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(71) Applicant (for all designated States except US): ECAPS AB [SE/SE]; P.O. Box 4207, S-171 04 Solna (SE).
(72) Inventors; and
(74) Agent: BRANN AB; P.O. Box 12246, S-102 26 Stockholm (SE).

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(54) Title: LOW-TEMPERATURE OPERATIONAL AND STORABLE AMMONIUM DINITRAMIDE BASED LIQUID MONOPROPELLANT BLENDS
(57) Abstract: Ammonium dinitramide based liquid monopropellants containing ADN, water, ammonia and, optionally, methanol, exhibiting improved low-temperature operational range are disclosed.
LOW-TEMPERATURE OPERATIONAL AND STORABLE AMMONIUM DINITRAMIDE BASED LIQUID MONOPROPELLANT BLENDS

FIELD OF THE INVENTION

The present invention relates to ammonium dinitramide (ADN) based liquid monopropellant blends exhibiting improved storability and operational range in terms of having a reduced lower operational temperature limit. The inventive monopropellant belongs to a type of monopropellants generally being referred to as High Performance Green Propulsion (HPGP) monopropellants. The monopropellants are especially suited for rocket propulsion, other vessel or vehicle propulsion, and gas generation. More particularly the present invention relates to such propellants especially suited for space, and deep space applications, and suitable for storage, and operation in close proximity to cryogenic propulsion systems, and land/sea/air-based systems operating in cold environments.

BACKGROUND OF THE INVENTION

WO 2002/096832 discloses stable, liquid monopropellants based on ammonium dinitramide, having improved combustion characteristics. The propellants are low-hazardous both from a handling point of view and from an environmental point of view, and exhibit a low toxicity, low flammability, a high theoretical specific impulse, high density. Moreover such propellants are easily ignitable by means of a controlled ignition mechanism, and at the same time exhibit a low sensitivity. For space applications, and in order to be competitive with hydrazine, which solidifies at 1°C, such propellants must be storable and operational at temperatures within the range of 10°C and 50°C.

The most preferred propellants of WO 2002/096832 are composed of ADN, water, glycerol, and a stabilizer, or ADN water, methanol, and a stabilizer. Especially preferred is a composition consisting of about 64.3% ammonium dinitramide, about 24.3% water and about 11.4% by weight of methanol, (this composition is also being designated as LMP-103) to which composition a stabiliser is added in an amount of 0.1 to 5%, more typically 0.5-3 and preferably 0.5-1 by weight based upon the other components. The above monopropellant is an example of a
newly developed type of monopropellants referred to as High Performance Green Propulsion (HPGP) monopropellants.

The monopropellants of WO 2002/096832 can for example be used for the purpose of orbit manoeuvring and attitude control of satellites, and other space vehicles, in which case rocket engines, or thrusters are often used in short bursts or pulses, the duration of which typically can be fractions of seconds to several hours. For such purposes small rocket engines, or thrusters are commonly used with a nominal thrust of typically 0.5 N to 3 kN.

It has recently been found that the monopropellant designated LMP-103S, which is composed of 63.0% by weight of ADN, 18.4% by weight of methanol, 4.6% by weight of ammonia, the balance to 100% being water, and which is an example of the monopropellants disclosed in WO 2002/096832, tends to undergo saturation with respect to the dissolved ADN, which forms solid crystals in the mixture of liquid solvents when the temperature of the monopropellant is being lowered to about −7°C.

Accordingly, it would be desirable to provide a propellant for the above-mentioned purposes, which propellant should exhibit the above-mentioned desired characteristics of the above-mentioned liquid ADN-based HPGP monopropellant, and which propellant should remain a homogenous solution at temperatures below −7°C. Preferably, the propellant should remain homogeneous at temperatures down to −15°C. More preferably, the propellant should remain homogeneous at temperatures down to −30°C.

It is therefore an object of the present invention to provide such monopropellant.

According to the present invention, for an ADN-based, liquid monopropellant comprising ADN, water, and ammonia of the preamble of claim 1, the above object has been solved by means of the features of the characterising portion of claim 1.
SUMMARY OF INVENTION

The present inventors have surprisingly found that the low-temperature storability and operational range of a HPGP monopropellant comprising ADN, water, and ammonia, such as LMP-103S, could be substantially improved.

More particularly, it has been found that monopropellants having a composition comprising:

- 55-62 % by weight of ammonium dinitramide;
- 0-22 % by weight of methanol;
- 4-12 % by weight of ammonia; and
- the balance water;

will exhibit a saturation temperature of $-10^\circ$C, or below.

