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Rocket Solid Propellant Alternative Based on Ammonium Dinitramide

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Abstract: Due to the continuous run for a green environment the current article proposes a new type of solid propellant based on the fairly new synthesized oxidizer, ammonium dinitramide (ADN). Apart of having a higher specific impulse than the worldwide renowned oxidizer, ammonium perchlorate, ADN has the advantage, of leaving behind only nitrogen, oxygen and water after decomposing at high temperatures and therefore totally avoiding the formation of hydrogen chloride fumes. Based on the oxidizer to fuel ratios of the current formulations of the major rocket solid booster (e.g. Space Shuttle’s SRB, Ariane 5’s SRB) which comprises mass variations of ammonium perchlorate oxidizer (70-75%), atomized aluminum powder (10-18%) and polybutadiene binder (12-20%) a new solid propellant was formulated. As previously stated, the new propellant formula and its variations use ADN as oxidizer and erythritol tetranitrate as fuel, keeping the same polybutadiene as binder.

Key Words: ammonium dinitramide, rocket, propellant, green, specific impulse

1. INTRODUCTION

The space industry is under an exponential growth and advances are made on a daily basis regardless of their field application. Whether is for surveillance, telecommunication or research purposes, satellites are being sent into space by dozens each year, with 52 orbital launches (including ISS logistics) to take place in 2016 alone [1]. Adding to these figures the flourishing business that space tourism is predicted to create, there is only one direction for this industry. But while the number of yearly launches goes up, the impact created by chemical propulsion upon the environment also increases and therefore raising serious concerns on a global scale.

Most of the current space launchers use solid propellant in one or several of their stages and almost all of them use *ammonium perchlorate* (AP, $\text{NH}_4\text{Cl}_4\text{O}$) [2] based propellant while alternating the type of fuel, majority still using aluminum (Al) powder. Binding the oxidizer and the fuel together through a polymer matrix, the composite propellant has excellent performance characteristics, good thermal stability, as well as low friction and shock sensitivity. Unfortunately its combustion results in the formation of various chlorinated and

hazardous exhaust products. The flagship of the European Space Agency, Ariane-5 as well as the newly commissioned Vega launcher contains no less than 476 and 122 tons of composite propellant, respectively. For each launch this burns into the equivalence of 270 and 71 tons of concentrated hydrochloric acid, respectively. Even the American prime orbital launcher, the Space Shuttle, had its solid rocket boosters containing 998 tons of ammonium perchlorate based propellant. From the complete combustion, 580 tons of concentrated hydrochloric acid was exhausted [3].

Even when it comes to altitude or maneuverability thrusters or monopropellant rocket engines, their liquid fuel is commonly based on *hydrazine* (N_2H_4) derivatives such as mono methyl hydrazine (MMH) or unsymmetrical dimethyl hydrazine (UDMH). Due to its high toxicity this fuel even creates occupational hazards during handling and fueling [4], [5]. All these facts lead to the necessity of replacing the ammonium perchlorate and hydrazine-based formulations with more *green propellants* and searching for replacements has proved to be a difficult task due to the reduced options for a green oxidizer.

Hydrazinium nitroformate (HNF, $N_2H_5^+ + C(NO_2)_3^-$) is one of the oxidizers that are being seriously considered as a replacement but due to unresolved problems concerning thermal stability and friction sensitivity, as well as various compatibility problems [6]. HNF can hardly be considered an option, especially that is also expensive to produce and presents carcinogenic risks.

Ammonium nitrate (AN, $NH_4^+ + NO_3^-$), the most popular, used as a high-nitrogen fertilizer in agriculture could be a cheap and stable alternative but lacks the performance of the ammonium perchlorate presenting a way lower energy content while also having diminished burning rates as it can only be used with magnesium as fuel. AN also has many different crystal phases, which transform into one another, close to ambient temperatures. This causes inhomogeneity in solid formulations, which can lead to cracks and bubbles [7].

Hydroxylammonium nitrate (HAN, $NH_3OH^+ + NO_3^-$) is primarily considered a possible hydrazine monopropellant replacement. It hasn't yet reached practical applicability due to problems regarding ignition catalysts, complicated combustion mechanisms, high sensitivity and material incompatibility [8].

Given the above oxidizing alternative, the current article proposes a new propellant formula comprised of a mix of *ammonium dinitramide* and erythritol tetranitrate bonded together in a hydroxyl terminated polybutadiene matrix. The following chapter contains descriptions and properties of these components.

2. COMPONENTS AND PROPERTIES

Ammonium dinitramide (ADN, $NH_4^+ + N(NO_2)_2^-$, Figure 1, Table 1) [9] is a chlorine free oxidizer that has been considered a possible AP replacement for the last 20 years.

