SP2016_3125163

GREEN SOLID PROPELLANTS FOR LAUNCHERS

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KEYWORDS: Green solid propellant, perchlorate, dinitramide, ADN, performance, formulation.

ABSTRACT

Due to environmental and health concerns related to ammonium perchlorate, AP, alternative solid propellants based on the green oxidizers ammonium dinitramide, ADN, and ammonium nitrate, AN, are developed in the EU funded project GRAIL. By using non-energetic binders and by varying the ratio between ADN and AN, it seems possible to develop a green propellant with properties similar to state-of-the-art, AP based solid propellants.

1. INTRODUCTION

Solid rocket motors are today the most cost effective, competitive and reliable propulsion technology for space launch systems. State-of-the-art solid rocket propellants are based on the oxidizer ammonium perchlorate, AP, and aluminum powder, embedded in a polymer binder. AP has been used since the 1940s [1] and is in many ways an excellent oxidizer. However, AP has a negative impact on the environment and on personal health due to ozone depletion, thyroid gland interference and acid rain formation [2-6].

Sustainable Development has become a top priority on the European and international agendas. With ever increasing environmental concerns, industries in Europe need to adapt to more restrictive environmental legislation in order to stay competitive and to enhance social acceptance. The space industry is in this case no exception which is reflected by ESA´s Clean Space Initiative and the Green Propulsion Harmonisation Process [7, 8].

The GRAIL project (www.grail-h2020.eu), funded by the European Union's Horizon 2020 research and innovation programme, has been granted to determine if it is possible to develop a green AP-free solid propellant. This paper gives an overview of the project and present current work performed at FOI and TIA, concerning propellant formulation and system analysis.

2. GREEN ALTERNATIVES TO AP

Developing an alternative to AP is a challenging task. Currently only two useful green oxidizers exist:

- Ammonium nitrate, AN (NH_4NO_3), and
- Ammonium dinitramide, ADN ($NH_4N(NO_2)_2$).

AN is a very cheap oxidizer, mainly used as fertilizer. Propellants based on AN have low performance and low burning rate. Thus AN-based propellants have mainly been used in low performance applications, such as gas generators. ADN is a new, very powerful oxidizer still in the development phase. It provides high performance and high burning rate, but it is costlier and more explosively hazardous (1.1D) compared to AP.

In Table 1, some of the properties of ADN and AN are presented qualitatively in comparison to AP. From this it seems that neither AN, nor ADN are able to replace AP. However, by combining ADN and AN it seems possible to combine their properties to meet the properties of AP. For instance, it has previously been shown that adding AN to ADN decreases the burning rate [9], and it is expected that low hazard properties can be obtained if a low amount of ADN is used.

Table 1. Properties of AN and ADN vs. AP.

Property	AN	ADN
Performance (Isp)	Low	High
Burning rate	Low	High
Explosive hazard	Low	High
Cost	Low	High
Environmental impact	Low	Low

3. THE GRAIL PROJECT

The aim of the Horizon 2020 project GRAIL, which started in the beginning of 2015, is to develop a green solid propellant based on ADN, AN, aluminum powder and a polymer binder. The propellant developed will be compared with state-of-the-art solid propellants with respect to safety, performance and cost, in order to determine if replacing AP with ADN/AN is a feasible option.

This three-year project, which is coordinated by FOI, can be seen as a continuation of the EU project HISP (www.hisp-fp7.eu). The partners in the project are shown in Table 2. More information about the project can be found on www.grail-h2020.eu.

Table 2. The GRAIL project partners

Partner	**Country**
Swedish Defence Research Agency, FOI	Sweden
Fraunhofer Institut für Chemische Technologie, ICT	Germany
The Inner Arch, TIA	France
Politecnico di Milano, POLIMI	Italy
EURENCO Bofors, EUB	Sweden
AVIO	Italy
Centre National de la Recherche Scientifique - Institute of Chemistry of Poitiers: Materials and Natural Resources, CNRS-IC2MP	France

The technical work in the project is performed in six work packages (WP):

1. System analysis and feasibility study
2. Oxidizer development
3. Binder development
4. High energy fuels
5. Propellant formulation
6. Motor testing

In WP1 (System analysis and feasibility study) the requirements of the propellant to be developed are defined. The output from WP1 is used to guide the development in the other work packages.

In WP2 (Oxidizer development) the properties of prilled ADN is improved and phase stabilized AN (PSAN) is developed. The required amount of ADN and PSAN is also manufactured in WP2.

The binder is developed in WP3. In WP4 the high energy fuels considered are developed and manufactured. This includes nano-aluminum, aluminum hydride, micron-sized aluminum, and mixtures thereof.

After selection of binder composition and fuel, the final propellant composition will be optimized and characterized in WP5 (Propellant formulation). The combustion properties and performance will be determined in WP6 (Motor testing).

