustion gas turbine fuels in any suitable manner. For example, they can be added singly or in combination, either as such, or in diluted form to the fuels either promptly after distillation or after storage for an indefinite period of time. When the diethylene glycol monoesters and the supplemental anticlogging agents are added to the fuels in admixture it frequently will be advantageous to add the agents in the form of a concentrated solution, say, a 50 percent solution, in a solvent such as Oxo-octyl alcohol or other suitable solvent, as the addition agents disclosed herein are frequently not otherwise mutually soluble. Alternatively, the addition agents disclosed herein can be added to aviation turbine fuels in admixture with other addition agents adapted to improve one or more characteristics of the fuels. For example, the addition agents disclosed herein can be added to the fuels in admixture with corrosion inhibitors, such as, amine salts of organic esters of orthophosphoric acid, antioxidants such as 2,6-di-tertiary-butyl-4-methylphenol, or 2,4-dimethyl-6-tertiary-butylphenol.

The diethylene glycol monoesters disclosed herein can be employed in aviation combustion gas turbine fuels in any proportions sufficient to improve the thermal stability of the fuels. A noticeable improvement in thermal stability, especially as regards reduction of heat transfer surface deposits, normally will be obtained by the use of as little as 2.5 pounds of diethylene glycol monoester per thousand barrels of fuel, but it is usually desirable to employ at least five pounds per thousand barrels of fuel of the diethylene glycol monoester in order to obtain a substantial improvement in thermal stability. A major improvement will ordinarily be obtained by the use of proportions in the range of about 10 to 20 pounds per thousand barrels of fuel. No additional benefits, insofar as thermal stability is concerned, are obtained with greater proportions. When a supplemental anticlogging agent of the kind disclosed herein is employed in the fuel, these materials can be used in the same range of proportions as the diethylene glycol monoesters and the respective materials can be employed in varying proportions with respect to one another. Normally, it is preferred to employ the diethylene glycol monoesters and the supplemental anticlogging agents in approximately equal proportions, but this is not essential as other relative proportions can be employed, provided that each of the respective agents is employed in proportions of at least 2.5 pounds of agent per 1,000 barrels of fuel. By way of illustration, the diethylene glycol monoesters and the supplemental anticlogging agents can be employed in weight ratios of about 1:8 to 8:1, and preferably 1:4 to 4:1.

Combustion gas turbine fuels of the type whose use is included by this invention are liquid hydrocarbon mixtures, typical of which are ordinary aviation turbine fuels, that is, jet fuels. The properties of the most common aviation turbine fuels are defined fully in the following specifications: MIL-J-5161E (Referee JP-4 Fuel), MIL-J-5624D (JP-4, JP-5 Fuel), MIL-F-25656 (JP-6 Fuel), MIL-F-25524A (Thermally Stable Fuel), MIL-F-25558B (RJ-1 Fuel), MIL-R-25576B (RP-1 Fuel), and American Airlines Specification No. M6-4A. In general, aviation turbine fuels are characterized by the following common properties:

Gravity, ° API	32.5–57.
Existent gum, mg./100 ml. (max.)	5–7.
Potential gum, mg./100 ml. (max.)	4–14.
Sulfur, percent (max.)	0.05–0.4.
Mercaptan sulfur, percent (max.)	0.001–0.005.
Freezing Point, ° F. (max.)	—75 to —40.
Thermal value, B.t.u. lb. (min.)	18,300–18,500.
Aniline-gravity constant	>4,500, usually >5,250.
Aromatics, vol. percent (max.)	5–25.
Olefins, vol. percent (max.)	1–5.

In addition to these characteristics, it also may be noted that typical aviation turbine fuels employed for use in aviation turbine engines involving a high temperature fuel stability problem normally boil in the range of 250° F. to 700° F., that is to say, aviation turbine fuels normally boil above the gasoline range.