According to the invention, monopropellant blends within the above specified range have been found to be a homogenous solution down to $-30^\circ$C. It is believed that according to the invention monopropellants can even be obtained which remain homogeneous solutions down to temperatures of $-40^\circ$C.

An improved low-temperature operational range of the monopropellant will have the advantage of less energy being required for heating the monopropellant during storage and operation. Accordingly, an energy providing system having reduced capacity, complexity and weight can therefore be used. This will also reduce the associated costs. As will be understood, each degree C of reduced temperature that the monopropellant will be tolerable to will be of substantial importance.

Also, any crystallization occurring in the inventive monopropellants during cooling thereof has been found to be reversible, that is, the crystals formed will dissolve again upon heating of the monopropellant. The required heating has been found to generally correspond to an increase of 5-10°C from the point of the observed saturation temperature.
By virtue of the improved low-temperature operational range, the inventive monopropellant blends will also allow for being stored and used in a closer proximity to cryogenic tanks than the prior art ADN-based liquid HPGP monopropellants, while at the same time requiring reduced extent heating during storage.

The inventive monopropellant blends will generally not require heating from the above-mentioned low temperatures up to a propellant feed temperature of e.g. 20°C before they are injected and ignited in the thruster. Instead, the monopropellants, as long as they are still homogenous, can be used directly, already at a low temperature. That is, the inventive monopropellants are operational at low temperatures.

In the present disclosure all percentages are given by weight unless otherwise indicated.

The term "monopropellant", as used in the present disclosure, may more correctly be referred to as "monopropellant blend", since the inventive propellant comprises more than one chemical compound. In the present disclosure, the terms "monopropellant" and "monopropellant blend", however, have been used interchangeably to denote the inventive propellant.

The percentages given for ammonia herein refer to pure NH₃. Consequently, if aqueous ammonia is being used in preparing the inventive monopropellants, when establishing the water content of the monopropellant being prepared, the water contained in the ammonia must be taken into account.

The improved low-temperature operational range will also make the inventive monopropellants suitable for land/sea/air-based systems stored and used in cold conditions, such as e.g. artic conditions, in for example gas generators, APUs, underwater vehicles, etc.

Further advantages and embodiments of the invention will be apparent from the following detailed description and appended claims.
DETAILED DESCRIPTION

The reduced low-temperature operational limit of the ADN-based monopropellant has been found to be governed by the temperature at which saturation with respect to ADN will occur, or, the temperature at which solidification of the monopropellant blend will occur, whichever is the higher temperature of the two.

In an ideal situation, in the absence of any disturbing particles in the liquid ADN-based monopropellant containing ADN, water, ammonia, and, optionally, methanol, such monopropellant should withstand being subjected to temperatures down to near its solidification point (a super saturated solution). For example, the solidification point for LMP-103S is as low as about −90°C. In practice, however, saturation with respect to ADN is observed already at about −7°C for this propellant.

Above the saturation temperature of a given monopropellant composition of the invention, the inventive monopropellant will not be affected by moderate presence of particulate matter in the monopropellants.

The present inventors have been found that monopropellants having a composition comprising:
55-62 % by weight of ammonium dinitramide;
0-22 % by weight of methanol;
4-12 % by weight of ammonia; and
the balance water;
will exhibit a saturation temperature of −10°C, or below.

In a preferred embodiment the liquid monopropellant of the invention comprises:
55-62 % by weight of ammonium dinitramide;
5-20 % by weight of methanol;
4-11 % by weight of ammonia; and
the balance water.
Such monopropellant blend will remain a homogenous solution down to a temperature of −15°C, or below.

More preferably, the liquid monopropellant of the invention comprises:
55-62 % by weight of ammonium dinitramide;
10-18 % by weight of methanol;
4-10 % by weight of ammonia; and
the balance water.

The latter monopropellant blends will remain a homogeneous solution down to a temperature of −25°C, or below.

The water content of the inventive monopropellant, based upon the above ranges
of ADN, ammonia and methanol, as specified in respect of the above three different embodiments, will typically range from 4 % to 41 %, preferably from 7 % to 36 %, and more preferably from 10 % to 31 % by weight.

In practice, ammonia may conveniently be used as a 25% aqueous solution when preparing the inventive monopropellants. This will produce a ratio of ammonia to water of 1:3 in the resulting monopropellant, unless additional water, or additional pure ammonia is being added. Accordingly, in one embodiment of the inventive monopropellant the ratio of ammonia to water is about 1:3.

Additional water may for example be added in cases where a lower combustion temperature is desired.

EXAMPLES

The following examples are provided to further illustrate the invention.

In the examples, different monopropellant blends were prepared and then tested for ADN solubility using the following cooling and heating ramp. The blend was
first cooled from 20°C to −30°C at 0.5°C/min, then kept at −30°C for 60 hours, and thereafter heated to 20°C at 0.5°C/min.