Using the results and the knowledge gained, the propellant developed will then be assessed for launcher applications in WP1. This will finally determine the feasibility of replacing AP with ADN and AN.

During the first year of the project the work has mainly focused on development, processing, production and characterization of the chemicals needed for the propellant development. This includes improving the methods to produce ADN particles with suitable morphology, production of phase stabilized AN, characterization of the oxidizer particles produced and development of suitable binder materials. The high energy density fuels to be used have been characterized and a launcher system analysis has been performed.

4. SYSTEM ANALYSIS

In order to use the propellant on a civilian launcher the propellant must be of hazard class 1.3 (non-detonatable) and the burning rate must be tunable in the range of 7 to 15 mm/s at 7 MPa, with a pressure exponent below 0.5. Apart from this, the mechanical properties, ageing properties, cost and performance must also be acceptable.

The performance must be evaluated on a system level. For this the Vega launcher was selected as a suitable case. In the initial performance calculations, data for P80, which is the first stage of Vega, has been used. The geometry of P80 is shown in Figure 1. The vacuum specific impulse was calculated using the RPA computer code [10], and the data shown in Table 3 and Table 4.

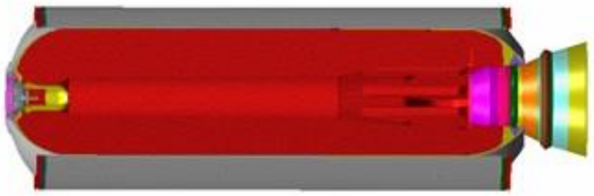


Figure 1. P80 SRM, 1st stage of the Vega launcher (credit AVIO).

Table 3. Data for P80.[a]

Pressure	67 bar
Nozzle area expansion	16
I_{sp} (vacuum)	280 s
Propellant HTPB 1912	Global composition Al: 19% HTPB: 12% AP: 69%

a) Data from AVIO.

In the calculations, two phase flow losses were taken in to account, which is required for propellants containing large amounts of aluminum. However, the model for calculating these losses are based on AP propellants. Due to the lack of more information, it was assumed that the model also is valid for ADN/AN propellants. It was further assumed that the erosive power on the carbon/carbon nozzle throat and the thermal dimensioning of the internal insulation are the same for the two types of propellants.

Table 4. Thermochemical data.[a]

Material	**Formula**	**ρ (g/cm^3)**	**ΔH_f (kJ/mol)**
AP	NH_4ClO_4	1,95	-295,3
AN	NH_4NO_3	1,72	-365,6 [11]
ADN	$NH_4N(NO_2)_2$	1,81 [12]	-134,6 [13]
HTPB	$C_{10}H_{15,09}N_{0,10}O_{0,23}$	0,93 [b]	-52,58 [b]
Al	Al	2,70	0

a) Data from reference [14] unless otherwise stated.
b) Measured at FOI.

The viscosity of an uncured propellant slurry increases with increasing volume fraction solid filler (AP and Al), and must be low enough to enable casting. Hence, to calculate the performance for a realistic HTPB/Al/ADN/AN based propellant, a reasonable solid loading must be used.

The propellant used in Vega, HTPB 1912, has a volumetric solid loading of 76,7%. To obtain such a high solid loading, particle fractions of different sizes are used. By using particle sizes similar to what is used in HTPB 1912, it is expected that a similar volumetric solid loading would be possible to obtain for a HTPB/Al/ADN/AN formulation. ADN and AN have lower density than AP. To not exceed a volumetric solid loading of 76,7% in an HTPB/Al/ADN/AN formulation, approximately 13 weight % HTPB is required.

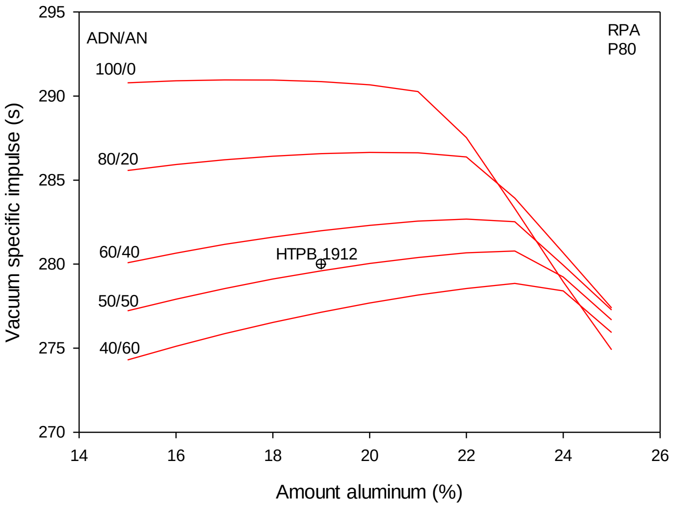


Figure 2. Delivered vacuum specific impulse as a function of Al content. Case P80.

