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# STORABLE LIQUID ROCKET PROPELLANTS CONTAINING TETRANITROMETHANE WITH DIFLUORAMINO COMPOUNDS AND METHOD OF USE

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This invention relates to high-performance liquid propellant compositions for use in rockets. It is concerned more particularly with a formulation of such liquid oxidizer compositions which are stable liquids under ordinary conditions and storable.

Known, high performance liquid propellants, including a liquid oxidizer, have the disadvantage of being non-storable, e.g., systems such as $H_2+F_2$, $N_2H_4+_2$ and $N_2H_4+O_2$. These systems involve the use of a liquefied normally gaseous oxidizer.

Now in accordance with the present invention a stable liquid propellant combination of high performance is found to be provided by using a liquid difluoramino substituted and saturated compound such as those containing 1 $NF_2$ group per carbon and containing at least 1 $NF_2$ group per 2 H atoms, with liquid tetranitromethane. These ingredients, which provide both fuel and oxidizer constitutents can be mixed and safely stored.

The liquid difluoramino saturated compounds include bis(difluoramino) ethane $C_2H_4(NF_2)_2$, tris (difluoramino) propane $C_3H_5(NF_2)_3$, tetrakis ($NF_2$) tetrahydrofuran tetrakis (difluoramino) butane $C_4H_6(NF_2)_4$, pentakis (difluoramino) pentane $C_5H_7(NF_2)_5$, $C_5H_8(NF_2)_4$,

$$C_6H_7(NF_2)_5$$

and $C_6H_8(NF_2)_4$, as particularly useful ingredients. In general, the useful liquid difluoramino alkanes for the present purposes contain 2 to 7 carbon atoms per molecule with an $NF_2$ group attached to each carbon atom. Mixtures of these compounds may be used satisfactorily together in combination with the oxygen supplying oxidizer tetranitromethane, $C(NO_2)_4$. The resulting liquid mixture may be made to be used as a monopropellant system which supplies both fuel and oxidizing constitutents (fluorine and oxygen).

To use the liquid propellant, it may be introduced into the combustion zone of a rocket where a suitable igniter, e.g. squib, spark or glow plug or a hypergolic material, initiates ignition.

The liquid mixtuer of the difluoramino alkane and tetranitromethane is useful in a bipropellant system which admixes a liquid borohydride, e.g. $B_4H_{10}$, $B_5H_9$, and $B_6H_{10}$, with these oxidizers in the combustion zone.

The following examples illustrate propellant formulations of the present invention.

## EXAMPLE 1

Using a liquid mixture of 0.2857 mole $C(NO_2)_4$ per mole of bis(difluoramino) ethane, the density of the mixture is about 1.53. The determined specific impulse (Isp) of this mixture in pounds thrust per pounds flow of the mixture per second is 305 seconds. The performance factor of this mixture is about 466, this factor being directly proportional to the product of the density and specific impulse. This performance factor is of most importance in evaluating the relative merits of various liquid propellants. Thus, the performance factor of 466 for the mixture of $C_2H_4(NF_2)_2$ plus $C(NO_2)_4$ is higher than that of other high performance liquid propellant compositions except $N_2H_4$ plus liquid oxygen, which is not a storable combination.

The liquid mixture of $C(NO_2)_4$ and bis ($NF_2$) ethane is a unique monopropellant in which oxidizing and fuel constituents are satisfactorily balanced even if the ratios of these compounds are varied. Although both these components have been thought of as oxidizers, no other fuel need be admixed.

In using the normally liquid propellant ingredients, e.g. $C(NO_2)_4$ and the liquid difluoramino alkanes, the container walls for storage in or out of the rocket casing can be thinner, thus increasing the propellant load capacity. The hardware for flowing and metering can thus be simplified, also.

The $C(NO_2)_4$ plus liquid difluoramino alkane mixture can be used in a bipropellant system with liquid borohydrides to obtain a still higher specific impulse.

