NOVEL IONIC MICROPROPELLANTS BASED ON N2O FOR SPACE PROPULSION

Application:

Applicant: Nicolas Pelletier, Le Fauga (FR)
Inventor: Nicolas Pelletier, Le Fauga (FR)
Assignee: CENTRE NATIONAL D'ETUDES SPATIALES, Paris (FR)

Serial Number: 13/751,774

Filed: Jan. 28, 2013

Foreign Application Priority Data:

Jan. 27, 2012 (FR) ........................................ 12 50794

Publication Classification:

Int. Cl. C06B 43/00 (2006.01)
U.S. Cl.
CPC .................................................. C06B 43/00 (2013.01)
USPC .................................................. 60/218; 149/1

Abstract:

Novel monopropellants are provided. The monopropellants are based on N₂O, to their preparation method and their uses for space propulsion.
FIG. 3

FIG. 4
NOVEL IONIC MICROPROPELLANTS BASED ON N₂O FOR SPACE PROPULSION

[0001] Priority is hereby claimed to FR Patent Application No. 12 50794 filed on Jan. 27, 2012, the entire disclosure of which is hereby incorporated by reference herein.

[0002] The present invention relates to micropelants and micropropellant mixtures.

BACKGROUND

[0003] Chemical propulsion of satellites is generally ensured by the decomposition or combustion of propellants thereby producing gases at very high temperature and very high pressure. The propellants may be of the monopropellant or bipropellant type.

[0004] Bipropellant propulsion is certainly one of the two technologies which are the most used today, in particular for satellites. Its large volume of use is notably explained by its adoption on telecommunications satellites (a major market), of high masses, where the thrusts set into play are of a higher range (10N to 400N). Their high performances (specific impulse (ISP) 320 s for an actual expansion e of 330) are further a parameter of choice which reduces the amount of propellant loaded on board for long maneuvers for transfer onto a geostationary orbit. On the other hand, bipropellants require the storage of two chemical compounds (an oxidizer and a fuel) in separate tanks, and therefore imply a complex architecture. The nitrogen peroxide (NTO)/monomethylhydrazine (MMH) bipropellant is presently the oxidizer/reducing agent combination of choice.

[0005] Monopropellant propulsion is the second technology which is the most used on satellites. Its most widespread form consists of using a monometable propellant which may be decomposed upon passing over a catalytic bed in an exothermic way, which has the effect of converting the propellant into gas products at a high temperature and with a low molar mass. Monopropellant propulsion in its generality is aimed at small thrusts (1N to 10N) and exhibits quite medium performances. Hydrazine (N₂H₄) is the most current monopropellant and exhibits an ISP of the order of 210 s with s=80 (actual). Its major advantage is to be based on a rather simple architecture because of the presence of a single propellant.

[0006] Nevertheless, the use of hydrazine and of its methylated derivatives (MMH or UDMH) has significant risks in terms of manufacturing, handling and operations because of their sensitivity to impurities and, to a lesser degree, to temperature and of their extreme toxicity. These constraints generate unwieldy operating procedures and high application costs. Further, hydrazine presently appears on the list of compounds listed by REACH (European Chemical Regulation), because of its dangerous nature (carcinogenic, mutagenic or toxic, persistent, bio-accumulable or toxic substance). In fact, a gradual potential ban on hydrazine and then on its derivatives is foreseen and its substitution may be required in the close future.

[0007] Many studies are presently conducted for identifying alternatives described as “green” alternatives because of their reduced toxicity as compared with that of hydrazine. The sought “green” propellants, observing the REACH regulations, will also have to meet requirements specific to the space domain, notably in terms of long term storage, thermal and mechanical stabilities (with regard to impacts, detonation, adiabatic compression, etc), wide compatibility with propulsion systems (tanks, pipings, valves . . . ), compatibility with space constraints (melting/boiling points, vapor pressure, etc), control of system impacts (bulkiness/mass, assembling, integration and tests) while having high performances (ISP, specific gravity).

[0008] Among the studied alternatives, monopropellants have been contemplated, based on AND (ammonium nitramide), HAN (hydroxylammonium nitrate) or further HNF (hydrazinium nitroformate). Their application is identical with that of hydrazine but, unlike the latter, these ionic monopropellants have the particularity of beginning combustion after their catalytic decomposition because of the presence of oxidizing and reducing species favorable to oxidation/reduction. This gives the possibility of attaining, under the effect of temperature, ISPs slightly greater than that of hydrazine (ISP 230 s with actual s=50). Patent application WO0503636 describes a formulation based on the dinitramide anion (N(NO₂)₂) associated with an energetic cation—preferentially ammonium (NH₄⁺), hydrazinium (N₄H₄⁺) or hydroxydiammonium (OHNH₂⁺), ammonium being preferred—the formed salt being dissolved in a reducing solution, either aqueous or not. The liquid reducing agent may thus be used as a solvent or be in equilibrium with a fraction of water so as to form a liquid ionic energetic solution. The reducing agent may notably be selected from alcohols, amines, aldehydes or ketones, large polarity being sought in order to favor solubility of the energetic salt. By increasing the polarity of the reducing agent, it is then possible to reduce the water content and thereby increase the ISP of the mixture. Theoretical ISPs are comprised between 245 s to 290 s (chamber pressure of 20 bars and 68 = 50). A formulation has received particular attention for its thermal stability upon storage: LMP-1035 (60-65% ADN, 15-20% methanol, 3-6% ammonia and balance of water), demonstrating a theoretical ISP of 252 s. However, in spite of the theoretical performances which are superior to those of hydrazine, such monopropellants have a major drawback related to their application in the thrusters: these propellants are actually decomposed by catalysis and their decomposition products then begin to combust because of the mutual presence of oxidizing and reducing agents and of a decomposition temperature above the self-ignition threshold. Consequently, the attained flame temperatures are higher (1,800° C.) than in the case of the hydrazine monopropellant (900° C.) and generate an intensive thermal stress for the catalytic bed. Among the problems related to this thermal stress, mention may be made of: deactivation of the catalyst by oxidation, erosion of the active phase or further sintering of the supporting particles. This loss of activity is expressed by a gradual decrease in the performances and a limitation of the lifetime of the thruster: in spite of a level higher than that of hydrazine in the “early life”, the ISP may strongly decrease during a mission so as to finally generate significantly lower global performances. It then appears that resorting to a catalytic device, historically used in monopropellant propulsion, seems to be inadequate if the trend is towards compounds with high energy density. An alternative application of the decomposition/reaction of the propellant in which the activation energy would be attained by a non-catalytic method, would then open the door to much more energetic compounds than hydrazine and even than ADN.

