GRAIL: A EUROPEAN INITIATIVE TO DEVELOP GREEN SOLID PROPELLANTS FOR LAUNCHERS

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Abstract

Due to environmental and health concerns related to ammonium perchlorate 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 a non-energetic binders and by varying the ratio between ADN and AN, the properties of the propellant can be tuned to meet, or even exceed, the properties of state of the art solid propellants. The background and an overview of the GRAIL project is presented, as well as recent work performed at FOI.

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 aluminium powder, embedded in a polymer binder matrix. AP has been used since the 1950s 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 [1-5].

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 [6, 7].

The objective of the GRAIL project (www.grail-h2020.eu), funded by the European Union's Horizon 2020 research and innovation programme, is to determine if it is feasible to develop a green AP free solid propellant based on the new high energy density oxidizer ammonium dinitramide, ADN, and the low cost oxidizer ammonium nitrate, AN. The high energy density green solid propellant developed will be compared with state of the art solid propellants with respect to safety, performance, ballistic and mechanical properties, and cost, in order to determine if replacing AP with ADN/AN is a feasible option.

2. Concerns related to AP

AP contains 30% chlorine which on combustion forms vast amounts of hydrochloric gas. From one launch of Ariane 5, 100 tons of hydrochloric gas is formed, and from one launch of Vega, 26 tons are formed, which corresponds to 270 tons and 70 tons respectively, of concentrated hydrochloric acid. The Space Shuttle produced even larger amounts of hydrochloric acid, see Table 1.

Table 1. Amount of HCl and concentrated hydrochloric acid formed per launch.

Launcher	Amount HCl gas formed (tons)	Amount concentrated hydrochloric acid formed[a] (tons)
Vega	26	70
Ariane 5	100	270
Space Shuttle	216	584

a) Maximum amount of HCl in concentrated hydrochloric acid is 37%.

Part of the chlorine emission is injected directly into the stratosphere where it catalytically promotes ozone depletion. At present, the global rocket launches don’t contribute significantly to the ozone layer depletion [1], but over the course of time, due to the expected increased numbers of launches, this contribution may become significant. It has even been suggested that this might require the number of launches to be regulated [2]. The impact of launchers on the ozone layer is currently assessed in a ESA Clean Space study [8].

Groundwater contaminated with perchlorate is of particular concern in the USA where drinking water supplies, that affect tens of millions of people, have been contaminated from the production of AP [3]. This might affect human health by interfering with iodine uptake into the thyroid gland as shown in Figure 1. Interference with both the thyroid and available thyroid hormones is known to produce adverse effects on neurodevelopment in humans, with fetuses and infants being most vulnerable [9]. Similar problems might also exist outside the USA, where perchlorate has been produced or used in large amounts.

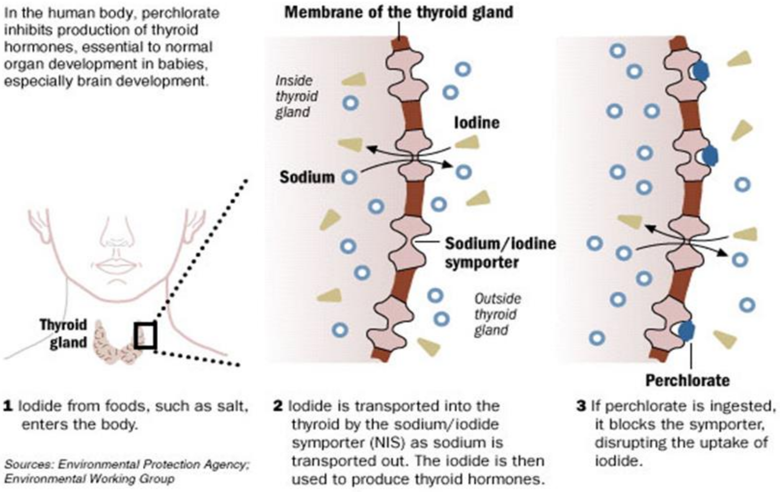


Figure 1. The thyroid gland and interference of perchlorate (credit US EPA).

