

## GREEN SOLID PROPELLANTS FOR LAUNCHERS

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### ABSTRACT

In the panorama of space launchers, solid propulsion has found a domain of application to first stage or strap-on boosters, in this one solid propulsion is always cost effective whatever the launcher size could be. Another domain of excellence is the boost stages of small launcher such as the Vega launcher.

All the civilian Solid Rockets converged on the use of a composite solid propellant based on polybutadiene as binder, ammonium perchlorate AP as oxidizer and aluminium as a fuel.

However, solid propulsion suffers of a lack of performance versus the liquid couple LOX/Kerosene and of a potential 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 (project following the HISP project). By using a 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.

This paper presents the methodology to select a domain of formulation to explore (based on the potential payload increase of a given launcher) and gives an overview of the project.

**INTRODUCTION** In the panorama of space launchers, Solid rocket motors are today cost effective and reliable propulsion technology for space launch systems. Their domain of use is mainly booster stages for small launchers like Pegasus, Vega, add-on boosters for heavy launchers like Atlas 5, H2, STS or even stage 1 like Ariane 5 and 6

Composite propellants were invented in the USA beginning of the 40s by Parson (GALCIT) [1]. Today all the civilian space launchers converged on the use of a composite solid propellant based on polybutadiene as binder,

ammonium perchlorate AP as oxidizer and aluminium as fuel.

This family of propellant is able to satisfy the requirements of the launcher system:

- ◆ A class of risk 1.3 (no detonation)
- ◆ A burning rate compliant with the required combustion time and with a high filling ratio
- ◆ A low cost of the propellant grain.

However, solid propulsion suffers of a lack of performance versus the liquid couple LOX/Kerosene and of potential environmental and health concerns related to ammonium perchlorate AP. [2-6].

The main way to improve a solid propellant is to replace:

- ◆ The oxidizer by a more energetic one or at least equivalent if "green"
- ◆ The fuel : Aluminium is very energetic and a way to increase significantly the specific impulse could be to use an hydride such as aluminium hydride AlH<sub>3</sub> Alane

Alternative solid propellants based on the green oxidizers ammonium dinitramide, ADN, and ammonium nitrate, AN, are developed in the EU granted project GRAIL (project following the HISP project) ([www.grail-h2020.eu](http://www.grail-h2020.eu)). By using a 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.

Sustainable Development has become a priority on the European agenda. 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].

This paper gives an overview of the project and present current work performed at FOI and TIA, concerning propellant formulation and system analysis.

## TOP REQUIREMENTS FOR A NEW SOLID PROPELLANT FORMULATION

- ◆ A safe Solid Rocket Motor.

The realized motor has to possibly be in the class of risk 1.3 even if one of its raw materials is of a class of risk 1.1 (risk of mass detonation)

Taking into account the cost of the launch pad, of the payload and of the launcher itself this risk cannot be taken. Moreover the cost of the storage will be increased (e.g. safety distances)

- ◆ SRMs have to be able to be stored several years (one or two) before use (worst case: production following on in case of launches stop)
- ◆ A conventional burning rate in the range 7 to 15 mm/s with a possible tuning of the selected formulation

This requirement result of an analysis of launcher specifications: launchers using solid propulsion-strap-on or main boosters- have a diameter in the range 1 to 3.7 meters and combustion time between 45 to 140 s ; for the current Vega and Ariane families the range is 7 to 11 mm/s.

- ◆ A low environmental impact.

Current solid propellants for launchers are based on the oxidizer ammonium Perchlorate, AP (NH<sub>4</sub>ClO<sub>4</sub>). 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:

- Thyroid gland interference (manufacturing process and waste elimination)
- Toxic aerosol (Mesosphere)
- Acid rain (Mesosphere)
- Ozone layer depletion (Stratosphere)
- Greenhouse effect / global warming (Stratosphere).

### Manufacturing process and waste elimination

Ammonium Perchlorate is a major component of solid propellant (annual production around 12,000 tons) AP is soluble in water and may readily contaminate surface and ground waters if released around facilities. Being chemically stable, it is able to persist for decades in typical ground conditions; in California the maximum guide level is of 18mg/litre of drinking water and 16mg/litre in Europe [9].

