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 being developed. By using a non-energetic binder, such as HTPB, 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 ongoing development of ADN in Europe is briefly described and the composition of four different ADN based propellants are optimized by using thermochemical calculations.

1 INTRODUCTION

Current solid propellants for launchers are based on the oxidizer ammonium perchlorate, AP (NH_4ClO_4). AP has many desirable properties such as high oxygen content, high density, low explosive hazard and good combustion properties. However, AP has a negative impact on the environment and on personal health due to:

- Ozone depletion
- Thyroid gland interference
- Acid rain formation

Sustainable Development has become a top priority on the European and international agendas. With ever increasing environmental concerns, the space industries in Europe need to adapt to more restrictive environmental legislation in order to stay competitive and to enhance social acceptance. Chlorine free green solid oxidizers to replace AP are thus of great interest.

Finding alternatives to AP is a challenging task and the numbers of alternatives are very limited. In the 1990s ESA supported the development of hydrazinium nitroformate, HNF ($N_2H_4CH(NO_2)_3$) based solid propellants at TNO/APP in the Netherlands [1, 2]. Theoretically HNF enables high performance but it is very sensitive to friction and has a poor thermal stability [3]. Even though HNF doesn't contain any chlorine it is a toxic (LD 50 oral 128 mg/kg) [4] salt of hydrazine, and it is thus questionable if it can be considered as green. Since a few years back the HNF development at TNO/APP is discontinued and the production equipment for producing HNF has been dismantled.

Currently only two feasible green oxidizers exist:

- Ammonium nitrate, AN (NH_4NO_3)
- 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 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 explosively hazardous compared to AP.

In the EU project HISP (www.hisp-fp7.eu) high performance solid ADN based propellants for in-space propulsion applications were studied. Typical applications considered were upper stages, interplanetary transfer stages and planetary ascend vehicles. To obtain very high performance an energetic binder based on glycidyl azide polymer, GAP, and high energy density fuels such as aluminum hydride (AlH_3), nano-aluminium and activated aluminum were studied.

In the beginning of 2015, the EU Horizon 2020 project GRAIL (www.grail-h2020.eu) started. The objective of the GRAIL project is to develop green solid propellants for launchers by using both ADN and AN. In Table 1, the properties of ADN and AN are presented in relation to AP. By combining ADN and AN it seems that the properties can be tuned to meet, or even exceed, the properties of AP.

Table 1. Properties of AN and ADN compared to AP.

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

This paper present results from the HISP project, and activities in the GRAIL project performed at FOI.

2 OXIDIZER DEVELOPEMNT

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 prize, ways to improve the synthesis of ADN were studied in the HISP project. The future prize of ADN, if produced in large scale, were estimated to be in the range of 20-60 €/kg depending on the assumptions made [5]. To obtain a better prize estimate and to further decrease the prize synthesis improvements are ongoing in GRAIL.

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. This method was scaled up in HISP 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 current method suffers from two disadvantages; the particle size distribution is broad, and the density of the prills are 1-2% below the theoretical value. A narrow particle size distribution will improve particle packing and thus performance, and 100% dense prills are desired to reduce the explosive sensitivity. Currently work at FOI is ongoing to use an ultrasonic spray nozzle. Initial results show that 100% dense, transparent 200 µm prills with narrow size distribution and reduced sensitivity can be produced. The improved prills are shown in Figure 1.

Figure 1. Improved 100% dense ADN prills with reduced sensitivity.

Jet milling has been shown to be an effective and fast method to manufacture small ADN particles in the range of 10-20 µm [6]. Even though the particles have an irregular shape they provide good castability in combination with 200 µm prilled ADN. Currently the jet milling apparatus at FOI is being equipped with a powder feeder to increase the milling capacity.