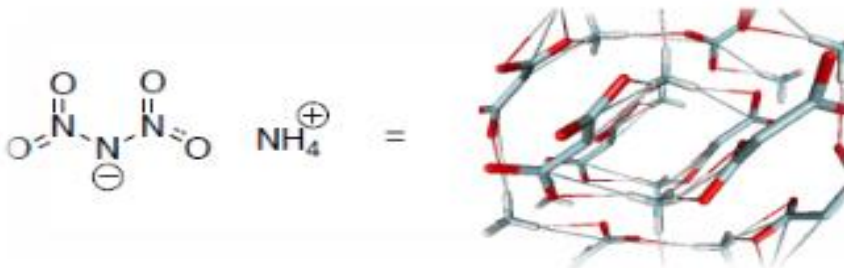


Figure 1. Ammonium dinitramide (ADN)

ADN was secretly discovered in 1971 [10] in the former USSR, and is believed to have been used in operational missile systems [11]. Its rediscovery in 1989 [12] by the US scientists initiated worldwide civil and military interest. ADN has several advantages over AP; it contains no chlorine and produces no hazardous combustion products. The absence of chlorine also enables low-signature (no smoke) combustion when combined with a suitable fuel. Furthermore, the dinitramide anion is more energetic, which enable higher performances than AP-based propellants. It has been estimated that if a propellant formulation based on ADN were to replace today's AP-based propellants the lift capacity of space launchers would increase by approximately 8% [13]. ADN is a colorless salt that becomes yellowish when non-dry. α -ADN has a monoclinic crystal structure, in the $P2_1/c$ space group [14]. A second monoclinic high pressure phase, β -ADN, has been reported over 2 GPa [15]. ADN is highly soluble in polar solvents whilst non-soluble in most low-polarity solvents [16]. Due to its high hygroscopicity, ADN dissolves itself if the relative humidity exceeds 55% [17]. Similar to all dinitramide salts ADN is photosensitive, and should not be subjected to excessive UV light [18]. There are several ways of synthesizing ADN, using standard industrial chemicals. For instance, nitration of primary amines, or ammonia, using mixed acids or other nitration agents, such as NO_2BF_4 or N_2O_5 [19]. Since 1996 ADN is produced in larger scale, at a pilot plant operated by Eurenco Bofors in Karlskoga, Sweden.

Table 1. Properties of ADN

Properties of ADN	
Molecular weight	124.07 g/mol
Density of solid (25°C)	1.81 g/cm ³
Density of liquid (100°C)	1.56 g/cm ³
Melting point	93 °C
Heat of formation	-35.4 kcal/mol
Heat of combustion	101.3 kcal/mol
Heat capacity	1.8 J/g
Oxygen balance	+25.79%
Critical relative humidity	55.2%
Friction sensitivity	72 N
Impact sensitivity	5 Nm
Electrostatic discharge sensitivity	0.45 J
UV absorption maxima in water	214 and 284 nm
Solubility in water at 20°C	357 g in 100 g solvent

Erythritol tetranitrate (ETN, $\text{C}_4\text{H}_6\text{N}_4\text{O}_{12}$ – Figure 2, Table 2) is an ester of nitric acid and erythritol. It is a low melting crystalline solid with explosive properties similar to those of pentaerythritol tetranitrate [21].

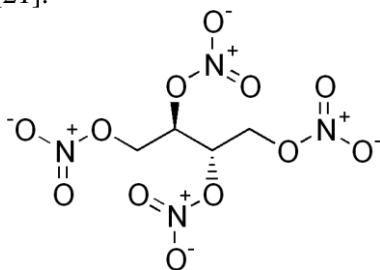


Figure 2. Erythritol tetranitrate (ETN)

Erythritol tetranitrate (ETN) was first synthesized in 1843 by Stenhouse [22]. In recent years, ETN has become a popular explosive for amateurs, since erythritol was first released onto the market as a sugar substitute (sweetener) [23]. At the moment there are two known methods of obtaining ETN (Figure 3):