## EXAMPLE 2

By introducing from separate storage chambers liquid $B_5H_9$ and a liquid mixture of $C(NO_2)_4$ plus $C_2H_4(NF_2)_2$ into a combustion chamber, the specific impulse obtained is 326 seconds, the molar ratio of the combination being 2.83/1.287/1.5 for the $B_5H_9$, $C(NO_2)_4$, and $C_2H_4(NF_2)_2$.

The following table compares the quality of the formulation by the present invention with other liquid propellant systems.

TABLE

| System | Isp | D (Density) | D Isp |
|---|---|---|---|
| $C(NO_2)_4+C_2H_4(NF_2)_2$ | 305 | 1.53 | 466 |
| $H_2—F_2$ | 372 | 0.82 | 305 |
| $N_2H_4—F_2$ | 362 | 1.32 | 478 |
| $N_2H_4—N_2O_4$ | 290 | 1.23 | 357 |

Of the systems liste din the table, the only system other than $C(NO_2)_4+C_2H_4(NF_2)_2$ which is liquid at ordinary atmospheric temperatures is $N_2H_4—N_2O_4$. It is evident that the $C(NO_2)_4+C_2H_4(NF_2)_2$ system is much better than the latter in performance. Moreover, $N_2H_4—N_2O_4$ components do not make a stable storable mixture.

## EXAMPLE 3

Mixing a molar ratio of 1.287 moles $C(NO_2)_4$ per mole of tris ($NF_2$) propane, this liquid oxidizer mixture can be stored indefinitely and can be supplied to a combustion chamber to burn $B_5H_9$ supplied thereto as liquid at a rate of 2.83 moles per mole of the tris ($NF_2$) propane in the $C(NO_2)_4$ mixture to give an impulse of 326 seconds.

The molar ratios of the mixed liquid oxidizers and of the borohydride fuel can be changed without substantial changes in the resulting impulse; however, for highest impulses the ratios are balanced to form as principal exhaust products, BOF, CO, HF, $H_2$.

Other variations may be made in selection of liquid fuels. For example liquefied diborane $B_2H_6$ may be used and also liquid alkyl decaboranes. If desired, small proportions of compatible thickening agents and powdered flammable metals e.g. boron, aluminum or the like may be dispersed in the liquid fuel.

The mixed, liquid oxidizers, $C(NO_2)_4$ and difluoramino alkanes, may be thickened with stable and compatible difluoramino polymers having close to 1 $NF_2$ per carbon without detracting drastically from their high performance. The amount of thickening is kept low to prevent sticking and to avoid undesired retardation of flow.

It is believed that by using the liquid mixture of oxygen oxidizer, $C(NO_2)_4$, and a liquid difluoramino alkane as fluorine oxidizer the highest specific impulse and performance is obtained in comparison to any other system using a stable oxidizer and fuel mixture.

While the stable $C(NO_2)_4$+liquid difluoramino alkane mixtures are of exceptional value in attaining very high thrust performance used by themselves or with particularly good liquid fuels, e.g. the borohydrides, they have still other exceptional values. They may be used to oxidize lower energy fuels, if desired. They are particularly interesting in being capable of high Isp values particularly with relatively low exhaust gas temperatures, which is of concern in preventing burning-out of exhaust nozzles. For this purpose, from about 0.2 to 1.4 mole of $C(NO_2)_4$ is mixed with 1 mole of the difluoramino compound represented as having the composition $C_nH_{n+2}(NF_2)_n$, $n$ being 2 to 7, and depending upon the proportion of the hydrocarbon group ($C_nH_{n+2}$) present. Thus, preferably the optimum mole ratio of the $C(NO_2)_4$ to the difluoramino alkane $C_nH_{n+2}(NF_2)_n$ is close to $n/7 \pm n/20$, wherein $n$ is 2 to 7.

The $C(NO_2)_4$+difluoramino compound liquid mixtures can have a varied ratio of oxygen to carbon over a range without substantial loss in performance and with the advantage of relatively low exhaust gas temperatures when the O/C ratio is low. This holds even when the difluoramino-hydrocarbon components do not have quite 1 $NF_2$ group per carbon. For example, in a system where the compounds having $CNF_2$ groups have the average composition $C_5H_8(NF_2)_4$ and these compounds are mixed for combustion with liquid $C(NO_2)_4$, the optimum ratio for maximum specific impulse is close to 1.25 mole $C(NO_2)_4$ per mole of the $C_5H_8(NF_2)_4$ liquid but this ratio can be lowered to 1 without much loss in performance yet with a drop of about 300° C. in the exhaust gas temperature. In this particular system the ratio of ($NF_2$) to hydrogen is 1:2, of F/H is 1:1 and of $NF_2$/C is 4:5.

