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ROCKET FUEL AND FUEL ADDITIVE

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This invention relates to rocket propellants, and more particularly to means and methods for effecting rapid, spontaneous ignition of liquid rocket fuels which do not undergo spontaneous ignition when admixed with common oxidizers.

From the viewpoints of military transport and supply, including handling and storage, hydrocarbon fuels, particularly the jet-fuel types, are preferred for rocket motors. The varieties of fuming nitric acid, white and red, are among the most important oxidizers for use with rocket fuels. A great difficulty, however, which is involved in the use of such hydrocarbon-nitric acid systems as rocket propellants, lies in initiating and continuing combustion therein.

A principal object of this invention is to provide a rocket fuel which will ignite spontaneously and with a minimum of delay after contacting said fuel with fuming nitric acid.

Another object is to provide an additive for a jet-type liquid hydrocarbon fuel which, in admixture with the fuel in a suitable proportion, causes the mixture, upon the addition of fuming nitric acid thereto, to exhibit a high rate of temperature rise in the pre-ignition liquid phase, and a marked reduction in minimum ignition temperature—in comparison with results obtained under like conditions of test, but in the absence of said additive.

Other objects and advantages of the invention will appear as the description thereof proceeds.

At the threshold of our description we shall state the respective meanings that we intend to be comprehended in certain words and phrases which may appear therein or in our claims, as follows:

Jet-type liquid hydrocarbon fuel.—Such a fuel is contemplated herein to meet U.S. military specifications (MIL–F–5624B) for high vapor pressure (JP–3) and low vapor pressure (JP–4) grades, when tested in accordance with prescribed methods (VV–L–791). The following relevant specifications are the same for each of grades JP–3 and JP–4, namely, 90 percent shall distill off at not above 470° F.; the maximum freezing point shall be minus 76° F.; the maximum volume percentage of aromatic hydrocarbons shall be 25.0; and the volume percentage of olefin hydrocarbons is not limited. Vapor pressure measurements (Reid) shall lie in the range of 5.0 to 7.0 p.s.i. for JP–3, and in the range of 2.0 to 3.0 for JP–4.

Hypergolicity.—This term, as well as hypergolic activity, means the property possessed by a rocket fuel, or by an additive therefor, of igniting spontaneously when brought into contact with fuming nitric acid. This property is not possessed by either of the jet-type liquid hydrocarbon fuels, JP–3 and JP–4; both are non-hypergolic.

O/F ratio.—The O/F or oxidizer-fuel ratio is the numerical value of the proportion, usually by volume, of oxidizer to fuel in a given oxidizer-fuel system.

Other technical terms, used but not defined herein, are conventional in the rocket art.

We have discovered that a chemical compound, whose molecular structure is made up of a symmetric diolefin, with an aliphatic, tertiary amino group attached to each of its alpha and delta carbons, provides a hypergolic rocket fuel. Examples of such a compound are 1,4-bis-(dimethylamino)-1,3-butadiene

$$(CH_3)_2NCH{:}CHCH{:}CHN(CH_3)_2$$

and 1,4-bis-(diallylamino)-1,3-butadiene

$$(CH_2{:}CHCH_2)_2NCH{:}CHCH{:}CHN(CH_2CH{:}CH_2)_2$$

We ordinarily shall designate the first of these two compounds as DMAB, and the second as DAAB.

We also have discovered that such a substituted diolefin, preferably DMAB, can establish hypergolicity in a rocket propellant, comprising a nonhypergolic hydrocarbon fuel in admixture with a minor proportion of DMAB.

DMAB.—This compound is a light brown or amber colored liquid, with a mild ammoniacal odor. It boils at 102° C./25 mm., and decomposes when heated above 150° C. It has been stored for more than 18 months at ambient temperatures and in the presence of air, without undergoing any noticeable decomposition.

Hypergolicity of DMAB and of DAAB.—This was demonstrated by spontaneous ignition, with production of flames and a large volume of yellow brown smoke when, for example, one drop of DMAB was added to 0.5 ml. of white fuming nitric acid. The hypergolicity of DAAB was demonstrated in similar fashion.

Ignition delay of DMAB and of DAAB.—This represents the time lag from the initial contact of a hypergolic fuel with fuming nitric acid to the appearance of a flame. This time lag is measured by means of an ignition delay apparatus which, in its essentials, comprises a thermostated, graduated pipette, for measuring the fuel, mounted so that its outlet is about 10 cm. above a thermostated reaction vessel containing ordinarily 2.5 ml. of acid; a horizontal beam of light refracted by a lens so that it converges to a focus at the surface of the acid, and then diverges to be picked up by a first photocell; an electronic timer; and a second photocell which is mounted so as to be sensitized by the flash of ignition. To obtain a value for ignition delay a predetermined fraction of a ml. of fuel is dropped from the pipette onto the acid. The resulting indentation in the surface of the acid alters the refraction of the light beam so that it does not reach the first photocell in its original intensity—thereby causing it to actuate the starting mechanism of the timer. The ensuing flash of ignition causes the second photocell to actuate the stop mechanism of the timer.

