Green Propellants: Oxidizers

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ABSTRACT: The research for low toxicity and no damage to the environment has stimulated the development of specific investigation lines in many areas. Inevitably, the criteria for safe handling, sensitivity and, above all, specific impulse (efficiencies) of propellant compositions are still superior in relation to ecological appeals. Nowadays, however, the solid or liquid propulsion, as aerospace as military, has already compounds to efficiency and eco-friendly characteristics. This study aimed at describing "green" alternatives to propulsive systems.

KEYWORDS: Propellant, Ammonium perchlorate, Ammonium dinitramide, Hydrazinium nitroformate, Hydroxyl-terminated polybutadiene, Glycidyl azide polymer.

INTRODUCTION

A publication (Silva and Iha, 2012) has approached the "green propellants", but what is its meaning? Nowadays, friendly or green compositions are looked for in many kinds of applications, such as fertilizers, building materials, energy generation, and so on. Thus, this classification (green) can be established after subjection of the compound to a thorough toxicity study. When such compound is a energetic material (green energetic materials – GEMs), it useful to search for a material with high oxygen balances and halogen and metal-free nature (Rahn, 2010).

Propellants are designed to produce high temperatures and pressures in a closed chamber to accelerate projectiles, rockets, or missiles by means of the resulting propulsive force of the gas produced by its decomposition (burn). The propulsion system can be liquid, solid, or hybrid and the propellant can be divided into two major groups: homogeneous and heterogeneous propellants.

In a liquid propulsion system, the mixture of liquid oxygen (LOX) and hydrogen (LH) may be used without the generation of dangerous substances, although they are unstable together and are generally stored separately, imposing complexity to the system (oxidizer and fuel propellants tanks, pressurizing system, plumbing, valves, and engine). Another liquid propulsion system can be reached with the hydrazine, which is one of the most used monopropellants, in spite of its high toxicity, volatile, and carcinogenic properties.

Hydrazine is the only liquid monopropellant widely used for generation of hot gases. In the case of hydrazine, the decomposition pathway occurs in two stages: first, hydrazine is catalytically decomposed into hydrogen and ammonia in an exothermal reaction, and thereafter the latter further does the same into hydrogen and nitrogen in an endothermal

reaction due to the high temperature generated in the first stage; secondly endothermal reduces the flame temperature and the specific impulse (Gronland *et al.*, 2006).

In a bipropellant engine, fuel and oxidizer liquids are injected, atomized, and mixed in a first zone of the combustion chamber. With regards to a hypergolic bipropellant, such as hydrazine and nitrogen tetroxide, there is an initial chemical reaction in the liquid phase when a droplet of fuel impinges with one of oxidizer. Bipropellants that are not hypergolic use some type of igniter to initiate the chemical combustion. In a bipropellant system that applies the hydrogen peroxide as the oxidizer, a catalyst may be used.

Liquid bipropellants generally offer higher specific impulse than liquid monopropellants. Bipropellant systems are thus more efficient than monopropellant ones, but they tend to be more complicated because of the extra hardware components needed to make sure the proper amount of fuel is mixed with that of oxidizer.

In a solid propulsion system, nitrocellulose, or nitrates of cellulose (NC), is the main constituent of a single-base (SB) solid propellant, which has stabilizers and energetic or inert plasticizers too. However, this kind of propellant is useful for small arms, cannons, howitzers, tank, aircraft, and anti-aircraft weapon (Stainhauser and Klapötke, 2008).

Normally, long distance shooting with large caliber cannons needing higher bullet speeds and thus more energetic propellants require double-base (DB) propellants. An useful DB propellant is composed by nitrocellulose and nitroglycerine (NG), or another liquid nitrate ester (Stainhauser and Klapötke, 2008). The DB propellant has many advantages over the SB one, for example, the latter has a greater variance in performance, since the process of SB production uses volatile solvent and its residue is retained into the SB propellant. On the other hand, the NC/NG DB can present exudation during the storage (the nitroglycerin has a tendency to migrate out of the composition, and thereby results in poorer firing accuracy due to variance in propellant strength) bringing instability to the system. Also, nitroglycerin is volatile and its resulting vapors cause sickness and headaches to humans, resulting in health problems in the manufacture, handling, and storage of any composition containing nitroglycerin (Mosher, 1978).

An important heterogeneous propellant used in modern solid-rockets and missiles is the composite propellant consisting of an oxidizer, like ammonium perchlorate (AP),

and a fuel, such as aluminum. Typically, the solid rocket propellant composition comprises yet additives, like plasticizer and burning rate modifiers, and a binder, like a hydroxy-terminated polybutadiene (HTPB) and hydroxy-terminated caprolactone, which holds the propellant together (Jones and Tzeng, 2005). AP is a larger oxidizer used in solid propellants for airspace and military industries.