[0009] Other avenues have been followed both in terms of alternative “green” monopropellants and of application of their reaction. Patent applications W001/51433 and WO2009/062183 teach as liquid monopropellants, mixtures
of nitrous oxide (N\textsubscript{2}O) as an oxidizer and of hydrocarbons as a fuel, such as propane (C\textsubscript{3}H\textsubscript{8}) or ethane (C\textsubscript{2}H\textsubscript{6}), ethylene (C\textsubscript{2}H\textsubscript{4}), acetylene (C\textsubscript{2}H\textsubscript{2}). As an example, NOFB34 is a mixture of N\textsubscript{2}O and of acetylene in a ratio O/G=4. The selection of nitrous oxide as an oxidizer is motivated by its very good oxidizing power and by its volatility providing the possibility of self-pressurization of the tank. On the other hand, the highly volatile hydrocarbons used lead, in the temperature interval used, to a gas phase containing both nitrous oxide and the hydrocarbon. This gas mixture is sensitive and has high detonation risks in response to thermal or mechanical stimuli. As such, mention may be made of the work dealing with the study of resistance to detonation of N\textsubscript{2}O/O\textsubscript{2} mixtures, of M. Kaneshige et al. (Hydrocarbon-Air-Nitrous Oxide Detonations, Western States Section/The Combustion Institute, Spring Meeting, Sandia National Laboratories, Livermore, Calif., Apr. 14 and 15, 1997). Further, the formed binary mixture N\textsubscript{2}O/hydrocarbon has a high saturation vapor pressure (38 bars at 10\textdegree\textsuperscript{C} for the monopropellant NOFB34) and very sensitive to temperature (48 bars at 20\textdegree\textsuperscript{C} for the same monopropellant), which requires certified equipment for a service pressure greater than those presently encountered on the one hand and makes its continuous thermal control delicate on the other hand. Further, the energy density of these mixtures still has to be improved in particular because of their specific gravity sometimes less than 700 kg.m\textsuperscript{-3}.

**SUMMARY OF THE INVENTION**

[0010] An object of the present invention may be therefore a monopropellant based on nitrous oxide not having the disadvantages stated hereinbefore, and notably the instability. Firstly, the problem related to the sensitivity of the mixture has been solved by generating a monopropellant in which the fuel in its isolated form is an energetic salt. Its putting into solution in nitrous oxide generates an ionic liquid phase. Because of its reduced saturation vapor pressure, the fuel is bound in the liquid phase, so that the vapor phase co-existing with the liquid exclusively contains nitrous oxide. Secondly, the specific gravity of the thereby formed monopropellants is high by providing the salt, thereby guaranteeing high energy density. The applied salts have formation enthalpies and structures such that their association with nitrous oxide provides theoretical ISPs comprised between 300 s and 350 s depending on the candidates.

[0011] According to a first object, the present invention therefore provides a monopropellant formed by a mixture comprising nitrous oxide (N\textsubscript{2}O) as an oxidizer, at least partly in liquid form, and a fuel as a salt in the liquid phase of N\textsubscript{2}O.

[0012] Nitrous oxide N\textsubscript{2}O, of molar mass 44.013 kg.mol\textsuperscript{-1}, is also called laughing gas, dinitrogen monoxide, nitrogen oxide, dinitrogen oxide. Its critical point is located at P\textsubscript{c}=72, 51 bars and T\textsubscript{c}=34.26\textdegree\textsuperscript{C}. Its saturation vapor pressure (pressure at which the gas phase is in equilibrium with its liquid phase) varies in the interval [9.20\textdegree\textsuperscript{C}] between 31.3 bars and 50.6 bars. In this same interval, the specific gravity of its liquid phase passes from 907.4 kg.m\textsuperscript{-3} to 786.6 kg.m\textsuperscript{-3}, while that of its gas phase increases from 84.9 kg.m\textsuperscript{-3} to 158.1 kg.m\textsuperscript{-3}. Nitrous oxide is therefore a strongly volatile compound. Depending on the temperature and pressure conditions, N\textsubscript{2}O may exist in a biphasic form (liquid/gas thermodynamic equilibrium) or in a monophasic form beyond its critical point. Under normal temperature and pressure conditions, nitrous oxide is in a liquid/gas equilibrium.

[0013] According to the present invention, nitrous oxide is in liquid form. It may partly be in the form of a gas.

[0014] The presence of N\textsubscript{2}O in liquid form may be particularly advantageous in that it allows solubilization of the fuel and thus plays the role of a solvent. Nitrous oxide is then in solution with the liquid fuel phase.

[0015] The liquid phase of N\textsubscript{2}O is then in a mixture with the fuel.

[0016] In fact, the oxidizing and combustible species are in a same phase.

[0017] The presence of a gas phase consisting of N\textsubscript{2}O in equilibrium in the monopropellant is also of interest in that gaseous N\textsubscript{2}O plays the role of a pressurization gas.

[0018] By “pressurization gas” is meant a neutral gas—i.e. not being intended to participate in the chemical reaction—used in the tanks for pressurizing the monopropellants and allowing their discharge into the fluidic lines towards the thrusters. The system associated with this operating mode is then said to be “with positive expulsion”. Helium (He) and dinitrogen (N\textsubscript{2}) are the most common pressurization gases. Resorting to an additional gas induces certain drawbacks such as the loss of effective volume in the tank and the presence of trace amounts of gas in the monopropellant by absorption.

[0019] According to the present invention, the fuel may be an ionic compound introduced into the liquid phase of the monopropellant.

[0020] The liquid phase may include:

[0021] 1) fuel in the form of a solid salt when isolated at room temperature and solubilized in N\textsubscript{2}O at least partly present in liquid form, or

[0022] 2) molten salt of the fuel in a binary mixture with N\textsubscript{2}O at least partly present in liquid form, or

[0023] 3) an ionic solution of the fuel dissolved in an organic or ionic energetic solvent, in a binary mixture with N\textsubscript{2}O at least present in liquid form. If an ionic solvent is used, this is a molten salt.

[0024] A liquid containing ions among the solvent is called an ionic solution.

[0025] According to the embodiment 1), the salt is generally polar, is solid under standard temperature conditions and is soluble in N\textsubscript{2}O.

[0026] As an illustration, mention may be made of 1,5-diamino-4-methyl-tetrazolium azide.

[0027] According to the embodiment 2), the salt is generally present in the form of a pure liquid at room temperature (RTIL: Room Temperature Ionic Liquid), has a melting temperature of less than −20\textdegree\textsuperscript{C}, and forms a binary mixture with N\textsubscript{2}O.

[0028] As an illustration, mention may be made of 3-azido-1,2,4-triazolium 5-nitro-tetrazolate.

[0029] According to the embodiment 3), the salt, a solid under the standard condition, is dissolved in a solvent in order to form an ionic solution itself in a mixture with N\textsubscript{2}O present in liquid form. The solvent is advantageously an energetic solvent, such as methanol for example.

[0030] As an illustration, mention may be made of 1,5-diamino-4-methyl-tetrazolium dinitramide in a mixture in methanol.

[0031] When N\textsubscript{2}O is at least partly present in liquid form, the liquid phase contains this share of N\textsubscript{2}O in solution.

[0032] The fuel in liquid form gives the possibility of guaranteeing advanced stability of the monopropellant against
thermo-mechanical stimuli, notably of detonative origin (impacts, adiabatic compression, etc) and electrostatic stimuli.

The fuel is such that it is compatible with N₂O and of reduced volatility because of its ionic nature. In particular, under the storage conditions of the propellant, the fuel may be considered as non-volatile. The term of "compatible" means here that the fuel is, according to its phase under standard conditions:

- soluble or miscible and able to form solid-liquid or liquid-liquid binary mixtures respectively with liquid N₂O;
- gives rise to a thermodynamically stable mixture with liquid N₂O under standard conditions.

The fuel should be a species which reduces N₂O but which may optionally include certain oxidizing groups.

In order to meet the energy density requirements required for space propulsion, the fuel is selected from the salts of energetic compounds.