Elimination of waste appears today manageable (risk for water pollution) with

development of new biological processes (LICORNE by Herakles [10] and another one by ATK) but the risk resulting of an accidental event remains...

Aside from the propellants themselves, all the toxic products used during the manufacturing process have to be under control. In Europe the REACH (Registration, Evaluation and Authorization of Chemicals) regulation is introducing new constraints.

The legislation was proposed under dual reasoning: protection of human health and protection of the environment [11]

### A minimum Flight environmental impact

This point concern the first stage and add-on booster, today it is negligible mainly due to the limited number of flight per year

Note that concerning the ozone layer depletion, launchers using the couple LOX/Kero with a gas generator cycle have also a negative effect (soot ejection)

- ◆ A reasonable cost

The cost of the propellant grain is in the range 25-35% of the total cost of SRMs .For the reference propellant cost of raw materials are around one third of the cost of the grain, the cost of the raw material is around 10% of the total cost of a motor. So, the cost of the raw material may increase a little considering the cost efficiency of solid propellant.

- ◆ Service life

Contrary to NATO specifications, SRMs for Civilian launchers such as VEGA or Ariane booster know a favorable expected life profile and time life from manufacturing to use or disposal (manufacturing then storage and use in Guyana); so the specified range of temperature could be narrow around 27°C (2012 max temperature 37.3°C min 17.8°C) and the storage time limited to one or two years)

## IMPROVED COMPOSITE PROPELLANT AND GREEN ALTERNATIVES TO AP

Modern composite propellants today on launchers in operation or into development are all a combination of the three main ingredients HTPB as binder, AP as oxidizer and aluminium as fuel.

In the past and since 1942 many formulations were explored including different powerful oxydiser (e.g. HNF)

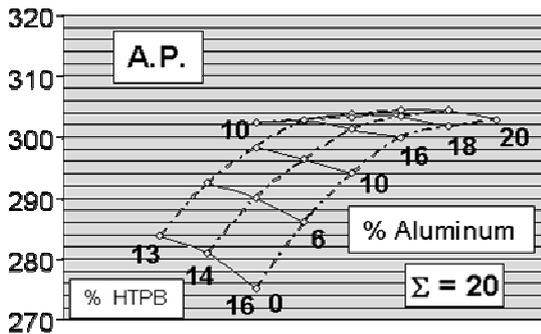


Figure 1. Ideal Vacuum specific impulse  $A_e/A_t=20$  for HTPB/AP/Al propellant [ ]

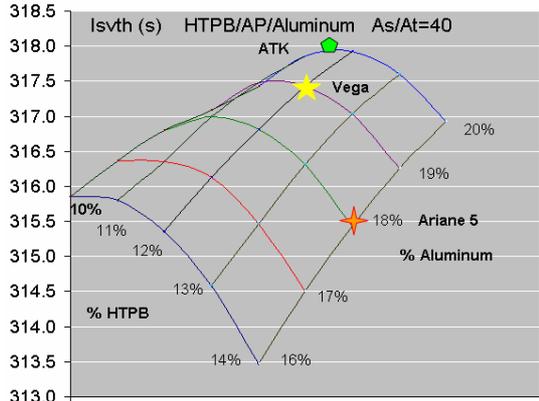


Figure 2 Ideal Vacuum specific impulse  $A_e/A_t=40$  for HTPB/AP/Al propellant [computed with FOI data ]

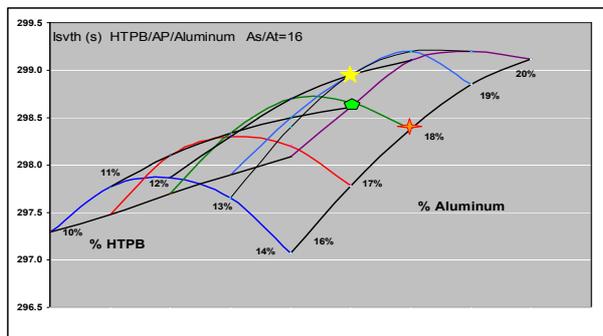


Figure 3 Ideal Vacuum specific impulse  $A_e/A_t=16$  for HTPB/AP/Al propellant [computed with FOI data]

Formulations converged on high solid volumetric loading .A particularity is a low variation zone of the theoretical Isp versus the percentage of aluminium in the range 18-20% (Figure 1), This zone is extended when taking into account the two phase flow losses that have as effect to reduce difference in specific impulse between two propellants with different % of aluminium. Some ATK motors for upper stages (STAR) uses formulation with 20% of Al and 11% of HTPB These two figures (2 and 3) show the influence of the kinetic losses on the choice of the formulation

that could be different if the SRM is a booster or an upper stage.