Differently from the liquid propellant, which is injected from external tank into the combustion chamber at the time of ignition, solid propellants are placed directly in it. Nevertheless, AP/aluminum solid rocket produces amounts of hydrogen chloride, aluminum oxide, and aluminum chloride, which affect the environment around rocket launch sites. A serious drawback in military applications is that the chlorine content causes yet smoke that may be detected with radar and, in the case of high air humidity, it can also be seen as a clear white smoke (Langlet *et al.*, 1999).

The concept of GEMs for defense and space applications is acquiring importance. Ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF) are emerging as potential eco-friendly replacements of AP. Although ADN and HNF have less oxygen balance and, substantially, less heat of reactants formation than AP, they have a superior specific impulse, and the exhausting gas of their burning has no hydrogen chloride. Moreover, they undergo highly exothermic combustion reactions near the surface unlike nitramines, leading to efficient heat feedback to the deflagrating surface enhancing the burning rates. Both the compounds have evinced interest all over the globe. However, severe ADN hygroscopicity and higher HNF sensitivity, particularly mechanical stimuli, are causes of concern (Nair *et al.*, 2010). Table 1 allows the comparison between the properties of AP, ADN, and HNF.

The concentration of oxygen atoms within the oxidizer, represented by "oxygen balance", is an important parameter to identify the potential of oxidizers. Oxygen balance is the amount of molecules remaining after oxidizing hydrogen, carbon, Mg, Al, etc., producing H_2O, CO_2, MgO_2, Al_2O_3, among others. The positive oxygen balance means that the composition has an excess of molecules remaining after the fuel oxidation.

The heat of explosion (H_{exp}) is determined by the difference between the heat of formation of reactants ($\Delta H_{f,r}$) and that of products ($\Delta H_{f,p}$). Then, in order to gain high H_{exp}, $\Delta H_{f,r}$ is expected to be as high as possible and $\Delta H_{f,p}$ as low as possible.

Table 1. Physicochemical properties of the following oxidizers: ammonium perchlorate (AP), ammonium dinitramide (ADN), and hydrazinium nitroformate (HNF).

Oxidizer	$\Delta H_{f,r}$ (MJ/kg)*	Oxygen balance [%]*	I_{sp} (s)*	Density (g/cm³)**
AP	-2.52	34.0	160	1.9
ADN	-1.22	-4.4	206	1.8
HNF	-0.39	25.0	265	1.9

*Kubota (2002); **Nair *et al.* (2010).

AMMONIUM DINITRAMIDE

The ADN is one of the most important compounds to replace the AP in solid propellants or the hydrazine in a liquid monopropellant. There are many routes for ADN production, but a large-scale production consists in the use of sulfamate salts and nitrating acid (Nagamachi *et al.*, 2009).

A new type of liquid monopropellant with a dinitramide compound salt and a fuel, which can show a high specific impulse, was taught by Anflo and Wingborg (2000). In agreement with them, the taught monopropellant had low hazardous from a handling and an environmental point of view, and does not develop smoke. Such propellant should exhibit the following properties: low toxicity, low flammability, higher theoretical specific impulse (as compared to hydrazine), higher density (as compared to hydrazine), easily ignitable, by means of a controlled ignition mechanism, storable at a temperature between -10 and 70ºC, and low sensitivity. The liquid propellants comprise an oxidizer, like ADN, and a fuel (for example alcohols, aldehyde, ketones, amino acids, carboxylic acids, amines, and mixtures thereof). The high ADN hygroscopicity is a major advantage, especially when the propellants contain water.

Langlet *et al.* (1999) taught a large-scale method of preparing dinitramide acid, $HN(NO_2)_2$, and salts thereof having the formula $M^{+n}(^-N(NO_2)_2)_n$, where M is a metal cation or a nitrogen-containing cation and n=1–3. The dinitramide salt can be used as an oxidizer in solid propellants. Dinitramidic acid is prepared by nitration of a compound selected from a group consisting of NH_2NO_2, $NH_4NH_2CO_2$, NH_2SO_3H, $NH(SO_3H)_2$, $N(SO_3H)_3$, and its salts with metal or organic cations, e.g. $NH(SO_3NH_4)_2$, and other products formed when a common nitrating acid such as nitric or sulphuric acids or nitric acid/acetic anhydride. In agreement with them (Langlet *et al.*, 1999), no aprotic solvent for the nitrating agent is required when nitrating

with such acids. Ammonium and potassium salts of the initial substances, and the fact that the neutralization after nitrating is carried out with NH_3 and KOH, results in an advantageous preparation direct to the products ADN and potassium dinitramide (KDN) respectively.