The ability of the materials disclosed herein to reduce formation of solid deposits in aviation turbine fuels at high service temperatures has been demonstrated by subjecting representative fuel compositions of the kind disclosed herein to the CFR Fuel Coker test procedure. This test procedure is described in detail in the Manual of ASTM Standards on Petroleum Products, ASTM D-1660-59T. In accordance with this test method, aviation turbine fuels are subjected to flow conditions and temperature stresses similar to those in combustion gas turbine or jet aircraft engines by circulation through a simulated aircraft fuel system, maintained at a temperature in excess of 300° F., at a rate of six pounds of fuel per hour for a period of 300 minutes. The test apparatus comprises a fuel system containing two heated sections, one of which is a preheater section that simulates the hot fuel line sections of an aviation turbine engine as typified by the engine fuel-lubricating oil cooler. The extent of fouling of heat transfer surfaces in the preheater section by fuel degradation deposits is determined by inspection, and the extent of such fouling is used as one index of the high temperature stability of the aviation turbine fuel in the heat exchanger section of an aviation turbine engine. Preheater deposits are rated according to the following scale: 0=no visible deposits; 1=visible haze or dulling, but no visible color; 2=barely visible coloration; 3=light tan to peacock stain; 4=heavier than 3.

The second heated section comprises a filter section that simulates the nozzle area, or fuel inlet area of the combustion zone of a jet engine where fuel degradation particles may be trapped. A precision, sintered stainless steel filter is employed in the filter section to trap fuel degradation particles formed during the test. The extent of the buildup of fuel degradation particles in the filter section is indicated by the pressure differential across the test filter, and this pressure differential is used as another index of the high temperature stability of the aviation turbine fuel. In carrying out the tests described, the temperature of the fuel at the outlet of the preheater section is maintained at 410° F. and the filter section temperature is maintained at 500° F.

In the fuel compositions subjected to the above-described test, the diethylene glycol monoester was a commercial material, Emcol RDC-D which was found to contain 89 percent diethylene glycol monolaurate and 11 percent ionized carboxylates composed of 50 mole percent lauric acid, 30 mole percent myristic acid, 15 mole percent palmitic acid, and 5 mole percent stearic acid. One of the supplemental anticlogging agents employed in the test was the 1:9 weight ratio copolymer of di(Oxo-octyl) aminoethyl methacrylate and lauryl methacrylate. This material was prepared by heating a mixture of 55 grams di(Oxo-octyl)aminoethyl methacrylate, 495 grams lauryl methacrylate, 3.3 grams azodiisobutyronitrile and 1100 grams of an SAE 10/W lubricating oil, with stirring, in a stream of nitrogen for six hours at 55° C. The resulting copolymer was obtained in a viscous solution slightly lighter in color than the solvent oil. The calculated nitrogen content of 0.13 for the solution was confirmed by analysis. A similarly prepared, oil-free copolymer had an average molecular weight of about 180,000. The Oxo-octyl substituents of the di(Oxo-octyl)aminoethyl methacrylate were derived from Oxo-octyl alcohol, that is, octyl alcohol prepared by the Oxo synthesis process. A typical sample of the Oxo-octyl alcohol from which the substituents were derived contained about 38 percent 4,5-dimethylhexyl alcohol, 30 percent 3,5-dimethylhexyl alcohol, 10 percent 5-methylheptyl alcohol, 19 percent 3,4-dimethylhexyl alcohol, and 3 percent 5,5-dimethylhexyl alcohol.

Another supplemental anticlogging agent employed in the tests described herein was a nitrogenous copolymer prepared just as described above except for the substitution of Oxo-octyl methacrylate for lauryl methacrylate. Still another supplemental anticlogging agent was a phosphosulfurized hydrocarbon product obtained by reacting P_2S_5 and pentapropylene in the mol ratio of 0.82:3.28 at about 220° C. for about 4.5 hours.