Developing an alternative to AP is a challenging task.

Currently to obtain a “green” propellant, 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 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. Today it is used in water blend as liquid propellant replacing Hydrazine (ECAPS engines propellant LMP-103S) (wikipedia)

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 [13], 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

### 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, aluminium 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.

The three year project, which is coordinated by FOI, can be seen as a continuation of the EU project HISP ([www.hisp-fp7.eu](http://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](http://www.grail-h2020.eu).

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: 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 aluminium, aluminium hydride, micron sized aluminium, 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 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.

## SYSTEM ANALYSIS

In order to use the propellant on a civilian launcher the propellant must be of hazard class 1.3 (non-detonable) and the burning rate must be tunable in the range of 7 to 15 mm/s, 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 with as main hypothesis that there are no major volume constraints on a civilian launcher.

The Vega launcher was selected as a suitable case for the study. The system study will follow several steps

1. select a domain of formulation and compute the lsv theoretical , density ,etc of propellants
2. With a trajectory computer code find the optimal performance of the launcher in terms of payload into orbit and determine a set of derivatives of payload versus inert mass and practical specific impulse
3. With a solid propulsion model rebuild each SRM that will be loaded with the new propellant
4. Verify the performance with a new computation of trajectory ( if the new propellant is implemented on all the stages )

### Propellant Domain Selection

The consequences of changing propellant on the level of performances of a SRM are multiples.

A basic hypothesis in this project is that the burning rate of the new propellant is the same ( $\alpha$  and  $n$ ); so the same combustion time and mass flow rate law can be achieved .At the end of the project this hypothesis will be reconsidered if needed.

So, performances of formulation will be based on variation of only two parameters: inert mass and effective Specific Impulse

The mass change will result of those of density and secondary of the combustion temperature.

The effective Specific Impulse change will result of those of:

- ◆ ideal Specific Impulse
- ◆ two phase flow losses
- ◆ average  $A_e/A_t$  for a given  $A_e$

This last one depends of the combustion temperature and of the composition of the exhaust gases (chemical erosion linked to water content mainly)

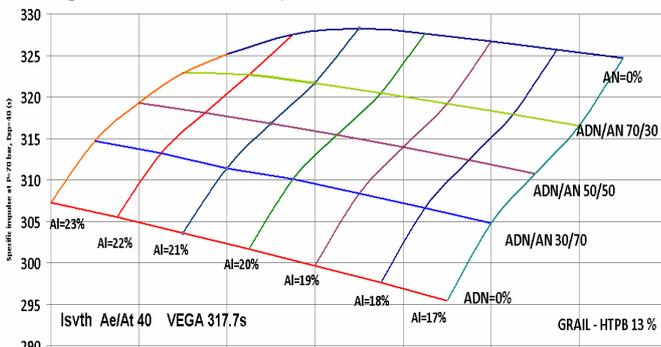
In a first approach, an analysis based on Ideal I Isv is performed. The computations use the values of Table 3