After the synthesis process, the ADN obtained in solution is crystallized in a conventional manner through the concentration, addition of a non-solvent and/or cooling, etc. The resulting crystals of crude ADN are in the form of small rods, or even of needles. However, such crystal morphology makes ADN unsuitable for formulation, because the feasibility of the compositions is greatly compromised due to the large increase in viscosity as soon as high loading rates are envisioned.

In order to solve such problem, Muscatelli *et al.* (2011) proposed the conditioning of the crude crystals, nor on crystallization in the presence of an added chemical element that is a crystal habit modifier, like taught by Benazet *et al.* (2009), but on controlling the parameters of crystal growth, resulting in (quasi) spherical crystals with a selected particle size range, which can be from a few microns to several hundred ones. The parameters under issue are: the nature of the solvent, in particular its viscosity for controlling the relative speeds of transfer and integration of the atoms into the crystal; the temperature cycles for shifting the equilibrium of the solution on the solubility diagram; the presence of impurities; the agitation, etc. The method characterized in that solvent has a viscosity greater than or equal to 0.25 Pa.s, when the spontaneous nucleation is implemented. The solvent is advantageously an alcohol, for example glycerol, 1,4-butanediol or mixture of alcohols, in particular one of glycerol and 1,4-butanediol. The crystallization process according to Muscatelli *et al.* (2011) makes possible to obtain ADN in energetic materials with a high charge level.

Gronland *et al.* (2006) taught a reactor for decomposition and combustion of liquid ADN-based monopropellants, such as for rocket propulsion and controlled gas generation for any

other purpose, such as rotary power in auxiliary power units. The combustion of the ADN-based liquid propellant can be divided into a series of steps, including the decomposition of the ADN oxidizer, which eventually generates free oxygen. In the final stage, combustible components created from thermal and catalytic decomposition will be oxidized in the homogenous gas combustion by free oxygen thus generated, without requiring catalysis. Then, the ADN-based monopropellant can be regarded as being decomposed into a bipropellant, which is combusted in a final step, during which the maximum temperature is reached. The most preferred monopropellants are: stabilized compositions of ADN, water, and glycerol or/and water and methanol; in case of methanol, a composition consisting of about 64.3% of ADN, 24.3% water and 11.4% by weight of methanol (LMP-103), to which a stabilizer is added in the above mentioned amount; in case of glycerol, a composition of about 61.0% of ADN, 26.1% of water and 12.9% by weight of glycerol (LMP-101), to which composition a stabilizer is added in such amount.

Roland (2007) analyzed a composite gunpowder comprising ADN and a thermoplastic elastomer (TPE) binder, which has a melting point of 60 to 90ºC and is based on an ethylene vinyl acetate (EVA) copolymer containing 9 to 30 weight% vinyl acetate and with a melt flow index greater than 100 g/ten minutes.

An energetic composition, with increased performance and total absence of hydrogen chloride in the combustion products, was done by Reed and Ciaramitaro (2004). The formulation avoids the use of halogen-based oxidizers to prevent the formation of their byproducts, using ADN as a primary oxidizer. The solid propellant formulation comprises about 5 to 10 weight% of at least one energetic binder; about 20 to 35 weight% of an energetic plasticizer; about 25 to 45 weight% of ADN, about 0 to 20 weight% of particulate aluminum having a particle size of around 1 to 60 mm; and about 0 to 20 weight% of ultrafine aluminum with less than 1 mm.

The use of ADN as an oxidizer can yet minimize the secondary smoke problem caused by the nucleation of HCl in AP. The energetic plasticizer is selected from those compounds, which are liquids and contain energetic moieties or groups in their chemical structures (for example: butanetriol trinitrate (BTTN), triethylene glycol dinitrate (TEGDN), nitroglycerin, glycidyl azide polymer terminated with azide (GAP azide or GAP plasticizer), etc.). The binder is selected from those oligomers and polymers known as "energetic binders", i.e., typically, GAP, copolymer of (bis-azidoethyl) oxetane (BAMO) with (3-nitratomethyl-3-methyl) oxetane (NMMO), called BAMO/NMMO, polyethylene glycol (PEG), hydroxy-terminated polycaprolactones, hydroxy-terminated polyesters, being preferably tetrahydroxy-terminated polyalkylene oxide (PAO).

HYDRAZINIUM NITROFORMATE

On one hand, HNF is a very desirable oxidizer to use in solid propellant formulations, because it is very energetic, thus providing high performance. On the other hand, the HTPB is the most applied binder in solid propellants. Unfortunately, the HNF cannot be used with this binder, because the HNF attacks its backbone, breaking down the binder chain. Pockets of gas are formed, therefore the propellant swells. In addition, due to the breakdown of the binder backbone, the material becomes soft. Thus, when a binder containing double bonds is utilized, a typical shelf life with HNF will range from 2 to 15 days at a temperature around 20 to 30ºC, in agreement with Low and Haury (1972). With the aim of solving this problem, the authors proposed using a small amount of nitroguanidine to the solid propellant formulations having unsaturated hydrocarbon binder and containing HNF, increasing the shelf life of the propellant to at least five months at ambient temperatures. The nitroguanidine should be added to the propellant during its mixing phase and will remain in the composition to prevent the undesirable reaction of the HNF with the binder.