In the tests reported below, the test fuels were commercial-type aviation turbine fuels having the following characteristics:

	Test fuel A	Test fuel B
Gravity: °API	43.7	43.6
Freezing point: °F	−65	−51
Sulfur, L: percent	0.011	0.054
Mercaptan sulfur: percent	0.001	<0.001
Existent gum: mg./100 ml	0.3	1.6
Potential gum: mg./100 ml	1.2	5.2
Aromatics: vol. percent	14.7	15.7
Olefins: vol. percent	1.0	1.7
Saturates: vol. percent	84.3	82.6
Thermal value: B.t.u./lb	18,581	18,587
Aniline-Gravity Constant	6,337	6,444
Distillation, kerosene:		
Over point: °F	354	330
End point: °F	514	524
10% evap. at	368	372
50% evap. at	398	420
90% evap. at	452	484

The make-up of the test samples and the results obtained in the above-described tests were as set forth in the following table:

Table A

	1	2	3	4	5	6	7
Make-up—Percent by Volume:							
Aviation Turbine Fuel A	100	100	100	------	------	------	------
Aviation Turbine Fuel B	------	------	------	100	100	100	100
Stabilizer Added—Lb./1000 bbls.:							
Diethylene Glycol Monolaurate	------	20	20	------	20	20	20
1:9 wt. ratio copolymer Di(Oxo-octyl)amino-ethyl methacrylate and lauryl methacrylate	------	------	------	------	------	20	------
1:9 wt. ratio copolymer Di(Oxo-octyl)amino-ethyl methacrylate and Oxo-octyl methacrylate	------	------	------	------	------	------	20
P_2S_5-pentapropylene reaction product	------	------	20	------	20	------	------
Inspections:							
Thermal stability, CFR—Fuel Coker:							
Filter Section:							
Time to reach a pressure drop of 10 In. Hg: Min	43	5	>300	195	>300	>300	>300
Time to reach a pressure drop of 25 in. Hg: min	60	10	>300	240	>300	>300	>300
ΔP at 300 min: in. Hg	>25.0	>25.0	1.10	>25.0	0.20	0.00	0.20
Preheater Section:							
Maximum preheater deposit rating	4	0	0	4	0	0	0
Average preheater deposit rating	1.8	0.0	0.0	1.6	0.0	0.0	0.0

From a comparison of results obtained in Test Runs 1 and 2, it will be seen that incorporation of a small amount of diethylene glycol monolaurate in aviation turbine fuel completely eliminated preheater deposits, i.e., heat transfer surface deposits. Comparison of the results obtained in Test Runs 1 and 3 and the results obtained in Test Runs 4 and 5, 6 and 7 indicates that the combination of the diethylene glycol monolaurate and the supplemental anticlogging agents effected essentially complete reduction of both preheater section, or heat transfer surface deposits, and the filter section deposits. The fact that the polymeric anticlogging agents reduce the filter clogging action of the diethylene glycol monolaurate without diminishment of the desirable characteristics of the latter indicates a coaction between the materials, as not every material that is capable as such of reducing filter section deposits retains its effectiveness in the presence of preheater deposit inhibitors such as the diethylene glycol monolaurate.

Examples of other fuel compositions included by the invention are set forth in the following table:

Table B

	1	2	3	4	5	6
Make-up: Percent by Vol.:						
Aviation Turbine Fuel	100	100	100	100	100	100
Improvement agents: lb./1000 bbl.—						
Diethylene glycol monooleate	20	-----	-----	-----	-----	----
Diethylene glycol monolaurate	-----	-----	-----	20	20	----
Diethylene glycol mono-oxo-octanoate	-----	20	-----	-----	-----	20
Diethylene glycol monostearate	-----	-----	20	-----	-----	----
1:9 wt. ratio copolymer of mixed octadecenyl and octadecadineyl trimethylammonium methacrylate and lauryl methacrylate	-----	-----	-----	20	-----	----
1:9 wt. ratio copolymer of di(oxo-octyl)-hydroxyethylammonium methacrylate and lauryl methacrylate	-----	-----	-----	-----	20	----
Pentapropylene-P_2S_5 reaction product	-----	-----	-----	-----	-----	20