Recently in Europe the presence of perchlorate in fruits and vegetables has attracted attention [10]. Extensive monitoring indicated that the presence of perchlorate in fruits and vegetables is more widespread than initially expected. Evidence was provided that the use of certain fertilizers is an important source of this contamination but other sources, such as manufacture, use and disposal of ammonium perchlorate used in rocket propellants, may also contribute. The European Food Safety Authority Panel on Contaminants concluded that the chronic dietary exposure to perchlorate is of potential concern. For this reason, the Commission Recommendation 2015/682 (EU), on the monitoring of perchlorate in food and drinking water was adopted 29 April 2015 [11].

The environmental and health issues related to AP as oxidizer in rocket propellants are debated and it is often argued that they are negligible on a global scale. However, this is also the case for every single source of pollutant and the space industry must, as any other industry, act responsibly to promote a healthy and sustainable environment for future generations. With future more restrictive environmental legislation, and increased concern with perchlorates, green alternatives to AP are desired.

3. The GRAIL project

Developing an alternative to AP is a challenging task. Currently only two feasible 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 a fertilizer. Propellants based on AN have low performance and low burning rate, and 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 more costly and more explosive 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 the properties can be tuned to meet, or even exceed, the properties of AP. For instance, it has previously been shown that adding AN to ADN decreases the burning rate [12], 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 in relation to AP.

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

The three year project, which started in the beginning of 2015, can be seen as a continuation of the previous EU project HISP (www.hisp-fp7.eu). The GRAIL consortium, represented by France, Germany, Italy and Sweden, was put together after analyses of the competences needed. The partners and their respective main activities in the project are shown in Table 2.

The technical work in the project is performed in six work packages:

- WP1: System analysis and feasibility study
- WP2: Oxidizer development
- WP3: Binder development
- WP4: High energy fuels
- WP5: Propellant formulation
- WP6: Motor testing

Table 2. GRAIL partners and their main activities in the project.

Partner	**Country**	**Type of entity**	**Main activity in the project**
Swedish Defence Research Agency, **FOI**	Sweden	Research institute	Prilling of ADN and propellant formulation. Project coordination.
Fraunhofer Institut für Chemische Technologie, **ICT**	Germany	Research institute	Manufacturing of phase stabilized AN, propellant formulation and combustion
The Inner Arch, **TIA**	France	SME	System analysis and definition of propellant requirements
Politecnico di Milano, **POLIMI**	Italy	University	High energy fuel characterization and combustion
EURENCO Bofors, **EUB**	Sweden	Industry	Synthesis development and production of ADN
AVIO	Italy	Industry	Propellant development and motor testing
Centre National de la Recherche Scientifique - Institute of Chemistry of Poitiers: Materials and Natural Resources, **CNRS-IC2MP**	France	Research institute	Phase stabilizers and combustion catalysts. AlH_3 synthesis development.

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 selecting 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 green solid propellants.

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. Work performed at FOI

4.1 Performance calculations

The Vega launcher was selected as a suitable case for the system analysis. In the initial performance calculations, data for P80, which is the first stage of Vega, was used. The geometry of P80 is shown in Figure 2. The vacuum specific impulse was calculated using the RPA computer code [13], and the data shown in Table 3 and Table 4. In the performance calculations, two phase flow losses were taken in to account, which is required for propellants containing large amounts of aluminium.

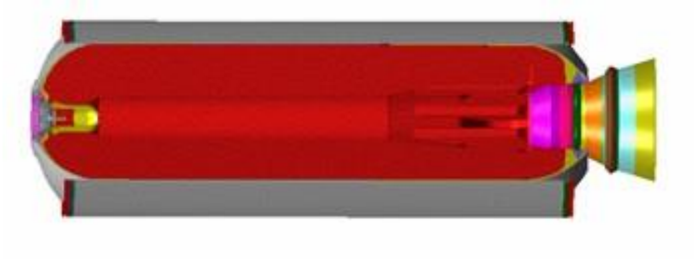


Figure 2. P80 SRM, 1st stage of the Vega launcher (credit AVIO).

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.

