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GRAIL: Green Solid Propellants for Launchers

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Abstract

Ammonium perchlorate (AP) is used in solid propellants for launchers. AP is in many ways an excellent oxidizer, but unfortunately it has a negative impact on the environment and on personal health. With ever increasing environmental concerns green solid propellants are desired. The aim of the EU funded project GRAIL is to determine if it is possible to replace AP with ammonium dinitramide (ADN) and ammonium nitrate (AN). An overview of the GRAIL project is presented as well as results obtained at FOI concerning ADN production improvements, propellant formulation and ballistic properties.

1. Introduction

Space based systems are a natural part of our daily lives for communication, navigation and much more, and the use of satellites is expected to increase in the future and so is the number of space launches. 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 (NH_4ClO_4), and aluminium powder, embedded in a polymer binder. AP has been used since the 1940’s [1] and is in many ways an excellent oxidizer. Unfortunately, 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 agenda. With ever increasing environmental concerns, industries in Europe need to adapt to more restrictive environmental legislation in order to be competitive and to enhance social acceptance. The space industry is in this case no exception as reflected by ESA´s Clean Space Initiative and the Green Propulsion Harmonisation Process [7, 8].

The EU Horizon 2020 research and innovation programme has granted the GRAIL project [9] to investigate if a green, chlorine free, solid propellant can be developed. The results will serve as important input for decision makers when considering development of future European launch systems. Successful development of a high energy green propellant will lead to a breakthrough in solid rocket propulsion technology with respect to performance, competitiveness and environmental impact.

2. The GRAIL project

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 a fertilizer. Propellants based on AN have low performance and low burning rate. Consequently, AN based propellants have mainly been used in low performance applications, such as gas generators. ADN is a new, 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. The conclusion is that neither AN, nor ADN, can replace AP on their own. However, by combining ADN and AN, it seems possible to meet the properties of AP with respect to performance, burning rate, cost and sensitivity.

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The aim of the GRAIL project is thus to develop a green solid propellant based on ADN, AN, aluminium powder and a polymer binder. To obtain high performance, high energy fuels such as aluminium hydride and nano aluminium are also studied in the project. The propellant developed will be compared with state-of-the-art solid propellants with respect to safety, performance and cost, to determine if replacing AP with ADN/AN is a feasible option. The project, which is coordinated by FOI in Sweden, started in the beginning of 2015 and ends in January 2018. The partners in the project are shown in Table 1.

Table 1. 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-aluminium, aluminium hydride, micron-sized aluminium, 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.

3. Performance

In order to use the propellant in a civilian launcher the propellant must be of hazard class 1.3 (non-detonatable) and the burning rate must be tuneable in the range of 7 to 15 mm/s at 7 MPa, with a pressure exponent below 0,5. Furthermore, the mechanical properties, ageing properties, cost and performance must also be acceptable.

Vacuum specific impulse calculations, using the RPA computer code [10] and the Vega P80 stage as a case study, have been performed [11]. In the calculations, two phase flow losses were taken in to account, which is required for propellants containing large amounts of aluminium. The current propellant in P80, HTPB 1912, contains 19% aluminium and 12% HTPB. Not to obtain a higher volumetric solids loading, 13% HTPB is required in an ADN and AN propellant due to the lower densities of these oxidizers. The specific impulse as a function of Al content for propellants containing different ADN/AN ratios and 13% HTPB, is shown in Figure 1. For comparison, the specific impulse for HTPB 1912 is also shown in the figure.