It will be understood that the invention is not limited to the particular diethylene glycol monoesters or supplemental anticlogging agents set forth in the preceding specific embodiments, and that other materials disclosed herein can also be employed with good results. For example, for the supplemental anticlogging agents of the preceding specific embodiments there can be substituted in proportions of, for example, 10 to 20 pounds per thousand barrels of fuel, quaternary ammonium salt copolymers such as the 1:9 weight ratio copolymers of monomeric distearyldimethylammonium methacrylate and monomeric lauryl methacrylate and the 0.05:1, the 0.1:1, the 0.5:1, and 1:1 weight ratio copolymers of monomeric dioctadecenyldimethylammonium, octadecenyldimethylethylammonium, distearyldimethylammonium, laurylbenzyldimethylammonium, lauryldimethyl(ethylbenzyl)ammonium acrylates and methacrylates, and monomeric n-octyl, lauryl, Oxo-octyl, 2-ethylhexyl, Oxo-tridecyl, and n-hexadecyl acrylates and methacrylates; addition salt copolymers such as the 3:7 weight ratio copolymer of monomeric di(Oxo-octyl)ammonium methacrylate and monomeric lauryl methacrylate, the 1:9 weight ratio copolymer of monomeric di(Oxo-octyl)hydroxyethylammonium methacrylate and monomeric lauryl methacrylate, and the 0.05:1, 0.1:1, 0.5:1, and 1:1 weight ratio copolymers of monomeric octylammonium, dioctylammonium, trioctylammonium, laurylammonium, octadecylammonium, octadecenylammonium acrylates and methacrylates and monomeric n-octyl, lauryl, Oxo-octyl, 2-ethylhexyl, Oxo-tridecyl, and n-hexadecyl acrylates and methacrylates; or aminoester copolymers such as the 0.05:1, 0.1:1, 0.5:1, and 1:1 weight ratio copolymers of monomeric n-octylaminoethyl, laurylaminoethyl, octadecylaminoethyl, and octadecenylaminoethyl acrylates and methacrylates.

In addition to their remarkable stabilizing characteristics, the improvement agents disclosed herein are distinguished by the fact that they impart unusually good water separation properties to combustion gas turbine engine fuels; that is, they do not promote or permit significant emulsification of water and fuel. Moreover, the preferred fuel compositions of this invention are advantageous in that they are essentially free from metallic ash-forming materials, neglecting impurities, especially heavy metal ash-forming materials, whereby they do not accelerate development of combustion deposits in engines in which they are consumed.

The combustion gas turbine fuel compositions of this invention can also contain various other addition agents adapted to improve one or more properties of the fuel. For example, the fuel compositions of this invention can contain in addition to the addition agents disclosed herein, corrosion inhibitors, freezing point depressants, antioxidants, metal deactivators, combustion and/or ignition improvement agents and the like.

Many modifications and variations of the invention as herein described will suggest themselves to those skilled in the art and resort may be had to such modifications and variations without departing from the spirit and scope of the invention. Accordingly, only such limitations should be imposed as are indicated in the claims appended hereto.

We claim:

1. A fuel composition comprising a major amount of a normally thermally unstable liquid hydrocarbon combustion gas turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel, of a combination of (A) a monoester of a fatty acid containing 8 to 18 carbon atoms per molecule and diethylene glycol, and (B) an oil-soluble nitrogen-containing anticlogging copolymer of (i) a monomeric copolymerizable alkyl ester of an acid selected from the group consisting of acrylic and lower alkacrylic acids whose alkyl ester substitutents contains 8 to 18 carbon atoms, and (ii) a monomeric, copolymerizable unsaturated compound containing an ethylenic linkage as the sole functional group that is copolymerizable with the aforesaid monomeric alkyl ester and a nitrogen-containing substituent group, said monomeric components being present, respectively, in the copolymer in a weight ratio of about 0.03:1 to 1:1, said small amount comprising at least about 2.5 pounds of each member of said combination per thousand barrels of fuel, and the members are present in the composition in a weight ratio with respect to each other of about 8:1 to about 1:8.

2. The composition of claim **1** where said small amount comprises about 10 to 20 pounds of each member of said combination per thousand barrels of fuel, and the members are present in the composition in approximately equal weight proportions.