**Table 3. Thermochemical data**

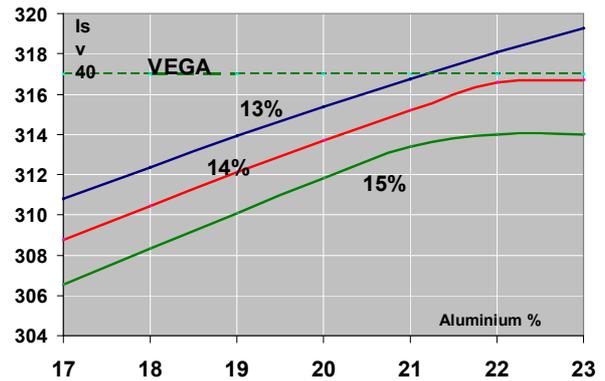
Material	Formula	$\rho$ (g/cm <sup>3</sup> )	$\Delta H_f$ (kJ/mol)
AP	NH <sub>4</sub> ClO <sub>4</sub>	1,95	-295,3
AN	NH <sub>4</sub> NO <sub>3</sub>	1,72	-365,6
ADN	NH <sub>4</sub> N(NO <sub>2</sub> ) <sub>2</sub>	1,81	-134,6
HTPB	C <sub>10</sub> H <sub>15,09</sub> N <sub>0,10</sub> O <sub>0,23</sub>	0,93 <sup>b</sup>	-52,58 <sup>b</sup>
Al	Al	2,70	0

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 high solid loading must be used, the performances in term of specific impulse being sensitive to this parameter. (Figure 5)

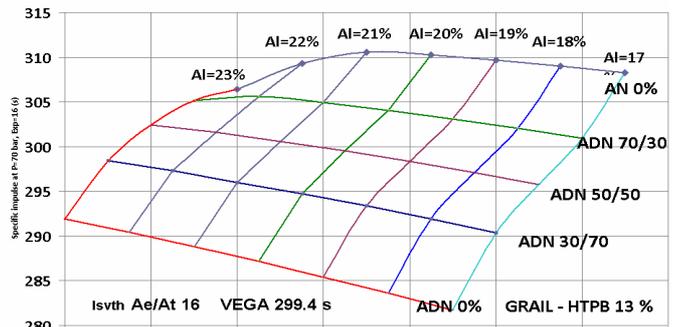
The propellant used in Vega, HTPB 1912, has a volumetric solid loading of 76, 7%. To obtain such a high solid loading, particle fractions of different sizes are used. By using particle sizes similar to what is used in HTPB 1912, it is expected that a similar volumetric solid loadings would be possible 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 4 Ideal Vacuum specific impulse Ae/At=40 for HTPB/AP/AN/Al propellant [computed with FOI data]**



**Figure 5 Ideal ISV Ae/At=40 HTPB/AP/AN/Al propellant: % Binder% effect for 50/50 ADN/AN**



**Figure 6 Ideal Vacuum specific impulse Ae/At=16 for HTPB/AP/Al propellant [computed with FOI data]**

Figures 4 and 6 show the increase of Isv with the aluminum percentage and with the amount of ADN. Contrary to AP propellants for a 50/50ADN/AN oxidizer the optimum of Aluminum % is over 20%.

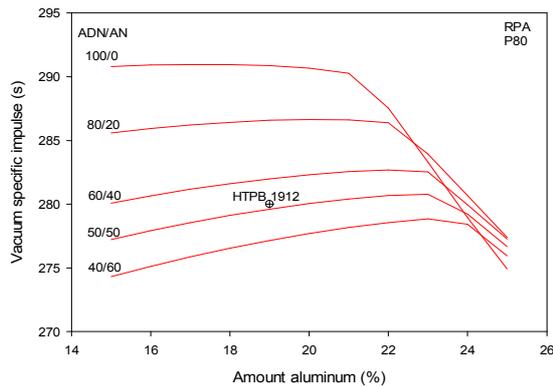
Figure 5 shows the importance to be able to realize propellant with a high Solid loading.

The effective specific impulse as a function of Al content for propellants containing different ADN/AN ratios and 13% HTPB, are shown in figure 7.

The vacuum specific impulse increases with increasing amount of ADN. However, as mentioned previously, addition of AN is probably needed to reduce the propellant explosive sensitivity and the burning rate

In a second step in the calculations of the practical specific impulse, two phase flow losses were taken in to account, which is required for propellants

containing large amounts of aluminium.



**Figure 7. Effective Vacuum specific impulse as a function of Al content. Case P80.  $A_e/A_t$  initial 16**

Assuming that the  $A_e/A_t$  remain unchanged, the effect of two phase flow losses on the  $I_{sp}$  was estimated with two methods ( RPA by FOI [8] and a semi empirical formula by TIA see latter)

The optimum aluminium content at respective ADN/AN ratios are shown (Fig.7) in Table , together with the data for HTPB 1912.

