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HYDROCARBON JET FUEL CONTAINING DECABORANE AND ALKANOLS OR PHENOLS

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This invention relates to hydrocarbon fuels for jet and rocket engines, and more particularly relates to a hydrocarbon fuel for such engines containing one or more particular additives for the purpose of decreasing the tendency of the fuel to form and deposit gum at high temperatures.

Modern jet engines impose special restrictions on the type of fuels which may be satisfactorily employed in their operation. This is because, in turbo-jet engines, the turbine and compressor may operate at shaft speeds of about 8,000 r.p.m., resulting in the generation of considerable heat at turbine and compressor shaft bearings. Bearing lubricants thus must not only reduce friction but must carry away large amounts of frictional heat. In the supersonic air-speed region where most military designed jets are operated, conventional air-cooled oil heat exchangers are useless, and consequently the growing trend is to use the engine fuel supply as a coolant for the lubricating oil.

This use of fuels as a lubricating oil coolant gives rise to a serious problem. In oil-fuel heat exchangers the fuel is subjected to quite high temperatures, on the order of 400–500° F. or higher, for a relatively short period of time. At these conditions, if the fuel is thermally unstable and particularly if it is susceptible to oxidative gum formation, the heat exchanger may become fouled with gum and hence ineffective, and as a result oil temperatures may rise and bearing failures may occur. Moreover, suspended gum and soluble gum which form in the exchanger are carried downstream with the fuel, where they plug fuel filters and combustor nozzles. Ultimately, engine roughness, cycling, reduced performance, and combustor warping may result from such plugging. Even complete engine flame-out may occur.

A similar problem arises in liquid-fueled rockets. Liquid fueled rockets may circulate the incoming hydrocarbon fuel around the combustion chamber before the fuel is injected into the chamber. Should gum or coke deposition occur during this short-time high-temperature exposure, the combustion chamber would overheat and ultimately cause destruction of the rocket engines and perhaps the rocket vehicle itself.

A primary object of the present invention is to provide a hydrocarbon fuel for jet or rocket engines which is inhibited against gum formation and gum and coke deposition at high temperatures. Another object is to provide an additive or additive combination for jet and rocket fuels to enable the use of hydrocarbons which, in the absence of the invention, would be too unstable from the standpoint of gum formation to be used in these engines. Other and more particular objects will become apparent as the description of this invention proceeds.

In accordance with the invention, a hydrocarbon jet or rocket fuel which normally would tend to cause gum formation and gum or coke deposition at high temperatures is inhibited against gum formation and deposition by the addition thereto of a minor amount of a boron compound selected from the group boron hydrides. It has been further discovered in accordance with the invention that the effectiveness of the foregoing boron compounds is greatly enhanced when the jet or rocket fuel also contains a minor amount of an alkanol having from

1 to about 8, preferably 1–4, carbon atoms per molecule, such as isopropanol, or a phenol of 6–8 carbon atoms.

Among the boron compounds useful in accordance with the invention are the boron hydrides, which have the formula B_nH_{n+4} and B_nH_{n+6}. Boron hydrides corresponding to the first mentioned formula are polymers of the hypothetical compound BH_3, formerly called borine, while the latter compounds are derivatives of the hypothetical compound B_2H_4. The boron hydrides are also termed "boranes," and since a borane having a given number of boron atoms per molecule may have either of two formulae, it is conventional to include in parenthesis, after the name of the compound, the number of hydrogen atoms per molecule. Thus according to this nomenclature the following suggested compounds may be employed in accordance with the invention: diborane (6), tetraborane (10), pentaborane (9), pentaborane (11), hexaborane (10), hexaborane (12), decaborane (14), etc. In general, while boranes having from 1 to about 20 or more boron atoms per molecule are useful, it is preferred to use a borane having from 4 to about 12 boron atoms per molecule, since these are relatively nonvolatile and have only a slight tendency to be pyrophoric.

The second but optional component used as an additive herein is a lower alkanol, i.e. an aliphatic alcohol having from 1 to 8 carbon atoms per molecule, preferably from 1 to 4 carbon atoms per molecule, or a phenol of 6–8 carbon atoms. Suitable alkanols include methanol, isopropanol, n-butanol, amyl alcohol, and hexanol. Suitable phenols include unsubstituted phenol, cresol, etc.

The amounts of each additive which are added to a particular jet or rocket fuel depend both on the service temperature and upon the inherent stability of the uninhibited hydrocarbon fuel. Where the fuel is highly unstable, particularly when derived from thermally cracked petroleum hydrocarbons, both additives may be used in relatively high concentrations, while an essentially virgin fuel or hydrogenated fuel requires very little of either. Ordinarily, the amount of boron compound may range from as little as 0.001 volume percent to about 5 volume percent based on total fuel, but usually is in the range of about 0.001 to 0.5%, preferably between 0.01 to 0.05% for the average JP–4 or JP–5 fuel. The amount of alcohol may be as little as 0.001 to as much as about 20 volume percent, preferably 0.01 to 15%; the amount of alcohol may be limited by allowable water absorption tolerances of the fuel. Since boron compounds vary considerably in molecular weight, the required amounts thereof may be defined on the basis of moles of boron compound per liter of hydrocarbon, and, in these terms, there may be used 0.0001 to 0.01, preferably 0.001 to 0.005 moles of boron compound per liter (m./l.) of fuel.