3. A fuel composition comprising a major amount of a normally thermally unstable liquid hydrocarbon combustion gas turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel of a combination of (A) a monoester of a fatty acid having 8 to 18 carbon atoms per molecule and diethylene glycol, and (B) an oil-soluble nitrogen-containing anticlogging copolymer of (i) a monomeric, copolymerizable alkyl ester of an acid selected from the group consisting of acrylic and lower alkacrylic acids whose alkyl ester substituent contains 8 to 18 carbon atoms, and (ii) a monomeric, copolymerizable ester of an acid selected from the aforesaid group and an amine having as at least one N-substituent an alkylol group containing 2 to 4 carbon atoms and as another N-substituent an aliphatic hydrocarbon radical containing 1 to 18 carbon atoms and as another N-substituent a member selected from the group consisting of hydrogen, aliphatic hydrocarbon radicals containing 1 to 18 carbon atoms and alkylol radicals containing 2 to 4 carbon atoms, said monomeric components being present, respectively, in the copolymer in a weight ratio of about 0.05:1 to 0.75:1, said small amount comprising at least about 2.5 pounds of each member of said combination per thousand barrels of fuel, and the members are present in the composition in a weight ratio with respect to each other of about 8:1 to about 1:8.

4. The composition of claim **3** where said small amount comprises about 10 to 20 pounds of each member of said combination per thousand barrels of fuel, and the members are present in the composition in approximately equal weight proportions.

5. A fuel composition comprising a major amount of a normally thermally unstable liquid hydrocarbon combustion gas turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel, of a combination of (A) a monoester of lauric acid and diethylene glycol, and (B) an approximately 1:9 weight ratio copolymer of (i) di(Oxo-octyl)aminoethyl methacrylate and (ii) lauryl methacrylate, said small amount comprising about 5 to 20 pounds of each member of said combination per thousand barrels of fuel, said members being present in the composition in a weight ratio with respect to each other of about 4:1 to 1:4.

6. A fuel composition comprising a major amount of a normally thermally unstable liquid hydrocarbon combustion gas turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel, of a combination of (A) a monoester of lauric acid and diethylene glycol, and (B) an approximately 1:9 weight ratio copolymer of (i) di(Oxo-octyl)aminoethyl methacrylate and (ii) Oxo-octyl methacrylate, said small amount comprising about 5 to 20 pounds of each member of said combination per thousand barrels of fuel, said members being present in the composition in a weight ratio with respect to each other of about 4:1 to 1:4.

7. A fuel composition comprising a major amount of a normally thermally unstable liquid hydrocarbon combustion gas turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel, of a combination of (A) a monoester of lauric acid and diethylene glycol, and (B) a phosphosulfurized pentapropylene product, said small amount comprising about 5 to 20 pounds of each member of said combination per thousand barrels of fuel, said members being present in the composition in a weight ratio with respect to each other of about 4:1 to 1:4.

8. A process for reducing formation of carbonaceous deposits by thermally unstable hydrocarbon oils on hot, heat transfer surfaces, comprising incorporating in a normally thermally unstable liquid hydrocarbon combustion gas turbine fuel that normally tends to form deposits upon hot, heat transfer surfaces contacted thereby, prior to contact with said heat transfer surfaces, a small amount, sufficient to reduce deposit formation of a monoester of a fatty acid containing 8 to 18 carbon atoms per molecule and diethylene glycol, and then heating the fuel by contact with a heat transfer surface at a temperature in excess of 300° F.

9. A fuel composition comprising a major amount of a normally thermally unstable liquid hydrocarbon combustion gas turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel, of a combination of (A) a monoester of a fatty acid containing 8 to 18 carbon atoms per molecule and diethylene glycol, and (B) an oil-soluble nitrogen-containing anticlogging copolymer of (i) a monomeric, copolymerizable alkyl ester of an acid selected from the group consisting of acrylic and lower alkacrylic acids whose alkyl ester substituent contains 8 to 18 carbon atoms, and (ii) a monomeric, copolymerizable unsaturated compound containing an ethylenic linkage as the sole functional group that is copolymerizable with the aforesaid monomeric alkyl ester, and also having a nitrogen-containing substituent associated with the group containing the copolymerizable ethylenic linkage through a linkage selected from the group consisting of ester, amine addition salt, amido and quaternary ammonium linkages, said monomeric components being present, respectively, in the copolymer in a weight ratio of about 0.03:1 to 1:1, said copolymer having an average molecular weight in the range of about 2,000 to about 500,000, said small amount comprising at least about 2.5 pounds of each member of said combination per thousand barrels of fuel, and said members being present in the composition in a weight ratio with respect to each other of about 8:1 to about 1:8.