So the interesting domain to select a propellant formulation will have a minimum percentage of binder 13 % mass or less , a limited amount of ADN to be able to be classified in class 1.3 ( and a relatively low burning rate) an enough Aluminium to be competitive with the Vega propellant.

**Table 4. Vacuum specific impulse for HTPB/Al/AP and HTPB/Al/ADN/AN propellants.**

Prop.	Ox.	Al	HTPB	$I_{sp}^{**}$	$I_{sp}^*$	$T_c$	Density
	(%)	%	%	s	s	K	Kg/m <sup>3</sup>
HTPB 1912	69 (AP)	19	12	279.6	280	3550	1808
ADN/AN 100/0	70/0	17	13	290.2	291	3370	1696
ADN/AN 80/20	53,6/13.4	20	13	285.9	287	3335	1701
ADN/AN 60/40	39/26	22	13	282	283	3254	1701
ADN/AN 50/50	32/32	23	13	280.1	281	3208	1701

\*Calculated using RPA. Case: P80.

\*\*Calculated using AFL +semi-empirical formula. Case: P80.

Already by using as low ADN/AN ratio as 50/50, the specific impulse of HTPB 1912 may be reached. However, the density of all HTPB/Al/ADN/AN (Table 4) is substantially lower (1700 kg/m<sup>3</sup>) compared to HTPB 1912 (1800kg/m<sup>3</sup>).

### Application to VEGA Launcher

First the propulsion of the concerned stages have to be modeled and the performance of the launcher with a trajectory optimisation

The propulsion modeling is based on the methodology and the design described in [14] chapters 5, 6 and 7; in a first step a geometrical

design is made considering the state of the art for an AVIO given set of data (propellant mass, combustion pressure, area ratio, propellant characteristics and performance,...), components masses are obtained using polynomial formulas involving geometrical data and operating parameters; for example, tanks are dimensioned taking into account the internal pressure (MEOP) with adjustment coefficients, masses of components are often issued of regression polynomial formulas as in [13]

And so an analysis can be made estimating the influence of a modification (such as the propellant characteristics) -or a new design- on the performance parameters (Dead mass,  $I_s$ ,  $I_{s,vac}$ ,  $A_e$ ,  $t_c$ ) needed for the trajectory computation.

Nevertheless, use of "Image" modeling knows the limitations of resulting of a lack of validation on the effect of some phenomena such for example for solids the internal Insulation ablation versus the characteristics of a new propellant: on this point, the ablation rate is function of the thermal flux at the power 0.78 and the flux depends on the Stanton number. A corrective factor has been introduced to the formula giving the thermal insulation mass issued of [14].

In the calculations aluminium particles have been assumed to be combusted and agglomerate in the same way as in AP based propellants, which may not be the actual case.

Even Computer codes estimating  $I_{sp}$  losses with a separate losses method (e.g. SPP [15]) are using experimental data. For example the Hermesen's Model uses particle diameter size (D43) issued of sampling in the exhaust gases without being able to give any correlation with the aggregate created by the chemistry of the combustion; moreover the data base of validation contain a limited [15] number (11) of motors all using AP and a polybutadiene binder; motor test using AN/ADN propellants with  $I_{sp}$  measurement will be a key point to determine if the two phase flow losses are affected by the chemistry of the combustion.

The code operates with a set of technological data by default when there is a lack of data. In the case of Vega motors, the technologies are known; so the main input are the propellant mass, the combustion time, the maximum pressure, the initial area ratio.