3 ADN PROPELLANT PERFORMANCE

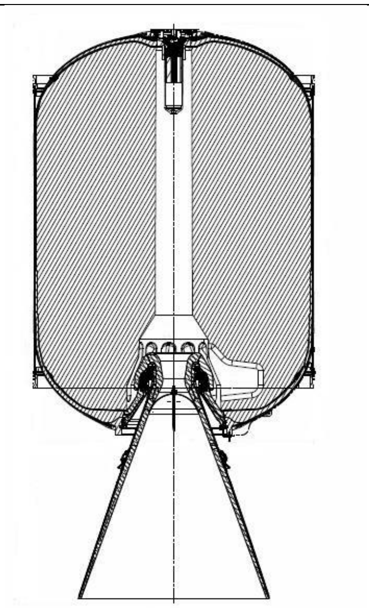
When calculating propellant performance one must distinguish between the ideal and the delivered specific impulse. The ideal specific impulse, ${I_{sp}}^i$, is the theoretical maximum that can be obtained and is often calculated using CEA [7]. The delivered specific impulse, ${I_{sp}}^d$, is what a specific motor can deliver and is calculated by applying k number of correction factors to the ideal value according to equation 1.

$$ {I_{sp}}^d = {I_{sp}}^i \prod \eta_k \quad (1) $$

Available computer codes to calculate the delivered specific impulse include SPP [8] and RPA [9]. Both these codes first calculate the ideal specific impulse in the same way as CEA, and then apply the calculated correction factors. In order to calculate the correction factors the nozzle geometry must be specified. In this case data from Zefiro 9 was used. The propellant in Zefiro 9, HTPB 1912, represents the state of the art and is selected as our benchmark. Some data for the Zefiro 9 rocket motor is shown in Table 2 and the thermochemical data used in the calculations is presented in Table 3.

Table 4 show the calculated specific impulse for Zefiro 9. The ideal specific impulse is 10% higher compared to the value shown in Table 2. When calculating the combustion efficiency, η_c, using RPA the specific impulse is underestimated by 1%. In order to obtain correct results the combustion efficiency was set to 99%. This value is used throughout the following calculations.

Table 2. Data for the Zefiro 9 motor used in the third stage of the VEGA launcher.[a]



	Average values during the burning time
	Pressure: 60 bar
	Nozzle area expansion: 57
	I_{sp} (vacuum): 295 s
	Nozzle half angle: 18°
	Propellant: HTPB 1912 - HTPB: 12% - AP: 69% - Al: 19% Burning rate: 7 mm/s at 7 MPa

a) Figure and data from AVIO.

Table 3. Thermochemical data used in the calculations.

Material	**Formula**	**ρ (g/cm³)**	**ΔH$_f$ (kJ/mol)**
AP	NH_4ClO_4	1,95 [10]	-295,3 [10]
AN	NH_4NO_3	1,72 [10]	-365,6 [10, 11]
ADN	$NH_4N(NO_2)_2$	1,81 [12]	-134,6 [13]
HTPB based binder	$C_{10}H_{15,09}N_{0,10}O_{0,23}$	0,93 [a]	-52,58 [a]
GAP based binder	$C_{10}H_{16,55}N_{8,44}O_{3,34}$	1,28 [a]	+221,7 [a]
Al	Al	2,70 [10]	0 [10]

a) Measured at FOI.

Table 4. Specific impulse for HTPB 1912 calculated using CEA and RPA.

	CEA ideal	**RPA ideal**	**RPA delivered**	**RPA delivered**
η_c	1	1	0,9825 [a]	0,99 [b]
I_{sp} (s)	323,5	323,5	293,2	295,4
Deviation (%) [c]	+10	+10	-1	0

a) Combustion efficiency calculated using RPA
b) Combustion efficiency set to 99%
c) Compared to the experimentally determined value shown in Table 2

In the HISP project a binder based on GAP was chosen in order to maximize performance. The viscosity of an uncured propellant slurry increases with increasing volume fraction solid filler. Hence, to find the optimum composition for a realistic ADN/Al/GAP formulation a reasonable solid loading must be used. The HTPB 1912 propellant used in Zefiro 9 has a volumetric solid loading of 76.68%. To not exceed a solid loading of 77 volume % in an ADN/Al/GAP formulation, at least 17 weight % GAP is required. The optimum ADN/Al ratio was determined using RPA. The results are presented in Figure 2 and Table 5. Similar optimization was also performed for HTPB/AP/Al and is shown for comparison.

The optimum composition for ADN/Al/GAP was found at 70% ADN, 13% Al and 17% GAP (HISP 1), with a vacuum specific impulse of 309.2 s at a volumetric solid loading of 76.61%. To obtain such a high solid loading particle size optimization and access to particles with correct size ratios are required. In the HISP project this was not possible but an ADN/GAP/Al 56/26/18 propellant (HISP 2) was developed and characterized. Even though the solid loading in HISP 2 is low the specific impulse and density is remarkably high, as seen in Table 5.