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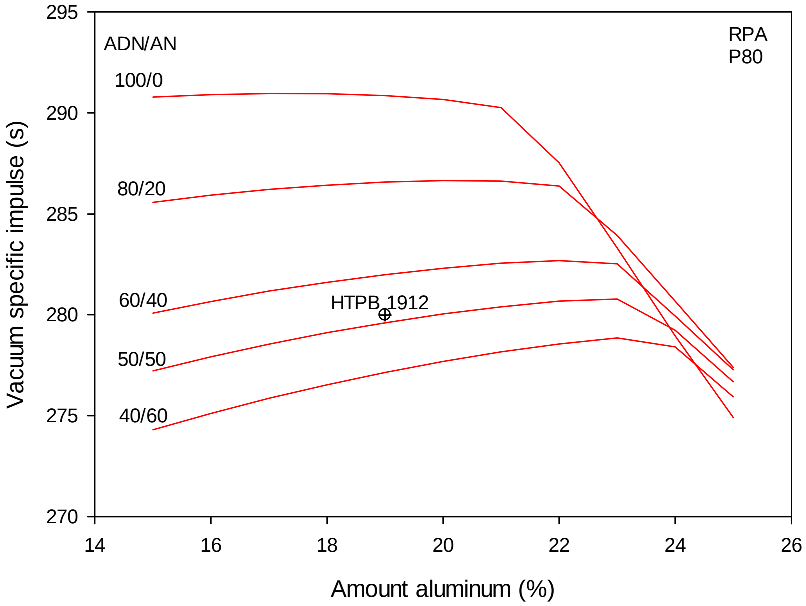

Figure 1. Delivered vacuum specific impulse as a function of Al content. Case Vega P80. ADN/AN propellants contains 13% HTPB.

The vacuum specific impulse increases with increasing amount of ADN. However, to obtain a non-detonatable propellant, addition of AN is needed. The optimum aluminium content at respective ADN/AN ratios are shown in Table 2, together with the data for HTPB 1912.

Table 2. Delivered vacuum specific impulse for HTPB/Al/AP and optimized HTPB/Al/ADN/AN propellants.

Propellant	Oxidizer (%)	Al (%)	HTPB (%)	I_{sp} (s)	T_c (K)	ρ (g/cm^3)
HTPB 1912	69 (AP)	19	12	280	3550	1,81
ADN/AN 100/0	70/0	17	13	291	3395	1,70
ADN/AN 80/20	53,6/13,4	20	13	287	3335	1,70
ADN/AN 60/40	39/26	22	13	283	3254	1,70
ADN/AN 50/50	32/32	23	13	281	3208	1,70

Calculated using RPA. Case Vega P80.

Already by using an ADN/AN ratio as low 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 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. Thus, the propellant, ADN/AN 60/40, with a specific impulse of 283 s seems to be an interesting option.

In the calculations it is assumed that aluminium particles 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 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 the calculations performed it seems possible to meet the system performance needed using an ADN/AN-based propellant containing about 40% ADN.

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4. ADN synthesis

ADN is today produced by EURENCO Bofors in Sweden in small scale according to the scheme shown in Figure 2 [12, 13]. First ammonium sulfamate is nitrated at low temperature to form dinitramidic acid which react with guanylurea sulphate to form guanylurea dinitramide (FOX-12). FOX-12 precipitates from the reaction mixture forming a pure product. FOX-12 is then converted by the use of potassium hydroxide to yield potassium dinitramide (KDN). In a final reaction step, KDN is further reacted with ammonium sulphate to yield ADN.

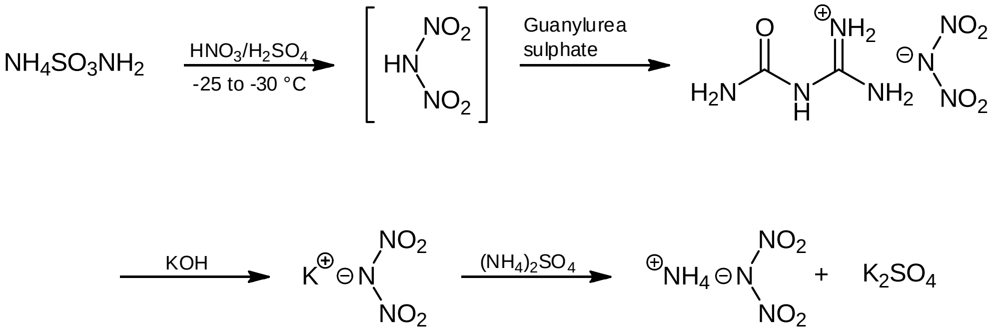

Figure 2. ADN synthesis method.