Parameters such as submergence of the nozzle, erosion of the throat area are tuned to obtain geometrical parameters, inert mass breakdown and performances parameters as close as possible of these of the motors

			VEGA P80		SoME Solid Motor Evaluation					
Main Characteristics			Flexseal 6 Degrees		Technologies	Dimensions (m,m2)		Masses [kg]		
Pmax	87	bars	VEGA P80 Propellant			Diameter	3.00	Propellant	87730	
Paverage	59.4	bars	Finocyl GRAIN			Ext L case	9.32	Structure	3147	
SUBMERGE	0.379		nD C-C 2 THROAT			Lemerging no	1.47	Igniter	117	
Tcu	110.0	s	Composite Case			L nozzle	2.36	Struct.		94
dm/dt average	797.5	kg/s	ΦThr.average	0.519		m	Lstage	8.63	Prop.	24
Thrust vaccuum	2188	kN	Φ exit	1.977		m	LHT	10.79	Intern. Ins.	1281
Isv Efficiency	0.943		Σ average	14.5			Exit Area	3.07	Nozzle	2214
Isp vac	279.6	s	Σ initial	15.9			A stage	7.08	Misc.	395
									TVC	344
									Mi	7153
									Mi with EPU	7497
									Mi/Mp	0.085
									M total	95227

Fig.8: Example of a simplified computation of the characteristics of the P80

In the initial performance calculations, AVIO open data has been used. As example the P80: The geometry is shown in Figure 9.

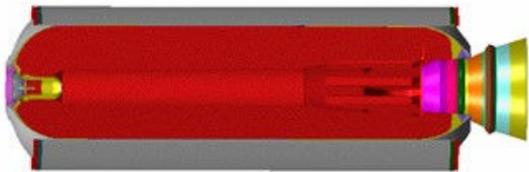


Figure 9. P80 SRM, 1<sup>st</sup> stage of the Vega launcher (credit AVIO).

L: 10.5 m	∅ : 3.0 m
Combustion time: 110 s	
Max Thrust (vacuum): 3015 kN	
Max pressure: 88 bar	
Propellant mass: 87730 kg	
Inert mass: 7330 kg	
Vacuum specific impulse: 280 s	
Nozzle expansion ratio: 16	
Nozzle deflection angle: +/- 6.5°	

With a less dense propellant, it has been considered in the system analysis a stretching the cylindrical part of the P80, to accommodate the same amount of propellant, leading to higher inert mass of the motor. The variation in terms of

payload into orbit is made with the same mass of propellant at lift-off

Using the data of the Vega Users manual and the data given by Avio, a set of data (mass flow rate versus time and characteristics of the stage) was defined and a nominal trajectory was established for the purpose of this study using the trajectory code Perfol (see following figure).

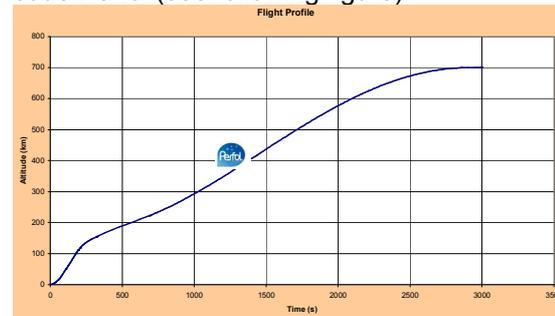


Fig.10: VEGA launcher typical trajectory (polar 700 km circ).

		P80	Z23	Z9
INERT MASS	kg/kg	-0.05	-0.15	-0.8
ISP	kg/s	16.2	10	15.6

A set of derivative coefficient was computed (table 5); are considered only the parameters subject to a variation; for example of an increase of inert mass of 100kg results a loss of payload:

- ◆ of 5kg in the case of P80

◆ of 80kg in the case of Z9  
 To evaluate the best amount of aluminium in a propellant formulation, three ones were selected, each ones contain 13% in mass of binder to be feasible, 19-20-21% of aluminium, and 67% of oxidiser ± 1% shared between AN and ADN. These propellants deliver an Isp in the same range than the current AP ones.

Assuming that new propellants will have the same burning law than the P80 and the nozzle the same erosion, the model of P80 was used to determine the mass (stretched case, lower combustion temperature) and the effective Isp variation of the motor

**Table 6.** Comparison of several propellants mixing AN and ADN.

		P80							
		d	Ae/At	Isvth	Isp	Cd	Water	Alumina	TC
	Formulation			s	s	s/m-1	moles/100g		K
GRAIL19	13/35.5/32.5/19	1.680	14.5	296.6	279.7	0.0006286	0.315	0.352	3106
GRAIL20	13/35/32/20	1.686	14.5	297.7	280.0	0.0006271	0.249	0.371	3140
GRAIL21	13/34.5/31.5/21	1.691	14.5	298.8	280.2	0.0006259	0.179	0.389	3140
Ariane 5	14/68/18	1.767	14.5	295.9	279.5	0.0006354	0.349	0.310	3393
VEGA	12/69/19	1.808	14.5	296.6	279.6	0.0006340	0.413	0.325	3533
Grail Formulation: binder ADN AN A1				Ae/At averag					