10. The composition of claim **9** where said small amount comprises about 10 to 20 pounds of each member of said combination per thousand barrels of said fuel, and the members are present in the composition in approximately equal weight proportions.

11. A fuel composition comprising a major amount of a normally thermally unstable liquid hydrocarbon combustion gas turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel, of a combination of (A) a monoester of a fatty acid containing 8 to 18 carbon atoms per molecule and diethylene glycol, and (B) a member selected from the group consisting of (1) an anticlogging oil-soluble phosphosulfurized aliphatic hydrocarbon selected from the group consisting of paraffins, olefins, petroleum fractions and olefin polymers having molecular weights in the range of about 50 to 10,000, and (2) an oil-soluble nitrogen-containing anti-clogging copolymer of (i) a monomeric, copolymerizable alkyl ester of an acid selected from the group consisting of acrylic and lower alkacrylic acids whose alkyl ester substituent contains 8 to 18 carbon atoms and (ii) a monomeric, copolymerizable unsaturated compound containing an ethylenic linkage as the sole functional group that is copolymerizable with the aforesaid monomeric alkyl ester, and also having a nitrogen-containing substituent associated with the group containing the copolymerizable ethylenic linkage through a linkage selected from the group consisting of ester, amine addition salt, amido and quaternary ammonium linkages, said monomeric components being present, respectively, in the copolymer in a weight ratio of about 0.03:1 to 1:1, said copolymer having an average molecular weight of about 2,000 to about 500,000, said small amount comprising at least about 2.5 pounds of each member of said combination per thousand barrels of fuel.

12. A fuel composition comprising a major amount of a normally thermally unstable liquid hydrocarbon combustion gas turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel of a combination of (A) a monoester of a fatty acid having 8 to 18 carbon atoms per molecule and diethylene glycol, and (B) an oil-soluble nitrogen-containing anticlogging copolymer of (i) a monomeric, copolymerizable alkyl ester of an acid selected from the group consisting of acrylic and lower alkacrylic acids whose alkyl ester substituent contains 8 to 18 carbon atoms, and (ii) a monomeric, copolymerizable ester of an acid selected from the aforesaid group and an amine having as at least one N-substituent an alkylol group containing 2 to 4 carbon atoms and as another N-substituent an aliphatic hydrocarbon radical containing 1 to 18 carbon atoms and as another N-substituent a member selected from the group consisting of hydrogen, aliphatic hydrocarbon radicals containing 1 to 18 carbon atoms and alkylol radicals containing 2 to 4 carbon atoms, said monomeric components being present, respectively, in the copolymer in a weight ratio of about 0.05:1 to 0.75:1, said copolymer having an average molecular weight in the range of about 2,000 to about 500,000, said small amount comprising at least about 2.5 pounds of each member of said combination per thousand barrels of fuel, and said members being present in the composition in a weight ratio with respect to each other of about 8:1 to about 1:8.

13. The composition of claim **12** where said small amount comprises about 10 to 20 pounds of each member of said combination per thousand barrels of fuel, and the members are present in the composition in approximately equal weight proportions.

14. A fuel composition comprising a major amount of a normally thermally unstable liquid hydrocarbon combustion gas turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel, of a combination of (A) a monoester of lauric acid and diethylene glycol, and (B) an approximately 1:9 weight ratio copolymer of (i) di(Oxo-octyl)aminoethyl methacrylate and (ii) lauryl methacrylate, said copolymer having an average molecular weight in the range of about 2,000 to about 500,000, said small amount comprising about 5 to 20 pounds of each member of said combination per thousand barrels of fuel, said members being present in the composition in a weight ratio with respect to each other of about 4:1 to 1:4.