By energetic compounds are meant molecules or combinations of molecules having high energy density and matter density. This is expressed by a positive and high standard formation enthalpy, which may attain several thousands of kJ·kg⁻¹ — typically 2,000 to 3,000 kJ·kg⁻¹ — and by a high specific gravity, generally greater than 1,000 g·cm⁻³. This is then referred to as HEDMs (High Energy Density Materials).

Certain HEDMs demonstrate uncommon performances but have limits of use because of their instability (uncontrolled release of energy) and are classified in the category of explosive materials. This is notably the case of the derivatives of pentazole. Further, an additional feature specific to space propulsion relates to the molar mass of the products from the combustion of these energetic compounds. The latter mass to be as low as possible — generally less than 30 g·mol⁻¹ — in order to guarantee a high flame temperature/molar mass ratio

\[ T_{\text{flame}} = \frac{E_{\text{th}}}{M} \]

guaranteeing a high specific impulse.

According to the present invention, the fuel (also called "a reducing agent") is any combination of a linear or heterocyclic cation and of a linear or heterocyclic anion meeting the criteria presented hereinbefore. The anion and/or the cation generally comprise one or several nitrogen-containing and/or unsaturated energetic groups such as amino, azido, cyano, propargyl, tripropargyl and guanidyl groups.

The fuel is generally a nitrogen-containing derivative, in the form of a salt. Thus, the anion and/or the cation of said salt may contain one or several nitrogen atoms.

Said cation may be selected from nitrogen-containing derivatives such as aliphatic, cyclic or aromatic, quaternary amines.

Said cation may notably be selected from:

- Linear cations, such as ammonium, hydroxylammonium, hydrazinium ions, and their derivatives;
- Saturated heterocyclic cations such as piperidinium, piperazine, and their derivatives; and
- Heterocyclic cations either aromatic or not, such as azinium, azolium, diazolium, triazolium et tetrazolium, notably pyridinium, pyrrolium, isoazolium, pyrazolium, oxazolium, pyrazolium, imidazolium, oxadiazolium, triazolium, oxatrizolium, tetrazolium,

pyrrolidium, triazinium, pyridazinium, pyrimidinium, pyrazinium, piperidinium, 1,2,3- or 1,2,4-triazolium, 1,4,5- or 2,4,5-tetrazolium, as well as their -inium and -imidium analogs, and their derivatives.

More particularly, said cation may be selected from ammonium, imidazolium, triazolium, tetrazolium ions and their derivatives.

The expression "ion derivatives" refers to compounds having a nitrogen atom in the form of said ion.

The -inium and -imidium analogs of the unsaturated heterocyclic compounds above refer to corresponding partly saturated (-inium) and saturated (-imidium) analogs resulting from a respectively complete partial hydrogenation, such as for example pyrrolium as a partly unsaturated analog and pyrrolidinium as a saturated analog of pyrrolium.

As ammonium derivatives, mention may notably be made of substituted ammoniums, such as ethylendiammonium, ethanalaminum, propylammonium, monopropargylandmonium, tetraethylammonium, N-tributyl-N-methylammonium, N-trimethyl-N-butylammonium, N-trimethyl-N-hexylammonium, N-trimethyl-N-propylandmonium.

As pyrrolinium derivatives, mention may for example be made of pyrroliniums notably substituted with an alkyl group, such as N-methylpyrrolinium.

As imidazolium derivatives, mention may be made of imidazoliums notably substituted with one or several alkyl and/or hydroxyalkyl groups, such as 1-butyl-2,3-dimethylimidazolium, 1-butyl-3-methylimidazolium, 1,3-dimethylimidazolium, 1-ethanol-3-methylimidazolium, 1-ethyl-3methylimidazolium, 1-hexyl-3-methylimidazolium, methylimidazolium, 1-octyl-3-methylimidazolium, 1-propyl-2,3-dimethylimidazolium.

As pyrrolidinium derivatives, mention may be made of substituted pyrrolidiniums, notably with one or more alkyl groups, such as 1-butyl-1-methylpyrrolidinium, 1-ethyl-1-methylpyrrolidinium, N-propyl-N-methylpyrrolidinium.

As piperidinium derivatives, mention may be made of piperidiniums substituted with one or more alkyl groups, such as 1-methyl-1-propylepiperidinium.

As triazolium derivatives, mention may be made of 1-methyl-1,2,4-triazolium, 3-azido-1,2,4-triazolium, 1-methyl-3-azido-1,2,4-triazolium, 4-amino-1,2,4-triazolium.

As tetrazolium derivatives, mention may be made of 1-amino-4,5-dimethyltetrazolium, 2-amino-4,5-dimethyltetrazolium, 1,5-diamino-4-methyltetrazolium.

As an illustration, mention may be made of the following families of cations:

<table>
<thead>
<tr>
<th>Family</th>
<th>Compound</th>
<th>Generic structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Azinium (8 atoms) Pyridinium (9 atoms)
wherein each of the R1, R2, R3, R4, R5 and R6, either identical or different, represent independently a hydrogen atom, or an alkyl group; CN; an alkyl substituted with CN; NRR'; azido(—N3); nitro; propargyl; tripargyl and guanidyl; wherein RR' represents independently a hydrogen atom or an alkyl group.

The anion of the fuel may be any anion having a negative charge either with nitrogen or not. It may, for example, be selected from:

- linear anions such as azide, nitrate, nitramide, nitroformate, dinitramide, nitrite, acetate, cyanamide, dicyanamide, phosphate, methylphosphonate, ethylphosphonate ions; and

unsaturated heterocyclic anions such as azolates (such as pyrrolate), diazolate (such as pyrazolate, imidazolate), triazolate (1,2,3- and 1,2,4-triazolate) and tetrazolate (such as nitrotetrazolate),

and their derivatives such as 4,5-dinitromida-zolate, 5-nitrotetrazolate.

By alkyl group is meant saturated hydrocarbon radicals with a linear or branched chain, with one 1 to 20 carbon atoms, preferably 1 to 5 carbon atoms. Mention may notably be made when they are branched or substituted with one or more alkyl rad-
cals, of isopropyl, tert-butyl, 2-ethylhexyl, 2-methylbutyl, 2-methylpentyl, 1-methylpentyl and 3-methylheptyl radicals.

More particularly, mention may, for example, be made of the following compounds as a fuel:

- Ammonium azide (AA),
- Tetraethylammonium azide,
- Triazolium nitrotetrazolate,
- Azidotriazolium nitrotetrazolate,
- Ammonium dinitramide (ADN),
- Hydroxylammonium azide (HAA),
- Hydrazinium azide (HA),
- Hydroxylammonium nitrate (HAN),
- Ammonium dinitramide (ADN),
- Hydrazinium nitrate (HN),
- Triethanolammonium nitrate (TEAN),
- Hydroxylammonium dinitramide (HADN),
- Azide, acetate, nitrate, dinitramide, dicyanamide, methylphosphonate, 4,5-dinitromiazidate, 5-nitrotetrazolate and ethylphosphonate salts of ammonium, ethyleneammonium, ethanolammonium, propylammonium, monopropargylammonium, tripropargylammonium, tetraethylammonium, tetracyclammonium, N,N-trimethyl-N,N-dimethylanilinium, N,N-dimethyl-N,N-dimethylanilinium, N,N-dimethyl-N-propylammonium, pyrroline, N,N-dimethylpyrrolinium, imidazolium, 1-butyl-2,3-dimethylimidazolium, 1-butyl-3-methylimidazolium, 1,3-dimethylimidazolium, 1-ethyl-3-methylimidazolium, 1-hexyl-3-methylimidazolium, methylimidazolium, 1-octyl-3-methylimidazolium, 1-propyl-2,3-dimethylimidazolium, 1-(2-butyl)-3-methylimidazolium, pyrrolidinium, 1-butyl-1-methylpyrrolinium, 1-ethyl-1-methylpyrrolinium, N-propyl-N-methylpyrrolidinium, piperidinium and 1-methyl-1-propylpiperidinium, of 1,2,4-triazolium, 3-azido-1,2,4-triazolium, 1-methyl-3-azido-1,2,4-triazolium, 4-amino-1,2,4-triazolium, 1-amino-5,5-dimethyltetrazolium, 2-amino-4,5-dimethyltetrazolium, 1,5-diamino-4-methyltetrazolium.