**Table 7.** Payload variation function of the % of aluminium (reference Vega propellant).

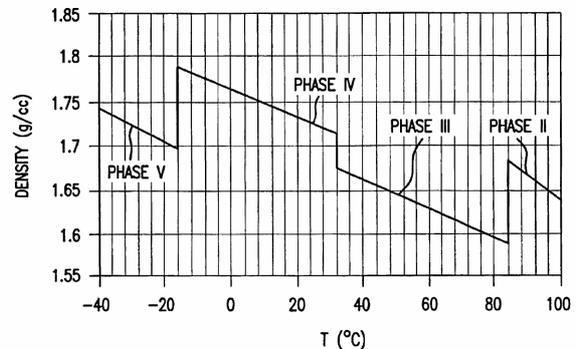
VEGA P80			
Al(%)	19	20	21
Dpayload (Kg)	-9.2	-4.2	-0.4
Disp (s)	0.1	0.4	0.6
Dmi (Kg)	216	213	202
DL (m)	≈0.6		

The table here above shows the results of the model (DMi and DIsv), using the derivatives payload variation is estimated: it appears possible for an amount of ADN limited to around 35% to develop a competitive solid “Green” propellant (over this percentage it will be better; it shows also a small interest to increase the aluminium percentage, nevertheless the limits of the model have to be taken into account (mainly on the internal insulation and two phase flow losses).

- ◆ Demonstration of propellant feasibility  
 To demonstrate the potential feasibility of a new propellant the first important point concerns the safety that implies studies on:
  - ◆ Stability, chemical incompatibilities, ageing
  - ◆ Ignition sensitivity to heat, impact, friction, spark, electrostatic discharge,...
  - ◆ Sensitivity to detonation (e.g. card gap test)

A particularity for AN is the phase change that implies to develop a PSAN (Phase Stabilized

Ammonium Nitrate). A civilian SRM is concerned by the III-IV phase change with possible propellant grain cracks



**Figure 11: AN phase change**

- The second important point is
  - ◆ Burn rate assessment
  - ◆ Study of ballistic modifiers
 To obtain the required burning rate associated to a pressure exponent lower than 0.5

The third important point is to improve the manufacturing cost of ADN and produce an economic and effective PSAN

Ballistic and sensitivity  
 For the replacement of AP propellants a mixture of ADN, AN is required associated to a high solid

loading (see above), the work done by ICT [17] shows that:

- ◆ □partial replacing of ADN by AN leads to a reduction of burning rate ,
- ◆ to a □. Ballistic exponent *increases* with decreasing ADN/AN ratio
- ◆ •Too high  $n$  at desired burning rates (7-15 mm/s)
- ◆ •Low  $n$  only at high amount of AN
- ◆ Propellants with polyester binder show an high pressure deflagration limit (PDL) at high ANcontent

So, Suitable burning rate modifiers have to be found associated or not with another binder than HTPB

Note: GAP/ADN propellant studied in the frame of HISP programme has a burning rate in the range 20-25mm/s at 7MPa with a low pressure exponent □. Requirements are often in contrast to each other,  $\bar{I}_{rb}$  and  $I_{sp}$  require high amounts of ADN  $\bar{I}_{rb}$  and sensitivity require high amounts of AN

The replacement of ammonium perchlorate (AP) by a mixture of ammonium dinitramide (ADN) and ammonium nitrate (AN) in propellant formulations with inert binder is still a challenge.