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 [14]
ADN	$NH_4N(NO_2)_2$	1,81 [15]	-134,6 [16]
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 [17] 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 needed. By using particle sizes similar to what is used in HTPB 1912, it is expected that a similar volumetric solid loadings would also 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, 13 weight % HTPB is required.

The specific impulse as a function of Al content for propellants with different ADN/AN ratios and 13% HTPB, is shown in Figure 3. The specific impulse for HTPB 1912, is shown for comparison.

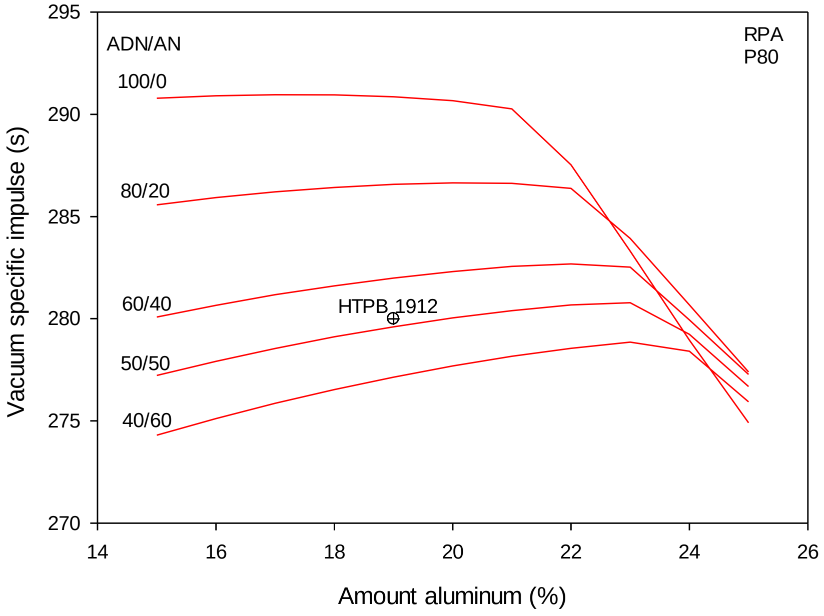


Figure 3. Vacuum specific impulse as a function of Al content. Case P80.

The vacuum specific impulse increase with increasing amount of ADN. However, addition of AN is probably needed to reduce the propellants explosive sensitivity and the burning rate. The optimum propellant compositions for respective ADN/AN ratio are shown in Table 5, together with the data for HTPB 1912.

Table 5. Specific impulse for optimized HTPB/Al/AP and HTPB/Al/ADN/AN propellants.

Propellant	Oxidizer (%)	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 densities of all HTPB/Al/ADN/AN propellants are substantially lower (1,70 g/cm^3) compared to HTPB 1912 (1,81 g/cm^3). To compensate for that, the specific impulse needs to be increased. The propellant, ADN/AN 60/40, with a specific impulse of 283 s thus seem as a reasonable option.

In the calculations, aluminium 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 aluminium content may also increase nozzle erosion. On the other hand, the combustion temperature for ADN/AN 60/40 is approximately 300 K lower compared to HTPB 1912, which will decrease nozzle erosion and require less thermal protection. A more detailed system analysis is needed to determine the actual performance, but from this initial study it seems possible to meet the performance needed using an ADN/AN based propellant containing less than 40% ADN.

4.2 ADN development

ADN is today produced by EURENCO Bofors in Sweden. The small scale production is performed in a plant initially built for producing other energetic materials and is 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 [18]. To obtain a better estimate and to further decrease the cost synthesis improvements are ongoing in GRAIL [19].

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 [20, 21]. This method was scaled up in the HISP project enabling prilling 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 are 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.