In addition, for each monopropellant blend stepwise testing was performed, wherein the monopropellant blend was kept at 0°C during one week, then at −5°C for one week, −10°C for one week, −15°C for one week, −20°C for one week, −25°C for one week, and, finally at −30°C for one week.

The objective of the present invention is to provide monopropellant blends having improved low-temperature operational and storability properties. Due to the reduced content of the highly energetic oxidizer compound ADN in the claimed monopropellants, the claimed monopropellant blends may in some instances exhibit a somewhat reduced, while still fully sufficient, performance, as compared to the preferred methanol-containing monopropellant of WO 2002/096832 referred to above.

EXAMPLE 1

A monopropellant blend was prepared consisting of

56.70 % of ADN,
21.54 % of methanol,
5.44 % of ammonia, and
16.32 % of water.

Crystallisation (of ADN) occurred at −15°C. The crystals dissolved again upon heating to about −8°C.

EXAMPLE 2

A monopropellant blend was prepared consisting of

56.70 % of ADN,
16.57 % of methanol,
4.19 % of ammonia, and
22.55 % of water.

Crystallisation (of ADN) occurred at −20°C. The crystals dissolved again upon heating to about −10°C.

EXAMPLE 3

A monopropellant blend was prepared consisting of 56.70 % of ADN, 13.57 % of methanol, 7.44 % of ammonia, and 22.30 % of water.

No crystallisation was detected during the testing.

Accordingly, the monopropellant blend of Example 3 is storable down to at least −30°C.

The performance of the monopropellant blend was verified on a 22 N thruster. The monopropellant readily ignited with a propellant feed temperature of about 20°C, and the combustion was stable.

Additional testing with a propellant feed temperature of 0°C (i.e. a temperature at which hydrazine is already in a solid state) showed the same results. The inventors believe that testing at temperatures down to the saturation point of the propellant blend (−30°C) also will prove to be successful.

The specific impulse ($I_{sp}$) of the monopropellant on the 22 N thruster was found to be essentially the same as that of hydrazine when used on a corresponding thruster of similar thrust designed for operation on hydrazine. The density of the monopropellant blend was found to be 20% higher than that of hydrazine.

EXAMPLE 4
A monopropellant blend was prepared consisting of
62.0 % of ADN,
13.1 % of methanol,
6.2 % of ammonia, and
18.7 % of water.

No crystallisation was detected during the testing.

Accordingly, the monopropellant blend of Example 4, having a higher ADN content than the blends of Examples 1-3, is storable down to at least −30°C.
CLAIMS

1. A liquid ADN-based monopropellant blend exhibiting improved low-temperature operational range, comprising a solution of ammonium dinitramide (ADN), water, and ammonia, characterised in that the ADN is contained in the monopropellant in an amount of 55-62 % by weight; the ammonia is contained in an amount of 4-12 % by weight; and in that methanol is contained in an amount of 0-22 % by weight, and the balance water.

2. The liquid ADN-based monopropellant blend of claim 1, wherein the methanol is contained in an amount of 5-20 % by weight; the ammonia is contained in an amount of 4-11 % by weight.

3. The liquid ADN-based monopropellant blend of claim 1 or 2, wherein the methanol is contained in an amount of 10-18 % by weight; the ammonia is contained in an amount of 4-10 % by weight.

4. The liquid ADN-based monopropellant blend of any one of the previous claims, wherein the water is contained in an amount of from 4 % to 41 %, preferably from 7 % to 36 %, and more preferably from 10 % to 31 % by weight.

5. The liquid ADN-based monopropellant blend of any one of the previous claims, wherein ratio of ammonia to water is about 1:3.

6. The liquid ADN-based monopropellant blend of claim 1 consisting of: about 56.7 % by weight of ADN; about 21.5 % by weight of methanol; about 5.5 % by weight of ammonia; and about 16.3 % by weight of water.

7. The liquid ADN-based monopropellant blend of claim 1 consisting of: about 56.7 % by weight of ADN; about 16.6 % by weight of methanol;
about 4.2 % by weight of ammonia; and
about 22.5 % by weight of water.

8. The liquid ADN-based monopropellant blend of claim 1 consisting of:

- about 56.7 % by weight of ADN;
- about 13.6 % by weight of methanol;
- about 7.4 % by weight of ammonia; and
- about 22.3 % by weight of water.

9. The liquid ADN-based monopropellant blend of claim 1 consisting of:

- about 62.0 % by weight of ADN;
- about 13.1 % by weight of methanol;
- about 6.2 % by weight of ammonia; and
- about 18.7 % by weight of water.