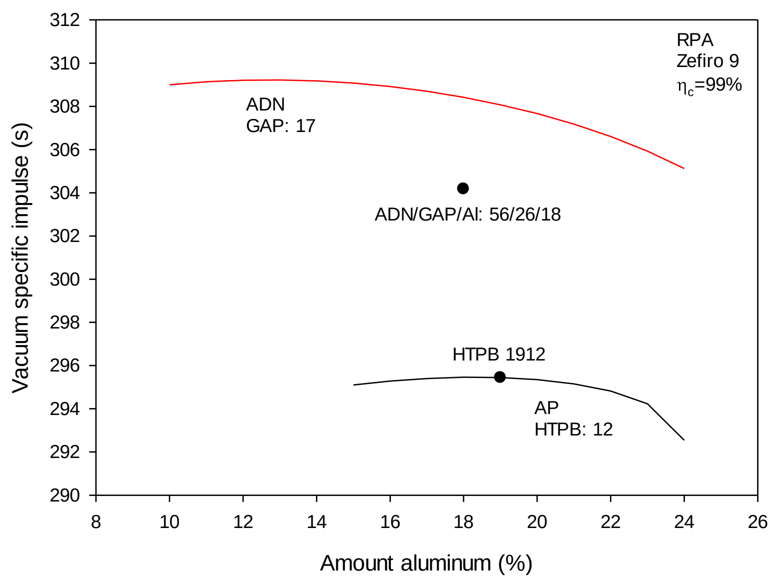


Figure 2. Vacuum specific impulse as a function of Al content.

Table 5. Calculated specific impulse for HTPB 1912 and GAP/ADN/Al.

Propellant	Oxidizer (%)	Al (%)	Binder (%)	Vol % filler	$I_{sp}{}^{d}$ (s)	ρ (g/cm^3)
HTPB 1912	69 (AP)	19	12 (HTPB)	76,68	295,4	1,81
HISP 1	70 (ADN)	13	17 (GAP)	76,61	309,2	1,76
HISP 2	56 (ADN)	18	26 (GAP)	64,93	304,2	1,85

Calculated using RPA. Case: Zefiro 9. Combustion efficiency 99%.

The burning rate as a function of pressure for the HISP 2 propellant is shown in Figure 3 and was found to be high (21 mm/s at 7 MPa) compared to HTPB 1912 (7 mm/s at 7 MPa). In the system analysis performed in HISP the conclusion was that for a motor similar to Zefiro 9, a burning rate in the range of

7 mm/s (for a radial burning grain) to 15 mm/s (for an end burning grain) is required. For long motors, such as boosters for launchers, an end burning grain geometry is not an option. By using non-energetic binder, such as HTPB, the burning rate of ADN/Al propellants can be reduced to approximately 15 mm/s [14]. It has previously also been shown that adding AN to ADN decreases the burning rate [15]. Using non-energetic polymers will also reduce cost which is important for launcher applications. In the GRAIL project it was thus decided to develop propellants based on ADN/AN/Al and a non-energetic binder.

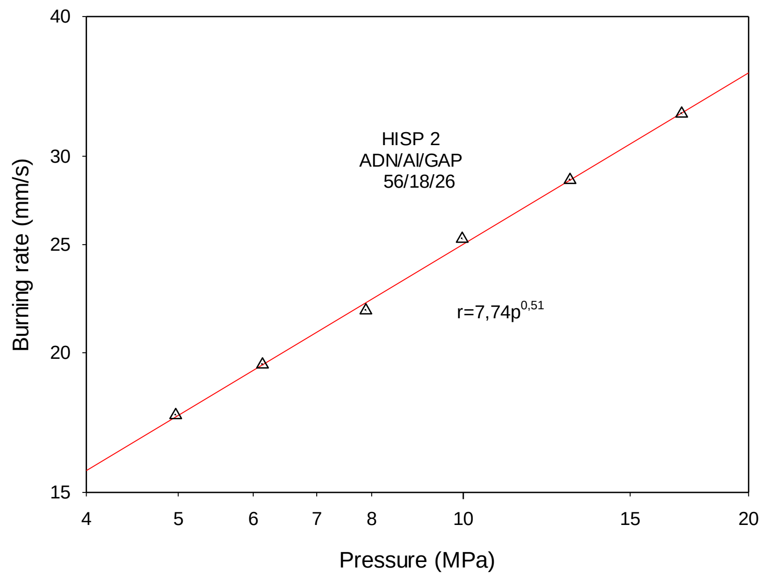


Figure 3. Burning rate for ADN/Al/GAP propellant, HISP 2.