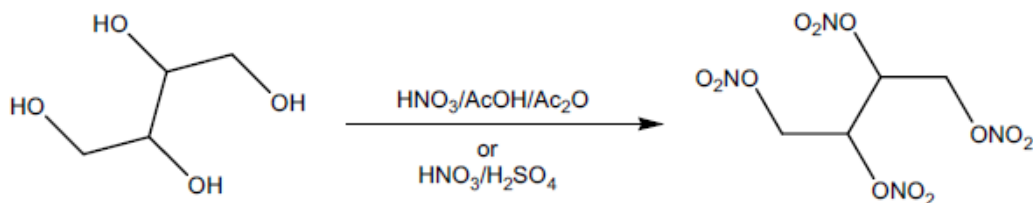


Figure 3. Scheme for erythritol tetranitrate preparation

1. Mixed acid nitration [24] – erythritol is dissolved in concentrated sulfuric acid, mixture that is added over a mixture of nitric/sulfuric acid. After addition is complete, the mixture is warmed and stirred. The reaction mixture is poured over ice, then filtered, rinsed with distilled water and later dried over a vacuum aspirator. The product is then dissolved in hot methanol adding ammonium carbonate to neutralize any remaining acid, and then filtered to yield recrystallized ETN.

2. Nitration with acetyl nitrate [20] – glacial acetic acid and acetic anhydride are mixed before being cooled. Fuming nitric acid is then added and the reaction mixture is stirred while adding erythritol. The reaction mixture is poured over ice, filtered, rinsed and then allowed to dry. The product is then dissolved in isopropanol and filtered resulting recrystallized ETN.

Table 2. Properties of ETN

Properties of ETN	
Molecular weight	302.11 g/mol
Density of solid (25°C)	1.6 g/cm ³
Melting point	61 °C
Boiling point	Decomposes at 160 C
Heat of formation	-113.48 kcal/mol
Heat release	2.8 kJ/g
Oxygen balance	+5.3%
Friction sensitivity	93 N
Impact sensitivity	2 Nm
Electrostatic discharge sensitivity	0.105J

Hydroxyl terminated polybutadiene (HTPB, $\text{C}_{667}\text{H}_{999.05}$ – Figure 4) [26] is a long-chain, cross-linked, and high molecular-weight polymer [25]. HTPB is a translucent liquid with a color similar to wax paper and a viscosity similar to corn syrup. The properties vary because HTPB is a mixture rather than a pure compound, and it is manufactured to meet customers' specific requirements.

HTPB is a legacy thermosetting polymer material frequently used as binder for solid rocket propellant grains made by combining two components [26]:

- 1) a hydroxyl-terminated polymer of butadiene,
- 2) a cross-linking agent, either isocyanate or methylene diphenyl diisocyanate (MDI), used to polymerize and set the material.

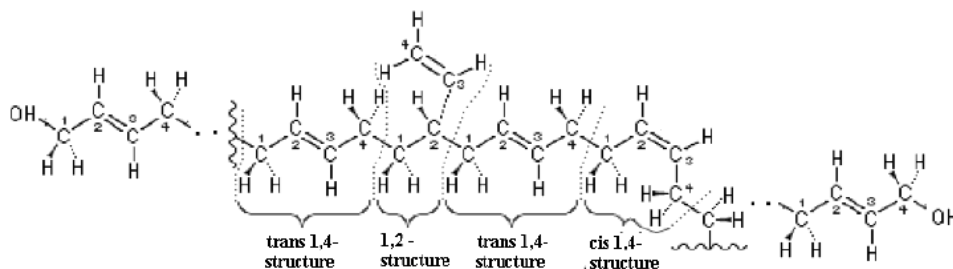


Figure 4. Chemical Structure of HTPB

3. CALCULATION OF THE PROPERTIES FOR ADN/ETN/HTPB

The considered formula for the proposed propellant is an improvement in the field of minimum smoke propellants using ADN as oxidizer. The theoretical properties have been obtained using PROPEP software developed by Arthur J. Lekstutis [30]. The mass percentages of components and the input for the thermochemical calculation are stated in table 3.

Table 3. ADN/ETN/HTPB components

Material	Formula	Mass (%)	Density (g/cm ³)	Heat of formation (cal/g)
ADN	NH ₄ N(NO ₂) ₂	70	1.81	-285
ETN	C ₄ H ₆ N ₄ O ₁₂	10	1.6	-395
HTPB (R45M*)	C ₆₆₇ H ₉₉₉₀₅	20	1.2	-30

*R45M is an already formulated hydroxyl terminated polybutadiene readily available on the market [27]

The assumptions for the thermochemical calculations are:

- Temperature of ingredients was set as default to 298K,
- Chamber pressure kept constant and set as default at 6.9 MPa,
- Exhaust pressure kept constant and set as default to 0.101 MPa.

From the calculation the following characteristics for the solid propellant were obtained:

- Specific impulse – 255.6 s,
- Adiabatic flame temperature – 3075K,
- Exhaust velocity – 5162.4 m/s.