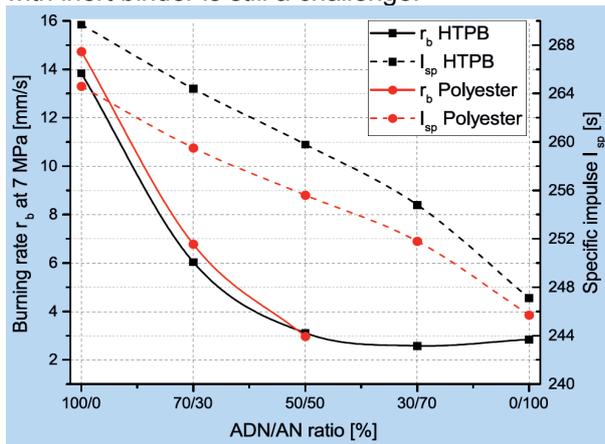


Figure 12. Burning rates (solid lines, left y-axis) and standard  $I_{sp}$  (dashed lines, right y-axis) at 7 MPa as a function of ADN/AN ratio [17]

#### ◆ 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. To obtain a better estimate and to further decrease the cost synthesis improvements are ongoing in GRAIL [18].

FOI in collaboration with EuB, a new synthesis improvement has recently been developed.[18] The new method has the potential to substantially decrease the cost of ADN, increase the purity and decrease the amounts of waste

The current work concerns the optimisation of the one-step synthesis of ADN from FOX-12, reducing the total number of steps from three to two, continues at FOI with the aim to develop a procedure sufficiently efficient to be transferred to EuB for industrialisation. The main focus of this work is to reduce the volumes of solvents required to obtain reproducible results in an economically viable way. Recent work in kilogram scale has shown this method to be very successful and it seems suitable for industrial scale up

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 [19,21]. This method was scaled up in the HISP project enabling prilling 30 kg 200  $\mu$ m 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  $\mu$ m prills with narrower size distribution and reduced impact sensitivity have been produced. The improved prills are shown in Figure . 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 13. Improved 100% dense ADN prills with reduced sensitivity.

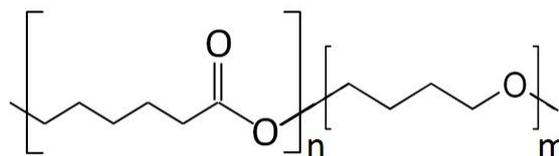
Jet milling has shown to be an effective and fast method to manufacture small ADN particles in the range of 10-20  $\mu\text{m}$  [22]. Even though the particles have an irregular shape they provide good castability in combination with 200  $\mu\text{m}$  prilled ADN. Recently, the powder feeder has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

### 5. FORMULATION

FOI has past experience on propellants based on ADN and the energetic polymer GAP [19]. 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 poly-caprolactone and polytetrahydrofuran (CAPA 7201A). The supplier of respective polymer is shown in Table , and the simplified structure of CAPA is shown in Figure .

**Table 8. Polymers and suppliers.**

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



**Figure 14. Simplified structure of CAPA**

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

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 15. ADN/polymer compatibility testing after 21 days at 75°C.**

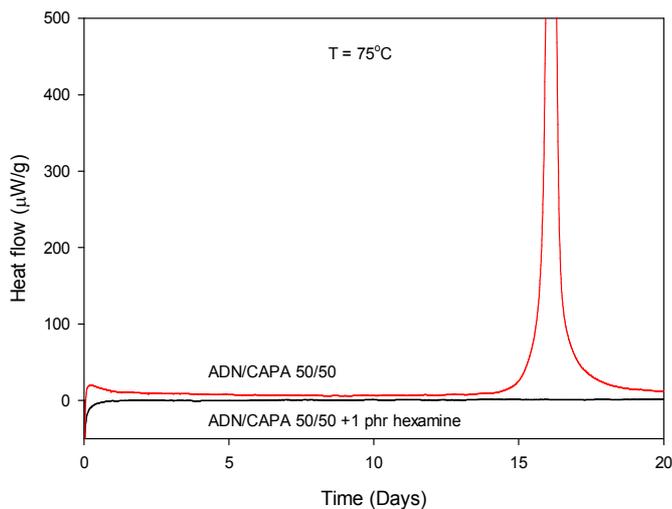


Figure 16. Heat flow from ADN/CAPA 50/50 and influence of hexamine.

## 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 has been assessed. Hexamine has shown to effectively improve the polymer/ADN compatibility.

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