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 are studied.

A way to convert FOX-12 in one step to ADN has been invented [14, 15]. The method has the potential to substantially decrease the cost of ADN, increase the purity and to decrease the amounts of waste. Successful small scale (~1 kg) laboratory synthesis has been performed, see Figure 3. The method is now further developed and scaled up to 100 kg batch size in cooperation with EURENCO Bofors.

Figure 3. Ion exchange reaction to the left and filtration to the right.

Improvements of the ADN synthesis is also performed in the Rheform project [16]. In this case the focus is to develop a continuous synthesis method. The low temperature nitration seems well suited for continuous synthesis, requiring less cooling power, and thus less energy and investments, compared to a batch process. However, the low temperature also makes the two-phase reaction mixture more viscous and thus poses an engineering challenge.

The future cost of ADN, if produced in large scale, has previously been estimated to be in the range of 20-60 €/kg depending on the assumptions made [17]. To obtain a better estimate, taking the recent advancements into account, a new cost estimate will be performed in the Rheform project at the end of 2017.

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5. ADN particle processing

In order to obtain high solids loading spherical ADN particles, prills, are required. The morphology of the ADN particles received from EURENCO are needle-shaped and thus not suitable for formulation. At FOI spherical ADN particles, prills, are manufactured by spraying molten ADN and collecting the solidified droplets formed [18, 19]. Two different types of spray nozzles have been tested. Atomisation using pressurized nitrogen yields ADN prills with large particle size distribution and particles with a density 1-2% below the theoretical value. By using an ultrasonic spray nozzle, the density increased and the size distribution became narrower, see Table 3, Figure 4 and Figure 5. However, the capacity of the ultrasonic nozzle decreased with time, possibly due to corrosion. After replacing the internal nozzle feed tube with one made of acid proof stainless steel, there has been no problems with the nozzle and the quality of the prills improved, see Table 3 and Figure 4.

Table 3. Properties of prilled ADN manufactured using different spray nozzles.

Method	**Batch**	**Density (g/cm^3)**	**Particle size, d_{50} , (µm)**	**Particle size distribution, *S***
Gas atomization	G130136	1,784	197	1,3
Ultrasonic nozzle	G150060	1,800	166	1,0
Improved ultrasonic nozzle	G170290	1,812	210	0,9

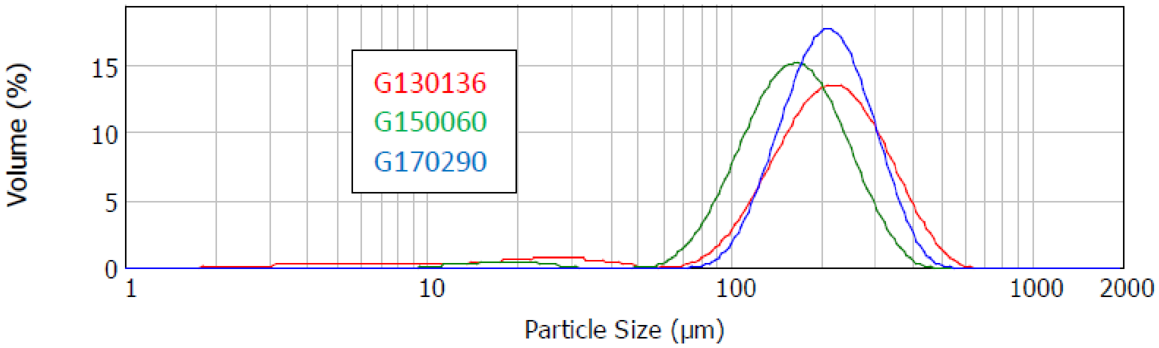

Figure 4. Particle size distribution for three different batches of prilled ADN.