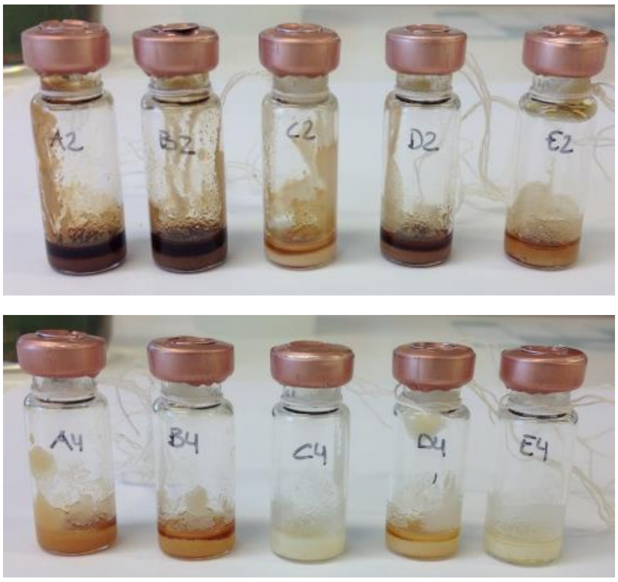
By using a an ultrasonic spray nozzle 100% dense, transparent 200 µm prills with narrower size distribution and reduced impact sensitivity have been produced. The improved prills are shown in Figure 4. Upcoming work in the project will show how these improved prills will influence the sensitivity when used in a formulation, and how much AN will be required in the formulation to obtain hazard division 1.3.

Figure 4. Improved 100% dense ADN prills with reduced sensitivity.

Jet milling has shown to be an effective and fast method to manufacture small ADN particles in the range of 10-20 µm [22]. Even though the particles have an irregular shape they provide good castability in combination with 200 µm prilled ADN. Recently, the powder feeder has been improved to increase the milling capacity and now one kg ADN can be milled in less than 5 minutes.

4.3 Formulation

FOI has past experience on propellants based on ADN and the energetic polymer GAP [23]. In the GRAIL project lower regression rate is desired and thus non-energetic polymers are studied such as different brands of HTPB (R45HT, R45V, Polyvest, Krasol LBH) and a co-polymer based on polycaprolactone and polytetrahydrofuran (CAPA 7201A). Respective polymer was mixed with ADN in a 50/50 ratio and the thermal stability was assessed at 75°C using a heat flow calorimeter. In all cases, large exothermal peaks and strong read brown discoloration were detected. By adding one part of hexamine to 100 parts of polymer, the compatibility improved substantially, as seen in Figure 5, and exemplified for CAPA in Figure 6. For all ADN/polymer mixtures, the exothermal peak disappear and the discolorations are 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.

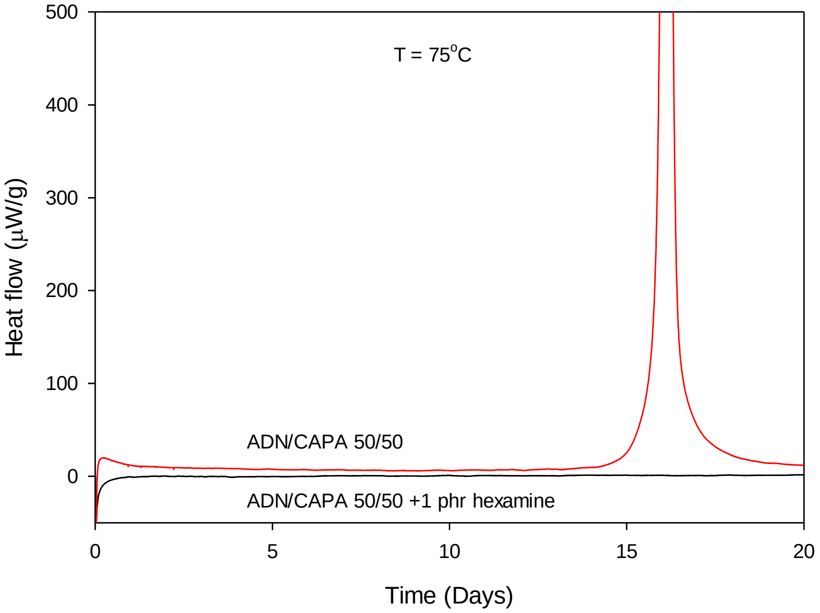


Figure 6. Heat flow from ADN/CAPA 50/50 and influence of hexamine.

5. 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. The three year project, which started in the beginning of 2015, is represented by seven partners from France, Germany, Italy and Sweden.

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 have 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.

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