15. A fuel composition comprising a major amount of a normally thermally unstable liquid hydrocarbon combustion gas turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel, of a combination of (A) a monoester of lauric acid and diethylene glycol, and (B) an approximately 1:9 weight ratio copolymer of (i) di(Oxo-octyl)aminoethyl methacrylate and (ii) Oxo-octyl methacrylate, said copolymer having an average molecular weight in the range of about 2,000 to about 500,000, said small amount comprising about 5 to 20 pounds of each member of said combination per thousand barrels of fuel, said members being present in the composition in a weight ratio with respect to each other of about 4:1 to 1:4.

16. A fuel composition comprising a major amount of a normally thermally unstable liquid hydrocarbon combustion gas turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel, of a combination of (A) a monoester of a fatty acid containing 8 to 18 carbon atoms per molecule and diethylene glycol, and (B) an anticlogging oil-soluble phosphosulfurized aliphatic hydrocarbon selected from the group consisting of paraffins, olefins, and olefin polymers having molecular weights in the range of about 50 to 10,000, said small amount comprising about 2.5 to 20 pounds of each member of said combination per thousand barrels of fuel, and the members are present in the composition in a weight ratio with respect to each other of about 8:1 to 1:8.

17. A fuel composition comprising a major amount of a normally thermally unstable liquid hydrocarbon combustion gas turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel, of a combination of (A) a monoester of a fatty acid containing 8 to 18 carbon atoms per molecule and diethylene glycol, and (B) a member selected from the group consisting of (1) an anti-clogging oil-soluble phosphosulfurized aliphatic hydrocarbon selected from the group consisting of paraffins, olefins, and olefin polymers having molecular weights in the range of about 50 to 10,000 and (2) an oil-soluble nitrogen-containing anti-clogging copolymer of (i) a monomeric, copolymerizable alkyl ester of an acid selected from the group consisting of acrylic and lower alkacrylic acids whose alkyl ester substituent contains 8 to 18 carbon atoms, and (ii) a monomeric copolymerizable unsaturated compound containing an ethylenic linkage as the sole functional group that is copolymerizable with the aforesaid monomeric alkyl ester and having a nitrogen-containing substituent group, said monomeric components being present, respectively, in the copolymer in a weight ratio of about 0.03 to 1:1, said small amount comprising at least about 2.5 pounds of each member of said combination per thousand barrels of fuel.

18. A fuel composition comprising a major amount of a normally thermally unstable liquid hydrocarbon combustion gas turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel, of a combination of (A) a monoester of a fatty acid containing 8 to 18 carbon atoms per molecule and diethylene glycol, and (B) an anti-clogging oil-soluble phosphosulfurized aliphatic hydrocarbon from a petroleum fraction, said small amount comprising about 2.5 to 20 pounds of each member of said combination per thousand barrels of fuel, and the members are present in the composition in a weight ratio with respect to each other of about 8:1 to 1:8.

19. A fuel composition comprising a major amount of a normally thermally unstable liquid hydrocarbon combustion gas turbine fuel and a small amount, sufficient to improve the thermal stability of said fuel, of a combination of (A) a monoester of a fatty acid containing 8 to 18 carbon atoms per molecule and diethylene glycol, and (B) a member selected from the group consisting of (1) an anti-clogging oil-soluble phosphosulfurized aliphatic hydrocarbon from a petroleum fraction, and (2) an oil-soluble nitrogen-containing anticlogging copolymer of (i) a monomeric, copolymerizable alkyl ester of an acid selected from the group consisting of acrylic and lower alkacrylic acids whose alkyl ester substituent contains 8 to 18 carbon atoms, and (ii) a monomeric copolymerizable unsaturated compound containing an ethylenic linkage as the sole functional group that is copolymerizable with the aforesaid monomeric alkyl ester and having a nitrogen-containing substituent group, said monomeric components being present, respectively, in the copolymer in a weight ratio of about 0.03 to 1:1, said small amount comprising at least about 2.5 pounds of each member of said combination per thousand barrels of fuel.

20. The composition of claim **16** where said small amount comprises about 10 to 20 pounds of each member of said combination per thousand barrels of fuel, and the members are present in the composition in approximately equal weight proportions.

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