The difluoramino compounds of the $C_5H_8(NF_2)_4$ type perform like $C_2H_4(NF_2)_2$ in having 1 F/1H atom ratio. Another compound of this type is tetrakis ($NF_2$) cyclohexane, $C_6H_8(NF_2)_4$.

Accordingly, in a broad sense the present invention discloses that the liquid oxygen oxidizer is mixed with a compatible (mutually stable in the mixture) liquid difluoramino compound, which contains 2 to 7 carbon atoms per molecule, is saturated (contains no C=C bonds), and contains at least 1 $NF_2$ group per 2 H atoms. For brevity, these difluoramino compounds are termed para-alkanes. The para-alkanes thus include the difluoramino-alkanes difluoramino-cycloalkanes, and difluoramino-epoxyalkanes (e.g. tetrakis ($NF_2$) tetrahydrofuran as tetrakis ($NF_2$) 1,4-epoxy butane).

Modifications and variations falling within the scope of this invention are defined in the claims.

What is claimed is:

**1.** A stable oxidizer and fuel liquid mixture consisting essentially of tetranitromethane in a 0.2 to 1.4 mole proportion and a 1 mole proportion of a compatible liquid $C_2$ to $C_7$ difluoramino para-alkane containing at least 1 $NF_2$ group for each two hydrogen atoms in the para-alkane molecule.

**2.** A composition as defined in claim **1** in which the para-alkane is an alkane.

**3.** A composition as defined in claim **1**, in which the para-alkane is a cycloalkane.

**4.** A composition as defined in claim **1** in which the para-alkane is an epoxy alkane.

**5.** A composition as defined in claim **1** in which the para-alkane contains 1 $NF_2$ group per carbon atom.

**6.** A stable oxidizer and fuel liquid mixture consisting essentially of a 0.2 to 1.4 mole proportion of liquid $C(NO_2)_4$ and a 1 mole proportion of liquid bis ($NF_2$) ethane.

**7.** A stable oxidizer and fuel liquid mixture consisting essentially of a 0.2 to 1.4 mole proportion of liquid $C(NO_2)_4$ and a 1 mole proportion of liquid tris ($NF_2$) propane.

**8.** A stable oxidizer and fuel liquid mixture consisting essentially of a 0.2 to 1.4 mole proportion of liquid $C(NO_2)_4$ and a 1 mole proportion of liquid tetrakis ($NF_2$) butane.

**9.** A stable oxidizer and fuel liquid mixture consisting essentially of a 0.2 to 1.4 mole proportion of liquid $C(NO_2)_4$ and a 1 mole proportion of liquid pentakis ($NF_2$) cyclohexane.

**10.** A method of developing thrust by combustion of bi-propellant oxidizer and fuel components in a combustion chamber which comprises injecting into the combustion chamber a liquid stream of liquid $C(NO_2)_4$ mixed in a 0.2 to 1.4 mole proportion with a 1 mole proportion of liquid $C_2$ to $C_7$ para-alkane containing at least 1 $NF_2$ group per 2 hydrogen atoms in the molecule and simultaneously injecting into the combustion chamber a stream of liquid borohydride as fuel.

**11.** A method of developing thrust by combustion of a liquid mono-propellant which comprises injecting into a combustion chamber a liquid stream consisting essentially of liquid $C(NO_2)_4$ mixed in a 0.2 to 1 mole proportion with a 1 mole proportion of liquid difluoramino $C_2$ to $C_7$ para-alkane containing 1 $NF_2$ group per two hydrogen atoms.

**12.** The method defined in claim **11**, in which the mono-propellant is a liquid mixture of $C(NO_2)_4$ and bis ($NF_2$) ethane.

No references cited.

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