As an illustration, mention may thus be made of:

- Ammonium azide (AA),
- Tetraethylammonium azide,
- Triazolium nitrotetrazolate,
- Azidotriazolium nitrotetrazolate,
- Ammonium dinitramide (ADN),
- Hydroxylammonium azide (HAA),
- Hydrazinium azide (HA),
- Hydroxylammonium nitrate (HAN),
- Ammonium dinitramide (ADN),
- Hydrazinium nitrate (HN),
- Triethanolammonium nitrate (TEAN),
- Hydroxylammonium dinitramide (HADN),
- Ammonium dicyanamide,
- Imidazolium dicyanamide,
- 1-butyl-3-methylimidazolium dicyanamide,
- 1-butyl-2,3-dimethylimidazolium acetate,
- 1-butyl-1-methylpyrrolidinium acetate, dicyanamide,
- 1,3-dimethylimidazolium methylphosphonate,
- 1-ethanol-3-methylimidazolium dicyanamide,
- 1-ethyl-3-methylimidazolium ethylphosphonate, methylphosphonate,
- N-triethyl-1-N-methylammonium dicyanamide,
- Ammonium dicyanamide,
- Ammonium azide,
- 1-butyl-3-methylimidazolium dicyanamide,
- 1,2,4-triazolium 4,5-dinitro-imidazolate,
- 1-methyl-1,2,4-triazolium 4,5-dinitro-imidazolate,
- 3-azido-1,2,4-triazolium 4,5-dinitro-imidazolate,
- 1-methyl-3-azido-1,2,4-triazolium 4,5-dinitro-imidazolate,
- 4-amino-1,2,4-triazolium 4,5-dinitro-imidazolate,
- 1,2,4-triazolium 5-nitro-tetrazolate,
- 1-methyl-1,2,4-triazolium 5-nitro-tetrazolate,
- 3-azido-1,2,4-triazolium 5-nitro-tetrazolate,
- 1-methyl-3-azido-1,2,4-triazolium 5-nitro-tetrazolate,
- 4-amino-1,2,4-triazolium 5-nitro-tetrazolate,
- 1-amino-4-5-dimethyltetrazolium nitrate,
- 2-amino-4,5-dimethyltetrazolium nitrate,
- 1,5-diamino-4-methyltetrazolium nitrate,
- 1,5-diamino-4-methyltetrazolium dinitramide,
- 1,5-diamino-4-methyltetrazolium azide,
- 1,5-diamino-4-methyltetrazolium tetrateside.

These salts are generally available commercially. Thus AA, HAA, HA, triazolium nitrotetrazolate, azidotriazolium nitrotetrazolate and ammonium dinitramide (ADN) are notably marketed by EURENCO Bofors (Sweden).

The other salts listed above may for example be marketed by Solvionic.

The salts according to the invention, when they are not available commercially may be obtained by applying or adapting known methods, notably according to the methods described by Keskin et al., J. of Supercritical Fluids 43(2007) 150-180, notably by coupling of its constituents, by metathesis or by an acid-base reaction. Thus, the sought salt may notably be prepared from the compound in neutral form, by salification for example by adding the acid including the desired anion, or from another ionic compound by exchange of ions, on a column for example, or by transsalification in the presence of an acid including the desired anion, or further by metathesis. Alternatively, it is possible to regenerate the fuel in free form in a basic medium and to regenerate a new ion by salification. It is also possible to regenerate a quaternary ion from the corresponding base by protonation or substitution (for example alkylaation), for example. The nitrate, dinitramide, azide salts may advantageously be prepared by metathesis in the presence of silver nitrate, dinitramide, azide salts from the corresponding halides.

Mention may thus be made of the methods described in U.S. Pat. No. 8,034,202; Asikigka et al. (Application of ionic liquids and microwave activation in selected organic reaction, Acta Univ. Oulu. A 502, 2008; Singh et al. Structure bond 2007, 125:35-83; Schneider et al. Inorganic Chemistry 2008, 47(9), 3617-3624.
It is understood that other salts may be used. Thus, depending on the anions and cations available commercially and on the optimization of the latter (depending on the energetic performances, and/or properties of compatibility with N₂O₅, stability, toxicity etc, as desired), it may be of interest to vary their structure. Different counter-ions may be obtained with a given cation or anion.

The monopropellants according to the invention are such that the N₂O₅/fuel ratio (by mass), known under the name of mixing ratio and often noted as O/F or OF (for Oxidizer/Fuel ratio) is generally comprised between 0.1 and 10, preferably between 1 and 6.

A means for quantifying the performances of a propellant is formed by the specific impulse, often noted as ISP. The specific impulse represents the duration during which the engine provides a thrust equal to the weight of consumed propellant. Thus, this is an indicator of the “soberness” and therefore of the energetic performance of a propellant. The ISP is expressed in the following way:

\[ \text{ISP} = \frac{C^*}{g_0} \gamma \sqrt{\left( \frac{2}{\gamma-1} \right) \left( \frac{2}{\gamma+1} \right)^{\gamma-1} \left[ 1 - \left( \frac{P_e}{P_r} \right)^{\gamma-1} \right]^2} \]

wherein \( C^* \), \( g_0 \), \( \gamma \), \( P_r \) and \( P_e \), respectively represent the characteristic velocity of the gases ejected by the nozzle, the gravity at the relevant altitude, the average isentropic coefficient of the ejected gases, the ejection pressure and the pressure within the chamber.

The characteristic velocity of the ejected gases is related to the speed of sound according to:

\[ C^* = \frac{a_0}{P_e} = \frac{a_0}{\sqrt{\frac{\gamma \cdot R \cdot T_{\text{ad}}}{M}}} \]

with the sound velocity:

\[ a_0 = \sqrt{\frac{R \cdot T_{\text{ad}}}{M}} \]

wherein \( R \), \( T_{\text{ad}} \) and \( M \) are the perfect gas universal constant, the adiabatic temperature within the chamber (a so-called “flame” temperature, if there is presence of combustion) and the average molar mass of the ejected gases, respectively.