Figure 5. Ultrasonic prilled ADN, batch G150060.

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6. Propellant formulation and ballistic properties

The most commonly used polymer in AP propellants is HTPB. Due to the vast experience with HTPB, it is desired to use it also in ADN propellants. However, ADN is substantially less chemically stable than AP, and the results from compatibility testing between ADN and HTPB are inconclusive. In the presence of oxygen, ADN seem to accelerate the degradation of HTPB, making it more brittle, but the compatibility can substantially be improved by using bases such as hexamine [11]. If this procedure is sufficient is currently examined in a long term test. Apart from different brands of HTPB, a saturated co-polymer based on polycaprolactone and polytetrahydrofuran, CAPA 7201A, Figure 6, is studied. Hexamine has also in this case shown to improve the compatibility with ADN [11].

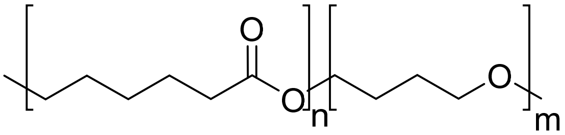

Figure 6. Simplified structure of CAPA.

CAPA has a higher glass transition temperature (Tg), than HTPB. By using DOA the Tg can be decreased substantially as seen in Figure 7.

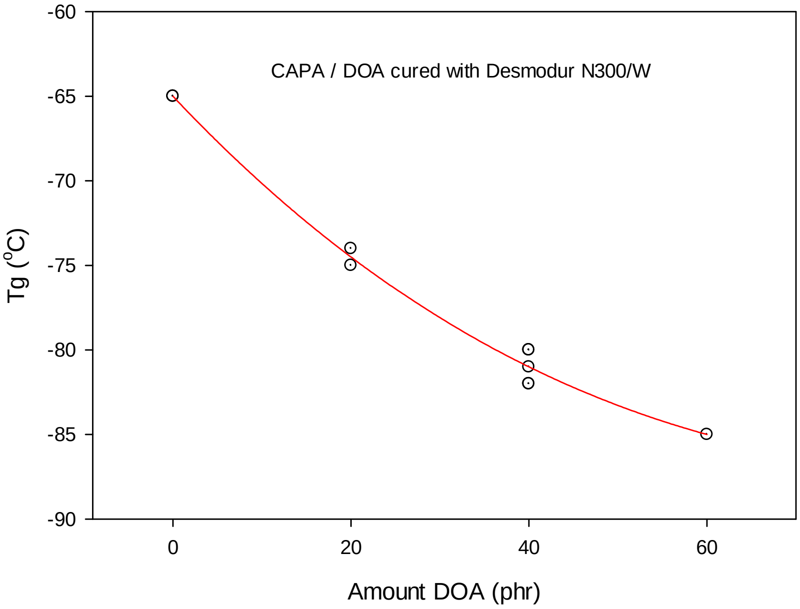

Figure 7. Tg (DSC 10 K/min, inflection point) for CAPA cured with Desmodur N3300/W with different contents of DOA.

In order to obtain a propellant with sufficiently low explosive sensitivity (hazard division 1.3), ADN need to partially be replaced with AN. Three different propellants with different amounts of AN were made. The prilled AN, supplied by Yara (PA165K), was sieved using a 250 µm sieve. The propellant compositions are shown in Table 4. In all cases 40 phr DOA was used in the binder.

Table 4. ADN/AN propellant composition.