In a second publication, Low and Haury (1973) taught a propellant formulation comprising HNF and saturated polymeric hydrocarbon binder, but without nitroguanidine. In this new case, they discovered that the reticulation of the binder with a curing agent type polyisocyanate can improve the shelf life of the composition. Polymethylene polyphenylisocyanate (PAPI) provides the best result when it is presented to provide a ratio of NCO to OH from 0.95 to about 1.3 in the composition.

Schöyer *et al.* (1990) investigated many formulations directed in particular to solid propellant combinations in the research for high-performance ones, which could be stored for a considerable time and used not only to change the position of a spacecraft that is in space, but also for launching one into space. According to their research, it could be constituted by a combination of GAP or BAMO with boron, aluminum or aluminum hydride and a compound selected from the group of HNF, nitronium perchlorate (NO_2ClO_4) or AP. The proportions of the components, oxidizer and fuel, in the propellant combinations were not critical. The components should be mixed prior to the reaction in such proportions that the mixing ratios were around the stoichiometric ratio to an amount of no more than 20%, calculated on the total mixture of the energetic binder (BAMO or GAP). In agreement with them, the preferred propellant combinations with HNF are: HNF – 70 to 80%, B – 10% and GAP or BAMO – 10 to 20%; or HNF – 59 to 69%, Al – 21% and GAP or BAMO – 10 to 20%. The same were based on HNF, aluminum and on an energetic binder such as GAP or BAMO, exhibiting an improvement of the specific impulse relative to conventional AP propellants of 214 m/s, with the combustion gases much more cleaner, because HNF does not include chlorine and the environment is not burned with hydrogen chloride gas.

Solid propulsion systems could provide very a high specific impulse by utilizing high performance oxidizers. Many of them offer significant gains on performance, reduced or low toxicity and have desirable exhaust signature characteristics, when compared to others using traditional solid ones. However, many oxidizers suffer yet from varying degrees and forms of instability, such as photosensitivity, shock, friction and impact sensitivity, decomposition in the presence of moisture, sensitivity to pH and incompatibility (such as hypergolic reaction) to other propellant materials. A typical example of incompatibility is the reaction between HNF and curing agents used in solid propellant binder systems such as HTPB and GAP. In order to improve the compatibility of the propellant and to reduce the risks by friction sensitivity during the mixing and casting operations, Cesaroni *et al.* (2002) taught an oxidizer package comprising a solid oxidizer in the form of discrete pellets from a predetermined geometric shape, the pellets were arranged in an array with spaces amongst the pellets and a holder for maintaining them in the array to receive a binder introduced to spaces amongst the array of pellets. The binder introduced provides a support matrix to give complementary burn rates for the pellets and the support binder matrix. The pellets were produced with HNF or ADN and the composition can present yet ballistic modifiers, other additives and, additionally, ultrafine aluminum.

A monopropellant used in the conventional manner for spacecraft propulsion in existing systems, whereby it is to be noted that due to the properties of the system, less strict requirements concerning storage, transport, and handling are possible, was proposed by van den Berg *et al.* (2004). Their research showed that solid high-energy oxidizers, such as HNF or ADN, when dissolved in water, provide a liquid monopropellant system with a specific impulse that could be equal to the specific one of the conventional monopropellant. The monopropellant can be done by the stabilization of HNF and/or ADN in water and/or a lower alkanol. Its amount in the solution is preferably between 0 and 70 weight%, whereas methanol and/or ethanol are preferred. An especially preferred system consists of 25 to 75 weight% of HNF, 5 to 50 weight% of water and 0 to 25 weight% of lower alkanol.

FINAL CONSIDERATIONS

In spite of the larger use of the AP in composite propellants and the hydrazine in liquid propulsion, they demonstrated the high risk to human health and environment. ADN and HNF are emerging as potential eco-friendly replacers to the AP and hydrazine. Despite the ADN hygroscopicity and HNF higher sensitivity, they have substantially higher specific impulse than AP, reduced or low toxicity and desirable exhaust gas signature characteristics, when compared to propulsion systems using traditional solid oxidizer (AP). They also do not contain chlorine and therefore the environment is not burned with hydrogen chloride gas produced in the burn of the propellant. These are the reasons of the increasing interest around them in all over the globe.

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