The ratio of the ejection and chamber pressures involved in the expression of ISP depends on the nature of the ejected gases but also on the geometrical characteristics of the nozzle:

\[ \frac{P_e}{P_r} = \left( 1 + \frac{\gamma-1}{2} \cdot M_e^2 \right)^{\frac{\gamma+1}{2\gamma}} \]

wherein \( M_e \) is the Mach number of the flow in the ejection section of the nozzle and may be obtained by the following implicit relationship involving the expansion ratio of the nozzle:

\[ \varepsilon = \frac{A_e}{A_{\text{ad}}} = \frac{1}{M_e} \left( \frac{2}{\gamma+1} \right) \left( 1 + \frac{\gamma-1}{2} \cdot M_e^2 \right)^{\frac{\gamma+1}{2\gamma}} \]

with \( \varepsilon \) being the nozzle expansion ratio equal to the ratio between the ejection sections (\( A_e \)) and the sections of the sonic neck (\( A_{\text{ad}} \)).

The monopropellants according to the invention generally have a theoretical ISP comprised between 300 s and 350 s when it is calculated under the following conditions: pressure in the combustion chamber of 10 bars, nozzle expansion ratio of \( \varepsilon = 100 \) and expansion in equilibrium in the nozzle.

According to another object, the present invention also provides a method for preparing the monopropellant according to the invention. Thus, said method comprises a step for mixing the fuel and N₂O₅. This mixing can be achieved at room temperature, but in the case when a solid salt is used under the standard conditions, the maximum solubility has to be considered at the minimum storage temperature of the monopropellant on orbit in order to get rid of any risk of saturation and recrystallization during flight. Therefore, during the synthesis of the monopropellant, this threshold should be observed. The minimum temperature of use of the monopropellant on orbit is typically 0°C.

The monopropellant according to the invention may be stored while making sure that the maximum allowed storage temperature is not exceeded, in order not to exceed a certain saturation vapor pressure, the MEO (Maximal Expected Operating Pressure, maximum pressure expected during operation) being comprised between 10 and 50 bars, typically between 20 and 40 bars. The maximum storage temperature is generally comprised between 0°C and 50°C. The monopropellant should have sufficient stability so as to be stored on orbit for a duration of several years—typically 5 years, but possibly for up to 15 years. The stability should notably be expressed by the absence of phase separation (demixing, decantation, etc).

According to another object, the present invention also provides a space propulsion method by means of the monopropellant according to the invention. By space propulsion is meant the propulsion of spacecraft such as launchers and satellites.

Advantageously, the monopropellant according to the invention is suitable for an operation with combustion. With combustion, it is possible to do without a catalytic bed and therefore without a complex thruster structure. Further, the lifetime of the thrusters may be extended insofar that the catalyst presently is the limiting element due to phenomena such as deactivation of the catalyst by erosion, oxidation, sintering, etc.

The method according to the present invention therefore comprises the combustion of the monopropellant according to the invention.

Combustion is generally achieved by controlled ignition. This may be carried out according to customary technologies, for example, by means of a high energy spark plug. The spark plug is generally positioned in the injection head, on arrival of the monopropellant into the combustion chamber, the thereby burnt gases being discharged through a nozzle placed at the opposite end of the combustion chamber.
the tank. Generally, present propellant systems called “cata-
lytic monopropellants” with hydrazine operate for pressures in the tank of the order of 20 bars during early life (initial pressure) and 5 bars at the end of life. This pressure decreases upon emptying the monopropellant due to the expansion of the pressurization gas in the space freed by the propellant. Certain systems provide regulation of the tank pressure in order to keep it constant over a certain portion of the mission of the satellite (optimization of the performances). Such is the case on a telecommunications platform, but this introduces a complex and costly piece of equipment.

[0143] In the case of the present invention, operating at a higher tank pressure may be contemplated—typically comprised between 25 and 40 bars in early life—in order to take into account the saturation vapor pressure of the mixture based on N₂O₅. Pressurization may advantageously be achieved by the solution of N₂O₅ itself, given its volatility, so that resorting to an additional inert gas is no longer required. This results in a gain on the filling level of the tank as well as on the apparent specific gravity of the liquid-gas pair.

[0144] As long as the liquid and vapor phases co-exist (equilibrium between the phases) the pressure remains constant (at an imposed constant temperature) due to the vaporization of the liquid, the effect of which is to generate a gas volume compensating the emptying of the tank. In this case, the pressurization means may be exclusively ensured by the filling of the propellant in the tank. In reality, re-establishing equilibrium between the liquid and vapor phases by vaporization of a liquid N₂O₅ fraction is accompanied by a slight lowering of temperature (endothermic phenomenon), so that a slight decrease in pressure will be observed. This phenomenon may be counter-balanced by exerting heating up of the tank via a thermal control (thermistors). This “self-pressurization” phenomenon represents a major advantage since, similarly to pressure regulators on biliquid engines, it allows operation of the thrusters close to their optimum of performances.

[0145] As soon as the liquid phase is depleted, phase equilibrium can no longer be achieved. The tank then conventionally operates in “blow down” mode similarly to pressurization with an inert gas.

[0146] The method according to the invention may also comprise the early step for loading the monopropellant into the tank of the space craft.

DETAILED DESCRIPTION

[0149] The following examples are given as an illustration and not as a limitation of embodiments of the present invention.

EXAMPLES

[0150] 1—Selection of the Energetic Salt

[0151] The tables hereafter give a few examples of energetic salts from among the ammonium, diazonium, triazoliu-

m and tetrazolium cations, some being provided with sub-
stitutive groups of the alkyl, azido or amino type. The associated anions are taken from among dicyanamide, azide, imidazolate, tetrazolate, nitrate or further dinitramide, either substituted or not with the nitro group. The atomic composition and a few of their properties are specified therein (melt-
ing point, thermal decomposition threshold, specific gravity of the salt under standard conditions, standard formation en-
thalpy).

[0152] Based on the ammonium cation:

<table>
<thead>
<tr>
<th>Atomic composition</th>
<th>Tₘp</th>
<th>T₇DComp</th>
<th>□</th>
<th>□Hf/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>C</td>
<td>N</td>
<td>H</td>
<td>O</td>
</tr>
<tr>
<td>Ammonium dicyanamide</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>Ammonium azide</td>
<td>0</td>
<td>4</td>
<td>4</td>
<td>0</td>
</tr>
</tbody>
</table>

[0153] Based on the diazolium cation (imidazolium):

<table>
<thead>
<tr>
<th>Atomic composition</th>
<th>Tₘp</th>
<th>T₇DComp</th>
<th>□</th>
<th>□Hf/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>C</td>
<td>N</td>
<td>H</td>
<td>O</td>
</tr>
</tbody>
</table>
| 1-butyl-3-methyl-
  imidazolium di-
  cyanamide         | 10  | 5       | 15| 0     | —6    | —     | 1050    |

(1) according to Emel’yanenko et al. JACS 2007, 129, 3919/3937.

[0154] 1-butyl-3-methyl-imidazolium dicyanamide may be prepared by applying the methodology described by Asikkala et al. (Application of tonic liquids and microwave activation in selected organic reaction, Acta Univ. Oul. A 502, 2008, page 134) by transesterification from 1-butyl-3-methyl-

imidazolium chloride in the presence of sodium dicyanamide, the chloride being prepared by reaction between 1-chlorobu-
tane and 1-methylimidazole.

[0155] Alternatively, 1-butyl-3-methyl-imidazolium dicy-

anide may be prepared by metathesis as described in, for example, U.S. Pat. No. 8,034,202, from 1-butyl-3-methyl-

imidazolium bromide in the presence of silver dicyanamide.