The ignition delay of DMAB with white fuming nitric acid, determined in the manner just described, was less than 10 milliseconds. The average ignition delay of DAAB, determined in the same manner, was 35.1 milliseconds.

Hypergolicity of jet-type hydrocarbon fuels containing DMAB.—A nonhypergolic, jet-type hydrocarbon fuel is rendered hypergolic to fuming nitric acid when DMAB is dissolved in the fuel. The optimal concentration of DMAB in the mixed fuel was found to lie within the range of about 12 percent to about 50 percent by weight.

Minimum ignition temperature of a jet-type hydrocarbon fuel as affected by addition of DMAB.—Minimum ignition temperature, as comprehended herein, is the lowest temperature at which the fuel, in intimate admixture with an oxidizer—here red fuming nitric acid—ignites spontaneously. The apparatus employed to determine such temperature comprises a furnace in the form of a solid Inconel cylinder, which can be heated to a desired temperature by current carried by an asbestos-covered Nichrome wire wound helically about the cylinder; a centrally located vertical hole in the cylinder,

adapted to receive a Pyrex glass ignition tube, which serves as a reaction vessel; a thermocouple located immediately below the bottom of the ignition tube; a potentiometer connected to the thermocouple; and a pair of gradulated pipettes for measuring acid and fuel, respectively—the pipettes being so positioned above the reaction vessel that, upon the opening of a singe stopcock, the acid and fuel are delivered to the bottom of the reaction vessel at the same time.

In determining minimum ignition temperature the furnace is brought up to a predetermined trial temperature, and the reaction vessel is allowed to reach thermal equilibrium therewith. The acid and fuel then are allowed to drop simultaneously into the reaction vessel. Spontaneous ignition at the trial temperature is evidenced by the appearance of a flame.

The minimum ignition temperature of a low vapor pressure fuel (JP–4), when mixed with an equal volume of red fuming nitric acid, was 324° C.; whereas, under like conditions of test, except that the fuel consisted of 90 percent by weight of JP–4 and 10 percent DMAB, the minimum ignition temperature was 270° C.

Rate of temperature rise in a hydrocarbon fuel-nitric acid system as affected by addition of DMAB to the fuel.—When fuming nitric acid is mixed with a jet-type liquid hydrocarbon fuel, a preignition, liquid phase, exothermic reaction occurs. The rise in temperature during a very short period subsequent to the mixing of fuel and acid can serve with other data in evaluating the effectiveness of a rocket fuel additive. Measurement of this initial rate of temperature rise was made with an apparatus comprising a thermistor encased in a short glass rod and positioned near the bottom of a 30-ml. beaker, which served as a reaction chamber; a recording potentiometer which automatically plotted the output of the thermistor against time; an acid pipette; and a constant speed electric stirrer for the reaction mixture. The potentiometer readings were converted into temperatures by calibrating the output of the thermistor with water at various temperatures.

The quantities of fuel and of acid (red fuming nitric acid) used in each test were 1.8 ml. and 3.0 ml., respectively, an O/F ratio of 1.7; the fuel being measured into the beaker, and the acid being dropped from the pipette into the fuel to start the reaction.

Thirteen determinations of the temperature rise in the fuel-acid system—the fuel being 100 percent JP–4—within the first 0.59 second following formation of the mixture, yielded an average rise of 7 degrees C.; whereas seven determinations under like conditions of test, except that the JP–4 contained an added 10 percent by weight of DMAB, yielded an average temperature rise of 24 degrees C.

Although the foregoing description relates to the preferred embodiment of our invention, all quantities, proportions or ratios given hereinabove are intended to be illustrative only; and various modifications and changes in details may be made without departing from the spirit of the invention as the same is defined in the appended claims.

We claim:

1. A rocket propellant, consisting of in combination, a liquid hydrocarbon fuel and 1,4-bis-(dimethylamino)-1,3-butadiene in an amount not substantially less than one part by weight to seven parts of said fuel.

2. In the process of propelling a rocket, the steps which comprise forming a hypergolic propellant by mixing not substantially less than one part by weight of 1,4-bis-(dimethylamino)-1,3-butadiene with about seven parts of a nonhypergolic jet-type hydrocarbon fuel, contacting said propellant with substantially an equal volume of fuming nitric acid and burning said propellant in the combustion chamber of a rocket motor.

3. In rocket propulsion, the process of causing hypergolic ignition in the fuel-oxidizer system which comprises using 1,4-bis-(dimethylamino)-1,3-butadiene in a liquid hydrocarbon fuel in an amount from about 12 percent to about 50 percent and fuming nitric acid in substantially equal volume and burning said propellant in the combustion chamber of a rocket motor as the oxidizer.

4. The process of reducing the minimum ignition temperature in a rocket motor combustion chamber of a jet-type hydrocarbon fuel from about 324° C. to about 271° C., when mixed with red fuming nitric acid in an oxygen-fuel ratio of 1.0 by volume, which comprises mixing with said fuel about 10 percent by weight of 1,4-bis-(dimethylamino)-1,3-butadiene.

5. A rocket propellant, consisting of in combination a liquid hydrocarbon fuel and 1,4-bis-(dimethylamino)-1,3-butadiene in an amount from about 12 percent to about 50 percent.

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