Propellant	**ADN/AN ratio**	**CAPA based binder (%)**	**Al (%)**	**ADN coarse, prills (%)**	**ADN fine, jet milled (%)**	**AN coarse, sieved (%)**
G160267	100:0	17	17	54,0	12,0	0
G160246	80:20	17	17	40,8	12,0	13,2
G160245	60:40	17	17	27,6	12,0	26,4

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The burning rate as a function of pressure was measured at room temperature using a strand burner. Nitrogen was used to pressurize the apparatus. Propellant strands, with the dimension: 5×5× ~120 mm, were cut from the cured propellants. Prior to testing, the strands were inhibited to ensure smooth burning. The burning rate was determined using break wires situated 80 mm apart. The results were evaluated using the burning rate equation,

$$r = ap^n$$

where p is the pressure, in MPa, and r is the measured burning rate in mm. The pressure exponent, n, and the burning rate constant, a, were determined by linear regression analysis of the logarithmic data. The results are shown in Figure 8 and Table 5. As expected the burning rate decreases with increasing amount of AN, but unfortunately the pressure exponent increases to unacceptable high values. In order to lower the pressure exponent to an acceptable value (<0,5) the search for suitable burning rate modifiers are currently ongoing in the project.

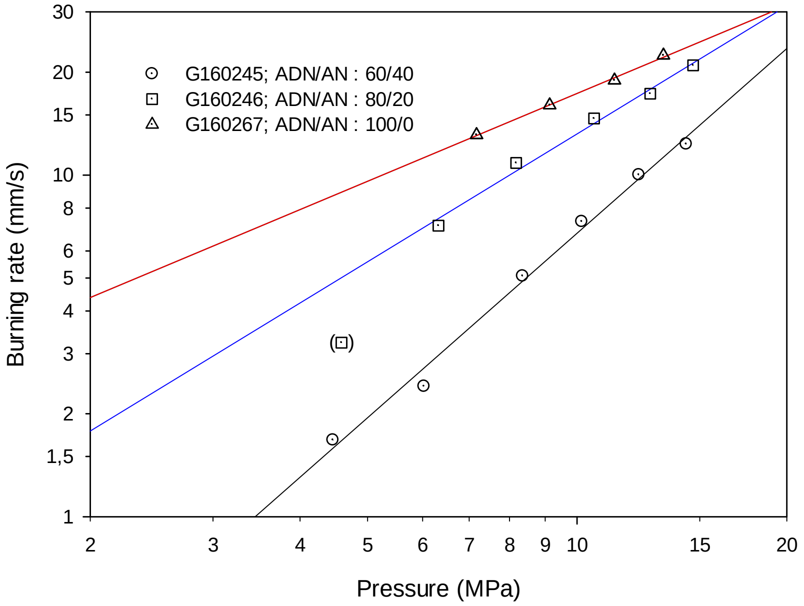

Figure 8. Burning rate as a function of pressure. Result within bracket excluded in the regression analysis.

Table 5. Evaluated burning rate parameters for ADN/AN propellants.

Propellant	**ADN/AN ratio**	***a***	***n***	**r_7 (mm/s) ***	**R^2 ***
G160267	100/0	2,42	0,85	12,7	0,997
G160246	80/20	0,75	1,24	8,4	0,989
G160245	60/40	0,11	1,79	3,6	0,992

* r_7 : burning rate at 7 MPa. R^2 : linear regression correlation coefficient.

As an intermediate solution AP have been used instead of AN to partially replace ADN. Even though not completely green, the propellant will become greener and the performance will increase. Two propellants, with compositions similar to the ADN/AN propellants shown in Table 4, but based on ADN/AP were made. The ratio between ADN/AP was in both cases 60/40. In propellant G160258, 0,5% Fe_2O_3 was added as burning rate modifier. The propellant compositions are shown in Table 6 and results from burning rate measurements are shown in Figure 9 and Table 7. The pressure exponent for ADN/AP 60/40 is high. By using 0,5% Fe_2O_3 the pressure exponent decreased, but not to the level desired. It might however be possible to reduce the pressure exponent further by using larger amounts of Fe_2O_3.

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Table 6. ADN/AP propellant composition.