[0156] Based on the triazoliu cation:

<table>
<thead>
<tr>
<th>Atomic composition</th>
<th>Tₘp</th>
<th>T₇DComp</th>
<th>□</th>
<th>□Hf/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>C</td>
<td>N</td>
<td>H</td>
<td>O</td>
</tr>
<tr>
<td>1,2,4-triazolium 4,5-dinitro-imidazole</td>
<td>5</td>
<td>7</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>1-methyl-1,2,4-triazolium 4,5-dinitro-imidazole</td>
<td>6</td>
<td>7</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>1,2,4-triazolium 4,5-dinitro-imidazole</td>
<td>5</td>
<td>7</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>1-methyl-1,2,4-triazolium 4,5-dinitro-imidazole</td>
<td>6</td>
<td>7</td>
<td>7</td>
<td>4</td>
</tr>
</tbody>
</table>

[0147] The present invention will be elucidated with reference to the drawings, in which:

[0148] FIGS. 1-3 represent the specific impulse (ISP) versus the mixing ratio for two expansion ratios (e=80 and e=330) for each of the monopropellants of Examples 1, 2 and 3 respectively; and FIG. 4 illustrates the solubility constraint as regards the optimum performances in the case of a monopropellant involving a solid salt under the standard condition (Example 1 or 3).
### Based on the tetrazolium cation

<table>
<thead>
<tr>
<th>Name</th>
<th>Atomic composition</th>
<th>$T_{mp}$</th>
<th>$T_{decomp}$</th>
<th>$\Delta H_f^{\circ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-amino-4,5-dimethyl-tetrazolium nitrate</td>
<td>3 6 8 3</td>
<td>170</td>
<td>1500</td>
<td>801.7</td>
</tr>
<tr>
<td>2-amino-4,5-dimethyl-tetrazolium nitrate</td>
<td>3 6 8 3</td>
<td>173</td>
<td>1550</td>
<td>750.0</td>
</tr>
<tr>
<td>1,5-diamino-4-methyl-tetrazolium nitrate</td>
<td>2 7 7 4</td>
<td>181</td>
<td>1510</td>
<td>986.4</td>
</tr>
<tr>
<td>1,5-diamino-4-methyl-tetrazolium dinitramide</td>
<td>2 7 7 4</td>
<td>184</td>
<td>1720</td>
<td>1744.8</td>
</tr>
<tr>
<td>1,5-diamino-4-methyl-tetrazolium azide</td>
<td>2 9 7 0</td>
<td>135</td>
<td>1420</td>
<td>4309.6</td>
</tr>
</tbody>
</table>

[0157] The salts above may be prepared according to Singh et al. Structure bond 2007, 125:35-83.

[0159] The theoretical performances of certain cation/anion pairs in a mixture with N$_2$O are given here on the basis of formation enthalpies found in the literature. The tables and figures below specify the time-dependent change of the specific impulse (ISP) in vacuo of the monopropellant versus the mixing ratio (O/F). The calculations are carried out for a pressure in the combustion chamber of 10 bars, a nozzle expansion ratio of $\varepsilon=100$ and expansion in equilibrium in the nozzle. The tables and curves are given for values around the maximum of ISP and the corresponding optimum mixing ratio. The examples given hereafter involve energetic salts put into solution according to each of the three methods described earlier, i.e.:

[0161] Example 1: monopropellant formed by a "crystal" salt dissolved in liquid N$_2$O;
[0162] Example 2: liquid salt in a binary mixture with liquid N$_2$O;
[0163] Example 3: solution formed with a "crystal" salt dissolved in an organic or ionic energetic solvent, itself in binary equilibrium with liquid N$_2$O;

[0164] The first case may be illustrated by the use of 1-(2-butynyl)-3-methyl-imidazolium azide, noted as [ByMIM] [N$_3$]. This compound may be prepared from 1-(2-butynyl)-3-methyl-imidazolium bromide on an azide exchange resin according to Schneider et al. Inorganic Chemistry 2008, 47(9), 3617-3624. It may be put into the solution by direct dissolution in N$_2$O. The following figure gives the structure of [ByMIM] [N$_3$]:

![Structure of [ByMIM] [N$_3$]](image)

[0165] The table hereafter and FIG. 1 provide the theoretical values of ISP for a chamber pressure of 10 bars and for two expansion ratios: $\varepsilon=80$ and $\varepsilon=330$. The maximum ISPs of about 311 s and 329 s are respectively found for an optimum mixing ratio of O/F=5. This corresponds to putting into solution 200 g of [ByMIM] [N$_3$] per kg of N$_2$O.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>O/F</td>
<td>[-]</td>
<td>1.0</td>
</tr>
<tr>
<td>ISP in vacuo ($\varepsilon=80$)</td>
<td>[s]</td>
<td>274.8</td>
</tr>
<tr>
<td>ISP in vacuo ($\varepsilon=330$)</td>
<td>[s]</td>
<td>291.3</td>
</tr>
</tbody>
</table>
Example 2

The second case may be represented by the liquid-liquid binary mixture between 1-butyl-3-methylimidazolium dicyanamide, noted as [BMIM][N(CN)₂⁻] (marketed by Solvionic), and N₂O. The following figure gives the structure of [BMIM][N(CN)₂⁻]:

![Structure of [BMIM][N(CN)₂⁻]](image)

The variation of the ISP with the mixing ratio is described in the table hereafter and FIG. 2, under the same conditions as those specified in example 1. The ISP maxima are obtained for an optimum mixing ratio of O/F=6 and respectively have the values of 304.6 s and 322.3 s for ε=80 and ε=330, respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>O/F</td>
<td>[—]</td>
<td>1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0</td>
</tr>
<tr>
<td>ISP in vacuo (ε = 80)</td>
<td>[s]</td>
<td>246.5 267.3 287.1 298.8 304.2 304.6 296.3 289.0 282.6</td>
</tr>
<tr>
<td>ISP in vacuo (ε = 330)</td>
<td>[s]</td>
<td>263.0 284.0 301.9 314.5 320.4 322.3 312.3 303.7 296.3</td>
</tr>
</tbody>
</table>

Example 3

The third case may be illustrated by the ternary equilibrium between 1,5-diamino-4-methyl-tetrazolium dinitramid, noted as [VAT][N(NO₂)₂] synthesized according to Singh et al. Structure bond 2007, 125:35-83, pyrrolidine and N₂O. The structure of [VAT][N(NO₂)₂] is the following:

![Structure of [VAT][N(NO₂)₂]](image)

As this is a ternary mixture, the notion of mixing ratio O/F is no longer used here. Instead, the ISP ternary diagram is studied and the mass fractions of the three compounds are swept. The table hereafter and FIG. 3 provide the maximum ISP values and the corresponding optimum mixing ratios for different salt mass fractions in the energetic solvent. The calculations are carried out under the same conditions as those of Examples 1 and 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt mass fraction in the solvent</td>
<td>[%]</td>
<td>0 10 20 30 40 50</td>
</tr>
<tr>
<td>Optimum O/F *</td>
<td>[—]</td>
<td>0.5 1.2 2.0 2.7 3.4 4.0</td>
</tr>
<tr>
<td>Maximum ISP in vacuo (ε = 80)</td>
<td>[s]</td>
<td>316.2 313.2 311.6 310.6 310.0 309.4</td>
</tr>
</tbody>
</table>

Example 4—Preparation of the Salt

The salt according to the invention may be prepared, for example:

1. Quaternization by alkylation according to Singh et al., Structure bond 2007, 125:35-83; U.S. Pat. No. 8,034,202; Asikkala et al. (Application of ionic liquids and microwave activation in selected organic reaction, Acta Univ. Oul. A 502, 2008)

2. Metathesis in the presence of silver nitrate, dinitramid, azide salts from the corresponding halides according to Singh et al. Structure bond 2007, 125:35-83; U.S. Pat. No. 8,034,202;

From another ionic compound by exchange of ions according to Asikkala et al. (Application of ionic liquids and microwave activation in selected organic reaction, Acta Univ. Oul. A 502, 2008; on a column: Schneider et al. Inorganic Chemistry 2008, 47(9), 3617-3624.