ADN and AN have lower density than AP. To not exceed a solid loading of 77 volume % in an ADN/AN/Al/HTPB formulation, at least 13 weight % HTPB is required. The optimum Al content for propellants with three different ADN/AN ratios were determined. The calculations were performed as described above using RPA with the combustion efficiency set to 99%. The results are presented in Figure 4 and Table 6. The results for HTPB/AP/Al is included for comparison.

The optimum Al content for ADN/AN 60/40 was found to be 23%. If no AN is used the optimum Al content is shifted to 21%. By replacing AP with ADN/AN 60/40, a specific impulse similar to HTPB 1912 can be obtained. When more ADN is used the specific impulse increase, but so will also the burning rate and the explosive sensitivity.

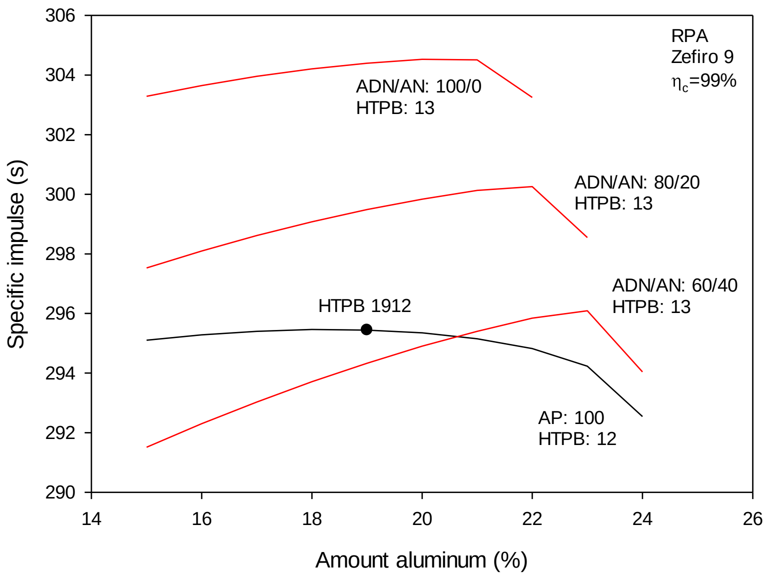


Figure 4. Vacuum specific impulse as a function of Al content.

Table 6. Calculated specific impulse for HTPB 1912 and ADN/AN/Al/HTPB.

Propellant	ADN/AN	Oxidizer (%)	Al (%)	HTPB (%)	Vol % filler	$I_{sp}{}^{d}$ (s)	ρ (g/cm^3)
HTPB 1912	---	69 (AP)	19	12	76,68	295,4	1,81
G1	100/0	66/0	21	13	75,99	304,5	1,72
G2	80/20	52/13	22	13	76,07	300,3	1,71
G3	60/40	38,4/25,6	23	13	76,14	296,1	1,71

Calculated using RPA. Case: Zefiro 9. Combustion efficiency 99%.

4 CONCLUSIONS

Propellants based on ADN/Al/GAP have been formulated and characterized, and methods to improve the production of ADN and ADN prills are ongoing in order to reduce cost, particle size distribution and sensitivity. Thermochemical calculations show that propellants based on ADN/Al/GAP have very high specific impulse but the burning rate is too high for launcher applications. By using non-energetic polymers, such as HTPB, the burning rate and cost can be reduced. To further reduce the burning rate and cost, and to decrease the explosive sensitivity, ADN can partially be replaced by AN. ADN and AN have lower density than AP. To obtain realistic solid loadings at least 13% HTPB is required. The optimum Al content in ADN/AN/Al/HTPB propellants with different ADN/AN ratios were determined. At an ADN/AN ratio of 60/40 a specific impulse similar to state of the art solid propellants is obtained. The promising results encourage further development of green solid propellants based on ADN.

5 ACKNOWLEDGMENT

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