Propellant	**ADN/AP ratio**	**CAPA based binder (%)**	**Al (%)**	**ADN coarse, prills (%)**	**AP fine, jet milled (%)**	**AP coarse (%)**
G160247 G160257	60/40	17,0	17	39,6	12,4	14
G160258*	60/40	16,5	17	39,6	12,4	14

* Propellant G160258 also contain 0,5% Fe_2O_3.

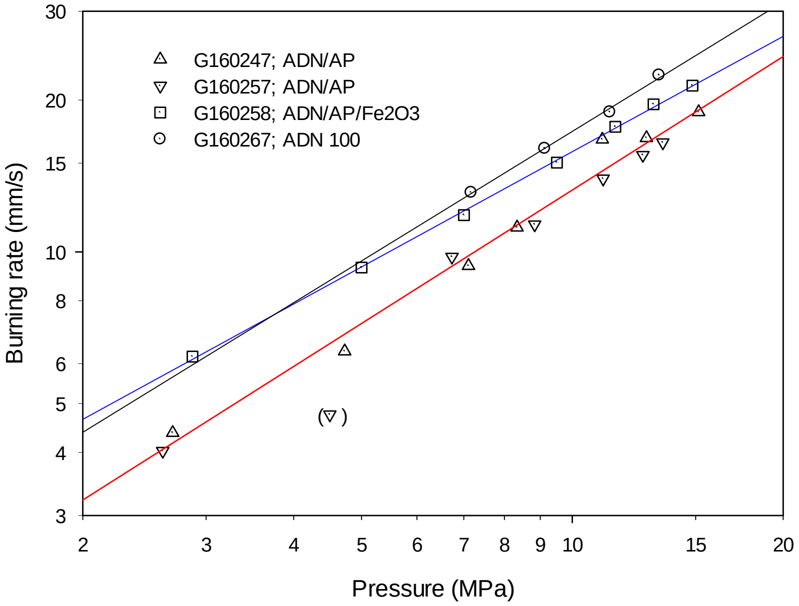

Figure 9. Burning rate as a function of pressure. Result within bracket excluded in the regression analysis.

Table 7. Evaluated burning rate parameters for ADN/AP propellants.

Propellant	**ADN/AP ratio**	***a***	***n***	**r_7 (mm/s) ***	**R^2 ***
G160267	100/0	2,42	0,85	12,7	0,997
G160247 G160257	60/40	1,75	0,88	9,7	0,987
G160258 *	60/40+ Fe_2O_3	2,74	0,76	12,0	0,999

* r_7 : burning rate at 7 MPa. R^2 : linear regression correlation coefficient.

4. Conclusions

The objective of the GRAIL project is to investigate if it is feasible to replace AP with a mixture of ADN and AN in order to develop a green solid propellant. By varying the ratio between ADN and AN, the demands for low sensitivity (hazard division 1.3) and high performance seems possible to meet. Calculations show that performance comparable to current AP based propellants can be obtained using less than 40% ADN. Substantial ADN synthesis improvements have been made and is now further developed and scaled up to 100 kg batch size in cooperation with EURENCO Bofors. Also the method to produce spherical ADN particles, prills, have been improved yielding narrower particle size distribution and 100% dense prills.

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At FOI the polymers HTPB and CAPA are assessed for use in ADN based propellants. It has been shown that the addition of hexamine substantially can improve the ADN–polymer compatibility. If this procedure is sufficient for HTPB is currently under evaluation. The burning rate of propellants based on CAPA and ADN/AN, in different ratios, have been measured. The burning rate decreases with increasing amount of AN, and the pressure exponent increases to unacceptable high values. For this reason, the search for suitable ballistic modifiers is ongoing in the project. As an intermediate *greener* solution, the burning rate of propellants based on ADN/AP 60/40 have been measured. Adding AP decreases the burning rate, but not as much as when using AN. By using 0,5% Fe_2O_3 the burning rate increases and the pressure exponent decreases to 0,76. Adding more Fe_2O_3 might further decrease the exponent. The work in the project has substantially advanced the technological level of green solid propellants but efforts are required to obtain better ballistic properties.

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