The specific impulse as a function of Al content for propellants containing different ADN/AN ratios and 13% HTPB, are shown in Figure 2. The specific impulse for HTPB 1912, is shown for comparison.

The vacuum specific impulse increases with increasing amount of ADN. However, as previously mentioned, addition of AN is probably needed to reduce the explosive sensitivity and the burning rate. The optimum aluminium content at respective ADN/AN ratios are shown in Table 5, together with the data for HTPB 1912.

Table 5. Delivered vacuum specific impulse for HTPB/Al/AP and optimized HTPB/Al/ADN/AN propellants.

Propellant	**Ox. (%)**	**Al (%)**	**HTPB (%)**	**I_{sp} (s)**	**T_c (K)**
HTPB 1912	69 (AP)	19	12	280	3550
ADN/AN 100/0	70/0	17	13	291	3395
ADN/AN 80/20	53,6/13,4	20	13	287	3335
ADN/AN 60/40	39/26	22	13	283	3254
ADN/AN 50/50	32/32	23	13	281	3208

Calculated using RPA. Case: P80.

Already by using as low ADN/AN ratio as 50/50, the specific impulse of HTPB 1912 is exceeded. However, the density of all HTPB/Al/ADN/AN propellants shown in Table 3 is substantially lower (1,70 g/cm^3) compared to HTPB 1912 (1,81 g/cm^3).

This has been considered in the system analysis by stretching the cylindrical part of the P80, to accommodate more propellant, leading to higher inert mass of the motor. To compensate for that, the specific impulse need to be increased by about 2 seconds. The propellant, ADN/AN 60/40, with a specific impulse of 283 s thus seems to be an interesting option.

In the calculations the aluminum particles are assumed to combust and agglomerate in the same way as in AP based propellants, which may not be the actual case. The higher aluminum content may also increase nozzle erosion. On the other hand, the combustion temperature for ADN/AN 60/40 is 300 K lower compared to HTPB 1912, thus requiring less thermal protection and leading to decreased nozzle erosion. A more detailed study is needed to determine the actual performance, but from this initial study it seems possible to meet the system performance needed using an ADN/AN-based propellant containing less than 40% ADN.

5. ADN DEVELOPMENT

ADN is today produced by EURENCO Bofors in Sweden. The small scale production is performed in a plant initially built for production of other energetic materials and thus not optimized for producing ADN. As a consequence, ADN is today very expensive. In order to reduce the cost, ways to improve the synthesis of ADN were studied in the HISP project. The future cost of ADN, if produced in large scale, were estimated to be in the range of 20-60 €/kg depending on the assumptions made [15]. To obtain a better estimate and to further decrease the cost, synthesis improvements are ongoing in GRAIL [16].

The morphology of the ADN particles received from EURENCO are needle-shaped and need to be processed to be used in a formulation. At FOI spherical ADN particles, prills, are manufactured by spray prilling [17, 18]. This method was scaled up in the HISP project enabling prilling of 30 kg 200 µm ADN per day. So far approximately 400 kg ADN has been prilled. Spray prilling seems as a suitable method for industrial production. However, the spray prilling method has two disadvantages: the particle size distribution is broad, and the density of the prills is 1-2% below the theoretical value. A narrower particle size distribution will improve particle packing and thus performance, and 100% dense prills are desired to reduce the explosive sensitivity.

By using an ultrasonic spray nozzle, 100% dense, transparent 200 µm prills with narrower size distribution and reduced impact sensitivity were produced. The improved prills are shown in Figure ***3***. Upcoming work in the project will show how these improved prills will influence the sensitivity when used in a formulation, and how much AN will be required in the formulation to obtain hazard division 1.3.

Figure 3. Improved 100% dense ADN prills with reduced sensitivity.

Jet milling is an effective and fast method to manufacture small ADN particles in the range of 10-20 µm [19]. Even though the particles have an irregular shape they provide good castability in combination with 200 µm prilled ADN. Recently, the powder feeder was improved to increase the milling capacity and now one kg ADN can be milled in less than five minutes.

6. FORMULATION

FOI has past experience on propellants based on ADN and the energetic polymer GAP [20]. In the GRAIL project lower regression rate is desired. Therefore, non-energetic polymers are studied such as different brands of HTPB (R45HT, R45V, Krasol LBH, Polyvest) and a co-polymer based on polycaprolactone and polytetrahydrofuran (CAPA 7201A). The supplier of each polymer is shown in Table 6, and the simplified structure of CAPA is shown in Figure 4.

Table 6. Polymers and suppliers.