Example 5—Optimization of the Salt

The specific impulse generated by the combustion of the monopropellant closely depends on the mixing ratio O/F between 1 eq N₂O and the fuel ("crystalline" salt dissolved or a liquid salt). A curve may then be described by plotting the development of ISP versus O/F any other parameter being maintained constant (chamber pressure, initial temperature, expansion ratio ε). An ISP maximum may then be identified as well as the corresponding optimum O/F. Ideally, the monopropellant has to be synthesized by observing this mixing ratio in order to provide the best propellant performances.

However, in the case of a crystalline salt (i.e., solid under standard conditions), the solubility of the salt in N₂O or in the solution combined with N₂O limits the accessible O/F interval. Indeed, the mixing ratio has to be greater than a threshold value dictated by the solubility of the salt at the minimum temperature of use (typically Tₘᵢₙᵦ = 0°C.). It clearly appears that for a given monopropellant, it is preferable that the optimum mixing ratio be found in a solubility zone which may be achieved in order to be able to attain the ISP maximum:

\[
(\frac{O}{F})_{opt} > (\frac{O}{F})_{min} = \frac{1}{S(F_{max})}
\]

This is illustrated in FIG. 4.

Therefore the crystalline salts of interest either have to have great solubility at the specified minimum temperature
(typically $S(T_{\text{min}}) > 100 \text{ g kg}^{-1}$), or exhibit an ISP optimum with a high mixing ratio (typically $4 \sigma/O/\sigma \geq 10$).

**Example 3**

[0180] given hereinafter actually illustrates this problem: without resorting to the solvent, the ISP maximum is found for $(O/F)_{\text{opt}} = 0.5$, which corresponds to a dissolution of 2 kg. kg$_{N_2O}$ of salt. This value is well beyond the maximum solubility of [DAMT] [N(NO$_2$)$_2$] at 0℃. By resorting to the energetic solvent, it is possible to enhance the optimum mixing ratio, to decrease the required amount of salt and therefore to observe the solubility ceiling. Thus, for a salt mass fraction of 40% in the solution of pyrrolidine, an optimum mixing ratio of 3.4 is found, which allows lowering of the required salt mass to 117 kg. kg$_{N_2O}$$^{-1}$. However, this approach alters the maximum ISP (hereby by about $-6 \sigma$), which shows all the importance of the energy density of the solvent used.

[0181] Observance of the condition on the minimum mixing ratio $(O/F)_{\text{min}}$ should be valid regardless of the progression of the emptying of the tank. Now, the phase change of N$_2$O during the emptying, due to following the saturation curve of the mixture will induce an increase in the salt content of the liquid phase. The mixing ratio will gradually decrease during the drawing off of the liquid phase. It is advisable to ensure that the increase in the salt concentration does not lead to exceeding the solubility, with the risk of recrystallization of the latter. The selection of the initial mixing ratio of the monopropellant should then take into account its condition at the end of the emptying. This is why in certain cases, in particular if $(O/F)_{\text{opt}}$ is very close to $(O/F)_{\text{min}}$ it is necessary to work with a low mixing ratio above the optimum value. In an unfavorable case, the maximum ISP is in a zone beyond saturation. The accessible ISP will be less than the maximum value and selected in a zone ranging up to the solubility maximum.

[0182] 5—Preparation of the Monopropellant

[0183] The volatility of the nitrous oxide involves a specific method for preparing the monopropellant, during which the mixing of the salt and/or solvent and N$_2$O mixture cannot be carried out in open air, but on the contrary in a closed enclosure. An illustrative procedure is the following, starting with a clean and decontaminated enclosure:

[0184] 1) Introducing into the enclosure, the salt in crystalline or liquid form, with a mass observing the optimization criterion presented hereinafter;

[0185] 2) If necessary, injecting the energetic solvent in the required proportions;

[0186] 3) Applying a vacuum to the enclosure (residual pressure typically of $10^3$ Pa);

[0187] 4) Injecting into the enclosure, nitrous oxide with control of the introduced mass by continuously weighing the admission enclosure or continuously weighing the initial container of N$_2$O;

[0188] 5) Stirring the mixture;

[0189] 6) Storage with control of the pressure-temperature conditions of the enclosure—or “storage cylinder”—in order to observe the specified temperature interval.

[0190] 6—Filling a Satellite

[0191] The filling of the tank on a satellite may then be carried out by putting the storage cylinder in communication with the tank of the propulsion module and by drawing off the liquid phase. The driving force allowing transfer of the monopropellant from the cylinder to the tank is directly ensured by self-presurization of the monopropellant. The use of an additional neutral gas may be contemplated for expelling the monopropellant from the storage cylinder.

[0192] 7—Operating and Combustion Conditions

[0193] The monopropellant [N$_2$O+ionic fuel] is stored in the pressurized tank is injected into the thruster via a customary fluidic line notably comprising a flow control valve, a so-called “engine valve”. The monopropellant is drawn off at the tank with its liquid phase insofar that only this phase includes both oxidizer and fuel. A drawing-off technique well adapted to the present innovation is the capillary network system (also known under the term of surface tension tank), well-known to one skilled in the art. Expulsion of the monopropellant through the fluidic line supplying the thrusters is ensured by the pressure generated by the N$_2$O gas in equilibrium with the liquid solution. Only the liquid phase is then expelled.

[0194] The value of the mass flow rate of the monopropellant injected into the thruster(s) is dictated by the total pressure drop in the fluidic lines from the tank to the engine(s), in particular by the singular pressure drop of the injector (dicated by its design). As long as the monopropellant has not crossed the injection head, it remains in the liquid phase as long as it exists in this state in the tank.

[0195] When the monopropellant passes through the injector located at the head of the engine (a so-called “front bottom”), the latter undergoes expansion. It then penetrates into the upstream portion of the combustion chamber and is led to undergoing a phase change. The cause of the phase change differs according to the condition of the combustion chamber, more specifically its pressure and temperature level. If this is ignition, it may be assumed that the monopropellant penetrates into a “fresh” vacuum medium or close to a vacuum (this is referred to as a rarefied medium) insofar that the chamber communicates with the space vacuum via the nozzle. The monopropellant will rapidly volatilize since its saturating vapor pressure will be clearly greater than the residual pressure within the combustion chamber. This phenomenon will be exacerbated if the monopropellant or the walls of the thruster are at a higher temperature.