The complete data obtain for the single run simulation for 100 g propellant can be found below:

Table 4. Chamber results

T (K)	P (atm)	Enthalpy(kcal)	Entropy(cal/K)	c _p /c _v	Gas
3075	68.02	-28.15	255.97	1.2172	4.189

Specific heat (molar) of gas and total=11.132

Number mols gas and condensed=4.1887

The molecular weight of the mixture is 23.874

Table 5. Exhaust results

T (K)	P (atm)	Enthalpy(kcal)	Entropy(cal/K)	c _p /c _v	Gas
1507	1	-106.31	255.97	1.244	4.135

Specific heat (molar) of gas and total=10.129
 Number of mols of gas and condensed=4.1347
 The molecular weight of the mixture is 23.874

Table 6. Propellant performance (frozen on first line, shifting on second line)

Impulse	Is Ex	T*	P*	C*	ISP*	OPT-EX	D-ISP	A*M	EX-T
255.6	1.2331	2754	37.97	5162.4		8.32	429	0.16049	1385
260.8	1.1881	2821	38.56	5241.0	202.6	8.63	437.8	0.16293	1507

Impulse – the specific impulse of the motor

IS EX – the isentropic exponent

T* – flow temperature at the throat measured in Kelvin degrees

P* – flow pressure at the throat measured in atmospheres units

C* – characteristic exhaust velocity measured in feet per second

ISP* – the vacuum impulse that would be obtained by a sonic nozzle in air-breathing motor work

OPT-EX - the Optimum Expansion Ratio is an important parameter in nozzle design. This value defines the ratio of the nozzle exit area to throat area, and as such, sizes the divergence cone exit diameter.

D-ISP – the Density Specific Impulse

A*M – the ratio of nozzle throat area to mass flow rate measured in square inch-second per pound

EX-T – the nozzle exit plane temperature measured in Kelvin degrees

In order to evaluate the results, thermochemical calculations have also been run for already known formulations of different solid propellants (Table 8).

For the completion of these formulations and due to the restricted access to sensitive/classified data (e.g. particle dimensions, coatings, additives) the ingredients in table 7 were used.

Table 7. Material inputs for thermochemical calculations

Material	Formula	Density (g/cm ³)	Heat of formation (cal/g)
Ammonium perchlorate (AP)	NH ₄ ClO ₄	1.95	-602
Aluminum (Al)	Al	2.7	0
Iron oxide (FeO)	Fe ₂ O ₃	5.1	-1230
Polybutadiene acrylonitrile terpolymer (PBAN*)	C ₆₇₁ H ₉₉₉ N ₁₉ O ₁₆	0.91	-160
Glycidyl azide polymer (GAP) [29]	C ₆₀ H ₁₀₂₆₀ NO ₂₁	1.29	282

*The characteristics of this ingredient are based on the Thiokol's PBAN

Table 8. Thermochemical calculations for different solid propellants

Propellant Designation	Ingredients	Mass %	Density (kg/m ³)	Specific impulse (s)	Adiabatic flame temperature (K)	Exhaust products (mols/kg)	
Ariane 5 Booster [28]	AP	68	1.87	256.4	3366	3.7651	H ₂
	Al	18				9.8872	CO

	HTPB	14				5.7613	HCl
						3.3347	Al ₂ O ₃
						2.8934	N ₂
						2.5813	H ₂ O
						0.3755	CO ₂
Space Shuttle booster [2]	AP Al PBAN FeO	69.9 16 14 0.1	1.75	254.9	3359	11.6113	H ₂
						9.0436	CO
						5.9049	HCl
						2.9647	Al ₂ O ₃
						3.1130	N ₂
						4.6021	H ₂ O
ADN/GAP[3]	ADN GAP	70 30	1.61	253.1	2928	0.7527	CO ₂
						6.6764	H ₂
						4.5387	CO
						4.46	CO ₂
						1.76E-04	NH ₃
						15.7843	N ₂
ADN/ETN/HTPB	ADN ETN HTPB	70 20 10	1.67	255.6	3075	12.2578	H ₂ O
						4.0084	H ₂
						4.1414	CO
						5.8371	CO ₂
						0	NH ₃
						12.6082	N ₂
						14.7516	H ₂ O

4. CONCLUSIONS AND FUTURE WORK

Given the new global requirements in regards of green environment and by diminishing the amounts of main pollution agents, the current paper, due to its results, offers a new viable, efficient and feasible propellant alternative.

As observed, the new solid propellant's performances are comparable to those actually used in orbital launchers, therefore, through its formulation, a new path to a cleaner sky can be opened.

As future work and in continuation to the current paper, efforts towards testing laboratory scale samples will be done. Through these tests the theoretical results are to be confirmed and a thorough study of combustion stability and key characteristics to be obtained.

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