Polymer	Producer/supplier
HTPB Poly bd R45HT LO	Cray Valley USA
HTPB Poly bd R45V	Cray Valley Italia
HTPB Krasol LBH 3000	Cray Valley Czech Rep.
HTPB Polyvest EP HT	Evonic Germany
CAPA 7201A	Perstorp UK

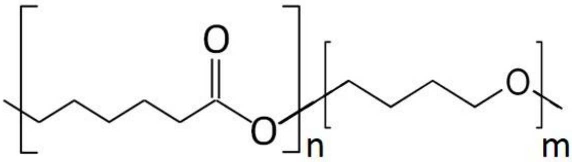
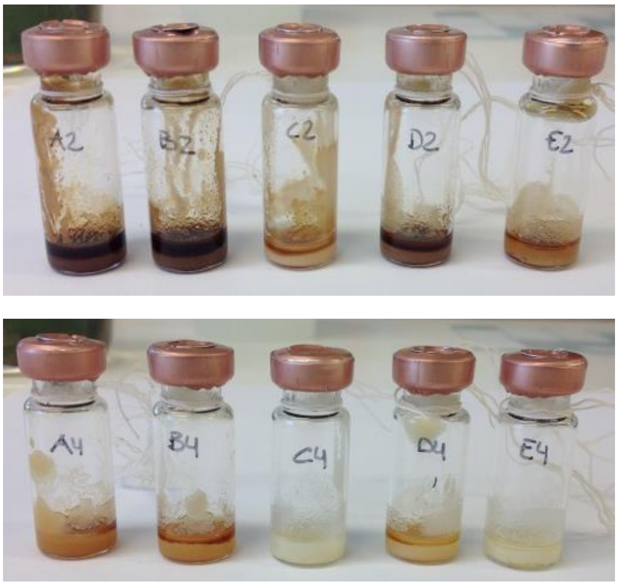


Figure 4. Simplified structure of CAPA.

ADN is substantially less chemically stable than AP, requiring proper compatibility testing with other propellant ingredients. Each polymer in Table 6 was mixed with ADN in a 50/50 ratio and the compatibility was assessed at 75°C by heat flow calorimetry. In all cases, large exothermal peaks and strong read brown discoloration were detected. By adding one part of hexamine to 100 parts of polymer (1 phr), the compatibility was improved substantially, as seen in Figure 5, and exemplified for CAPA in Figure 6.

For all ADN/polymer mixtures, the exothermal peak disappeared and the discolorations were reduced when adding hexamine. Among the polymers tested HTPB LBH and CAPA seems to be more compatible with ADN than the other polymers, and when using hexamine they show almost no discoloration.



ADN/polymer 50/50
A2: R45HT
B2: R45V
C2: LBH
D2: Polyvest
E2: CAPA

ADN/polymer 50/50 + 1 phr hexamine
A4: R45HT
B4: R45V
C4: LBH
D4: Polyvest
E4: CAPA

Figure 5. ADN/polymer compatibility testing after 21 days at 75°C.

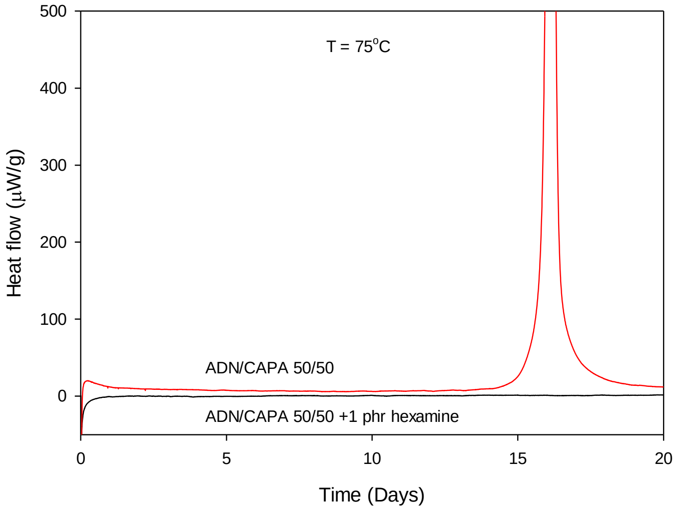


Figure 6. Heat flow from ADN/CAPA 50/50 and influence of hexamine.

7. CONCLUSIONS

The objective of the European research project GRAIL is to determine if it is feasible to replace AP in solid propellants with a mixture of ADN and AN. By varying the ratio between ADN and AN, the demands for low sensitivity (hazard division 1.3), low burning rate and high performance seems possible to meet. Initial performance calculations show that performance comparable to current AP based propellants can be obtained using less than 40% ADN.

Improved ADN prilling technology has been developed, enabling ADN particles with reduced sensitivity and narrower particle size distribution. The compatibility between ADN and different polymers have been assessed. Hexamine has shown to effectively improve the polymer/ADN compatibility.

8. ACKNOWLEDGMENT

The GRAIL project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement no. 638719.
The authors would like to acknowledge the good work performed by all members of the GRAIL project.

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