[0196] The ignition phase consists of synchronizing the triggering of the spark plug with the arrival of the flow of the monopropellant in order to generate “mild” ignition (the contrary of a “hard start” involving a transient and violent pressure peak which may be dangerous for the system). Guaranteeing quality ignition may also be achieved by producing a train of triggerings of the spark plug (electric arc bursts) at a relatively sustained frequency (a period of the order of a few tens of milliseconds to hundreds of milliseconds). The train of arcs may also be triggered with a slight phase advance on the injection in order to play the role of local preheating. Optimization of the ignition is thus based on the conjunction of optimized geometrical design and a sequence of triggerings.

[0197] In the case when the monopropellant penetrates into a “hot” chamber, which for example corresponds to several successive ignitions interrupted by relatively close in active phases (short cycles), ignition is facilitated since the monopropellant receives a provision of additional energy before the stimuli of the spark plug. These problems are well-known to one skilled in the art, notably as regards the ignition of turbine engines at high altitude or cryotechnical biliquid thrusters.

[0198] Advantageously, the combustion is sustained after ignition as long as the flow of monopropellant is maintained (open engine valve) and therefore does not require any addi-
tional spark plug triggerings. The energy released by the combustion of the monopropellant is sufficient for sustaining the reaction of the injected fresh species. The combustion consists in a reaction between the main oxidizer, i.e. N₂O, and the ionic fuel possibly comprising oxidizing groups (e.g. nitramides). The reaction produces high pressure hot gases. The combustion chamber is dimensioned so that thermodynamic equilibrium is reached before ejecting the burnt gases so as to attain maximum efficiency. The gases are ejected through a nozzle provided with a converging portion, with a sonic neck and a diverging portion so as to initiate and accelerate the flow in order to generate optimum thrust.

What is claimed is:

1. A monopropellant comprising a mixture comprising:
   nitrous oxide (N₂O) as an oxidizer, at least partly in liquid form, and
   a fuel in the form of a salt in the liquid N₂O phase.
2. The monopropellant according to claim 1, wherein the nitrous oxide is partly in the form of a gas.
3. The monopropellant according to claim 1, wherein the liquid phase includes:
   (i) fuel in the form of a solid salt when the fuel is isolated at room temperature and solubilized in N₂O at least partly present in liquid form, or
   (ii) a molten salt of the fuel in a binary mixture with N₂O at least partly present in liquid form, or
   (iii) an ionic solution of the fuel dissolved in an organic or ionic energetic solvent, in a binary mixture with N₂O at least present in liquid form.
4. The monopropellant according to claim 1, wherein the fuel is a salt of an energetic organic compound.
5. The monopropellant according to claim 1, such that the fuel is a salt of a nitrogen-containing derivative.
6. The monopropellant according to claim 1, wherein the cation of the salt is selected from the group consisting of:
   linear cations;
   saturated heterocyclic cations; and
   heterocyclic cations.
7. The monopropellant according to claim 6, wherein the cation is selected from the group consisting of ammonium, imidazolium, triazolium, tetrazolium ions and derivatives thereof.
8. The monopropellant according to claim 1, wherein an anion of the salt is selected from the group consisting of:
   linear anions; and
   unsaturated heterocyclic anions.
9. The monopropellant according to claim 8, wherein the anion is selected from the group consisting of azide, nitrate, dinitramide, dicyanamide, imidazolate and tetrazolate ions and their derivatives.
10. The monopropellant according to claim 1, wherein the fuel is selected from the group consisting of:
   ammonium azide (AA),
   tetranbutylammonium azide,
   triazolium nitrotetrazolate,
   azidotriazolium nitrotetrazolate,
   ammonium dinitramide (ADN),
   hydroxylammonium azide (HAA),
   hydrazinium azide(HA),
   1-(2-butylnyl)-3-methyl-imidazolium azide
   hydroxylammonium nitrate (HAN),
   hydrazinium nitroformate (HNF),
   ammonium nitrate (AN),
   hydrazinium nitrate (HN),
   triethanolammonium nitrate (TEAN),
   hydroxylammonium dinitramide (HADN),
   ammonium dicyanamide,
   imidazolium dicyanamide,
   1-butyl-3-methylimidazolium dicyanamide,
   1-butyl-2,3-dimethylimidazolium acetate,
   1-butyl-1-methylpyrroolidinium acetate, dicyanamide,
   1-ethanol-3-methylimidazolium dicyanamide,
   N-tributyl-N-methylammonium dicyanamide,
   1-butyl-3-methyl-imidazolium dicyanamide,
   1,2,4-triazolium 4,5-dinitro-imidazolate
   1-methyl-1,2,4-triazolium 4,5-dinitro-imidazolate,
   3-azido-1,2,4-triazolium 4,5-dinitro-imidazolate,
   1-methyl-3-azido-1,2,4-triazolium 4,5-dinitro-imidazolate,
   4-amino-1,2,4-triazolium 4,5-dinitro-imidazolate,
   1,2,4-triazolium 5-nitro-tetrazolate,
   1-methyl-1,2,4-triazolium 5-nitro-tetrazolate,
   3-azido-1,2,4-triazolium 5-nitro-tetrazolate,
   1-methyl-3-azido-1,2,4-triazolium 5-nitro-tetrazolate,
   4-amino-1,2,4-triazolium 5-nitro-tetrazolate,
   1-azido-1,2,4-5-trimethyltetrazolium nitrate,
   2-amino-4,5-dimethyltetrazolium nitrate,
   1,5-diamino-4-methyltetrazolium nitrate,
   1,5-diamino-4-methyltetrazolium dinitramide,
   1,5-diamino-4-methyltetrazolium azide and
   1,5-diamino-4-methyltetrazolium dinitramide.
11. The method for preparing a monopropellant according to claim 1 comprising the step of:
   mixing the fuel and N₂O in a closed enclosure.
12. A space propulsion method comprising the step of:
   using a monopropellant according to claim 1.
13. The propulsion method according to claim 12, further comprising the step of combusting the monopropellant by controlled ignition.
14. The method according to claim 12, further comprising a device for pressurizing the monopropellant in a tank.
15. The monopropellant according to claim 6 wherein the linear cations are selected from the group consisting of ammonium, hydroxyl ammonium, hydrazinium ions and their derivatives, the saturated heterocyclic cations are selected from the group consisting of piperidinium, piperazine cations and their derivatives, and the heterocyclic cations are either aromatic or not aromatic and are selected from the group consisting of azinium, azolium, diazolium, triazolium and tetrazolium, pyridinium, pyrrolium, isoxazolium, pyrazolium, oxazolium, pyrazinium, imidazolium, oxadiazolium, triazolium, oxatriazolium, tetrazolium, pyrrolidium, triazinium, pyridazinium, pyrimidinium, pyrazinium, piperidinium, 1,2,3- or 1,2,4-triazolium, 1,4,5- or 2,4,5-tetrazolium, as well as their -inium and -idinium analogues and their derivatives.
16. The monopropellant according to claim 16 wherein the linear anions are selected from the group consisting of azide, nitrate, dinitramide, dinitramide, nitroformate, nitrite, acetate, cyanamide and dicyanamide ions and the unsaturated heterocyclic anions are selected from the group consisting of azolates, diazolate, triazolate and tetrazolates and their derivatives.
17. The monopropellant according to claim 16 wherein the azolate is pyrrolate, the diazolate is pyrazolate or imidazolate, the triazolate is 1,2,3- or 1,2,4-triazolate, and the tetrazolate is nitrotetrazolate.

* * * * *