The hydrocarbon fuel or base component of the inventive jet or rocket fuel consists chiefly of a liquid hydrocarbon fluid boiling in the range of about 150 to 650° F. usually in the range of about 150–600° F. Jet and rocket fuels are usually prepared to conform with various military specifications, and existing jet fuels for military and civilian jets may be defined with reference to specification MIL–F–5616 (JP–1), and MIL–J–5624D (JP–3, –4, and –5). JP–4, the most commonly used present day (1959) jet fuel has a 20% distillation point of 290° F. and a 90% point of 470° F., an API gravity between 45 and 57, an existent gum of 7.0 max., a potential gum of 14.0 max., and may contain a maximum of 25 volume percent aromatics and 5 volume percent olefins. Various other requirements for JP–4 are described in the foregoing MIL–J–5624D. Other jet fuels are described in, for example, MIL–F–25656, MIL–F–25524A, MIL–F–5161E, etc. Ram jet engines currently employ grade RJ–1 fuel (MIL–F–2558–B) having a 430° F. minimum initial boiling

point and a 600° F. maximum end point in addition to other requirements. Hydrocarbon RP–1 grade fuels for rockets are described in MIL–F–25576A and MIL–F–19605 (SHIPS). It is contemplated that other requirements and other types of fuel may, from time to time, be substituted in whole or in part for the current jet and rocket fuel definitions.

Special-purpose hydrocarbon fuels for jets and rockets, such as technically pure alkyldicyclohexyl or alkyldecalin derivatives may also be inhibited against gum formation and deposition with the instant additive or additives.

In order to establish the efficacy of the presently described boron compounds, alone and in the conjoint presence of an alcohol, an unstable jet fuel was prepared from an ordinary JP–4 hydrocarbon jet fuel to which was added one part by volume of a highly unstable thermal naphtha per four parts of the JP–4. This fuel base, both with and without various inhibitors, was tested in a laboratory device for determining gum formation and deposition characteristics under short-time high-temperature conditions equivalent to those experienced in the oil-fuel heat exchangers of turbo-jet engines or on combustion chamber walls of rocket engines. The test device was a thermostatically controlled metal block through which ran a channel containing a removable aluminum specimen which specimen was weighed before and after each test to determine the amount of gum or coke deposition thereon. Test conditions were a block temperature of 400° F., and fuel flow rate of 400 ml. per hour, resulting in a fuel residence time of 12 seconds. The test was run for 2.5 hours. The following results were obtained:

JET FUEL HIGH TEMPERATURE STABILITY TEST RESULTS

Additive	Deposit Color	Deposit Weight (micrograms)	Appearance of Fuel following test
1—0.003 M decaborane plus 10 volume percent isopropanol.	Thin blue haze.	20	Clear.
2—0.003 M decaborane	Haze	110	Solid formation.
3—10 volume percent isopropanol.	Brown	450	Cloudy due to sediment formation.
4—None	do	400	Do.

It is particularly noted that only 0.003 M decaborane reduced deposit weight by about 70%, while 10 volume percent isopropanol alone actually increased the deposit weight. However, the combination of decaborane with isopropanol effected a 95% reduction in deposit weight. Moreover, the combination resulted in a fuel after testing which was water-clear and exhibited no cloudiness due to gum or other solid formation. It is also noted that isopropanol entirely eliminated solids formed by the apparent decomposition of decaborane.

The foregoing test data demonstrate that by adding a boron compound, optionally together with an alcohol, to a liquid hydrocarbon jet or rocket fuel, oxidative gum formation and deposition are at least partially inhibited. Consequently, the fuel side of a jet engine oil-fuel heat exchanger is maintained in more effective condition, with more effective heat exchange, than would be possible in the absence of said additives. Also, using the instant

additives there are several benefits to be gained in rocket or jet engines; the combustion chambers are maintained clean and cool, and the higher heat of combustion of boron compounds is advantageous in increasing the specific impulse of rocket fuels and in increasing the range or load-bearing capacity of jet aircraft. The boron compound and/or the alcohol or phenol may be incorporated in the hydrocarbon fuel during manufacture or introduced immediately before fueling the vehicle or alternatively, it may be introduced by injecting these additives in the form of a concentrate into the fuel just before the fuel passes into the engine. Such concentrate may contain at least 5 volume percent boron compound and at least 20 volume percent alcohol or phenol, the balance (if any) being inert for the present purpose.

We claim:

1. A jet and rocket fuel composition consisting essentially of a major proportion of a normally liquid hydrocarbon of the jet and rocket fuel boiling range normally tending to cause gum and coke deposits at high temperatures, from about 0.001 to about 5 volume percent of decaborane, and from 0.001 to about 20 volume percent of a member of the group consisting of alkanols having from 1 to 8 carbon atoms per molecule and phenols having from 6 to 8 carbon atoms per molecule.

2. The composition of claim 1 wherein said alkanol is isopropanol.

3. A jet and rocket fuel composition comprising a major proportion of a normally liquid hydrocarbon of the jet and rocket fuel boiling range (*a*) from about 0.001 to about 5 volume percent of decaborane and (*b*) from about 0.001 to about 20 volume percent of isopropanol.

4. The method of operating jet and rocket engines comprising burning in said engines a fuel composition consisting essentially of a major proportion of a normally liquid hydrocarbon of the jet and rocket fuel boiling range, from about 0.001 to about 0.5 volume percent of decaborane, and from 0.001 to about 20 volume percent of a member of the group consisting of alkanols having from 1 to 8 carbon atoms per molecule and phenols having from 6 to 8 carbon atoms per molecule.

5. The method of claim 4 wherein the alkanol is isopropanol.

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