BURNING BEHAVIOR OF AN/ADN PROPELLANTS

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Abstract

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 the fuel aluminum powder, embedded in an elastomeric polymer binder matrix. Unfortunately, AP has a negative impact on the environment and on personal health due to ozone depletion, thyroid gland interference and acid rain formation. The paper discusses first results of propellant formulations in which the oxidizer AP is replaced by a mixture of the new green high energy density oxidizer ammonium dinitramide (ADN), in combination with the low cost oxidizer ammonium nitrate (AN). It focuses on the burning behavior and stability issues of aluminized ADN/AN propellants with different oxidizer ratios of ADN and AN embedded in an energetic or inert binder systems.

Parts of the work were performed within the frame of the GRAIL project [1]. Further information about the project can be found in the paper V23 in this conference “GRAIL: A European initiative to develop green solid propellant for launchers” presented by Niklas Wingborg.

Introduction

In 2014, The European Commission, ESA (European Space Agency) and EDA (European Defence Agency) launched a new round of the European Non-Dependence Process with a view to establish a list of actions on critical space technologies for European non-dependence to be implemented in the time frame of 2015-2017 [2]. “Non-dependence” refers to the possibility for Europe to have free, unrestricted access to any required space technology. One item is the development of low cost, solid green propellants and environmental friendly, which will reduce application costs, and provide the same or similar efficiency as current propellant in use respectively; both demands fulfilled together.

The solid propellant formulations, commonly used for space access until today, contain mostly ammonium perchlorate in combination with hydroxyl-terminated polybutadiene (AP/HTPB). One of the main combustion products from AP is hydrogen chloride (HCl), which should be considered critical under pollution aspects, since it contributes to acid rains and causes environmental damage and corrosion around the launch base. The boosters that contain this type of solid propellants, burn propellant in the order of tons per second, releasing large quantities of HCl, which can reach more than 20% of the reaction products at the nozzle. Also aluminum chloride and other intermediate reaction products, which are not more than 2% [3], will cause additional serious problems, when the huge quantities of expelled masses are considered. Furthermore there are some health concerns regarding AP. The perchlorate ion is toxic for human beings and animals, the production of AP is contaminating the groundwater and perchlorate was found in fruits and vegetables [4][5][6][7].

In order to develop a green solid propellant, AP has to be replaced by a chlorine-free oxidizer. Unfortunately, the number of oxidizers for the preparation of green propellants is limited and only two with respect to chemical stability, compatibility and achievable pressure exponent [8] exist , namely ADN and AN. Ammonium dinitramide [ADN, $NH_4N(NO_2)_2$] has a dual advantage over the workhorse oxidizer AP in terms of clean combustion and superior heat of combustion. Due to lower oxygen content it is not possible to replace AP by ADN one-to-one and for high performance propellants ADN has to be combined with an energy-rich binder. Ammonium nitrate [AN, NH_4NO_3] on the other hand is usually not used in high performance propellants due to the low performance and low burning rate. This

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means neither ADN, nor AN are able to replace AP on its own.

Table **1** summarizes and compares some properties of AN and ADN [1] [9].

Table 1. Properties of AN and ADN [1][9]

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

A combination of both suggests that the properties and performance of AN/ADN based propellants are equal or even exceed the properties of AP based propellant and match the requirements for space applications.

Ingredients

ADN was purchased from Eurenco Bofors and prilled (48µm and 212µm) at ICT. Also AN was used in a spherical form. It was produced and phase stabilized with NiO (120µm) and KNO_3 (30µm) at ICT. The amount of aluminum was fixed at 18% by mass. For a better processing, two different particle sizes were used: 4µm (Alcan 400) and 20µm (X81). The selected binders were GAP-diol (Glycidyl azide polymer, Eurenco) and HTPB (R45HTLO, MACH I INC.). The GAP-binder was plasticized with bis-azido-triethylenglycol (BATEG) and cured with Desmodur™ N-100 and Desmodur™ E305 (BayerMaterial Science). For HTPB based formulation, DOA (dioctyl adipate)was used as plasticizer while IPDI (isophorone disocyanate) was the curing agent. The thermodynamic calculations were performed by ICT code with a combustion chamber pressure of 7 MPa and a nozzle expansion ratio of 70:1. The I_{sp} values were computed under the hypothesis of shifting equilibrium and as a function of the total amount of oxidizer and the ADN/AN ratio. The ADN/AN propellants are compared with the standard propellant based on AP, Al and HTPB.

GAP based aluminized ADN/AN Propellant

Thermodynamic calculations show that propellant with an energetic binder outperforms the current state of the art propellant in a wide range of total amount of oxidizer and ADN/AN ratios. As can be seen in Figure 1, GAP based propellants exhibit a kind of plateau for a total amount of oxidizer between 51% and 70%. This allows several solutions to adapt both mechanical and burning characteristics, since it is possible varying the amount of binder and the ADN/AN ratio with a minimal loss of performance.

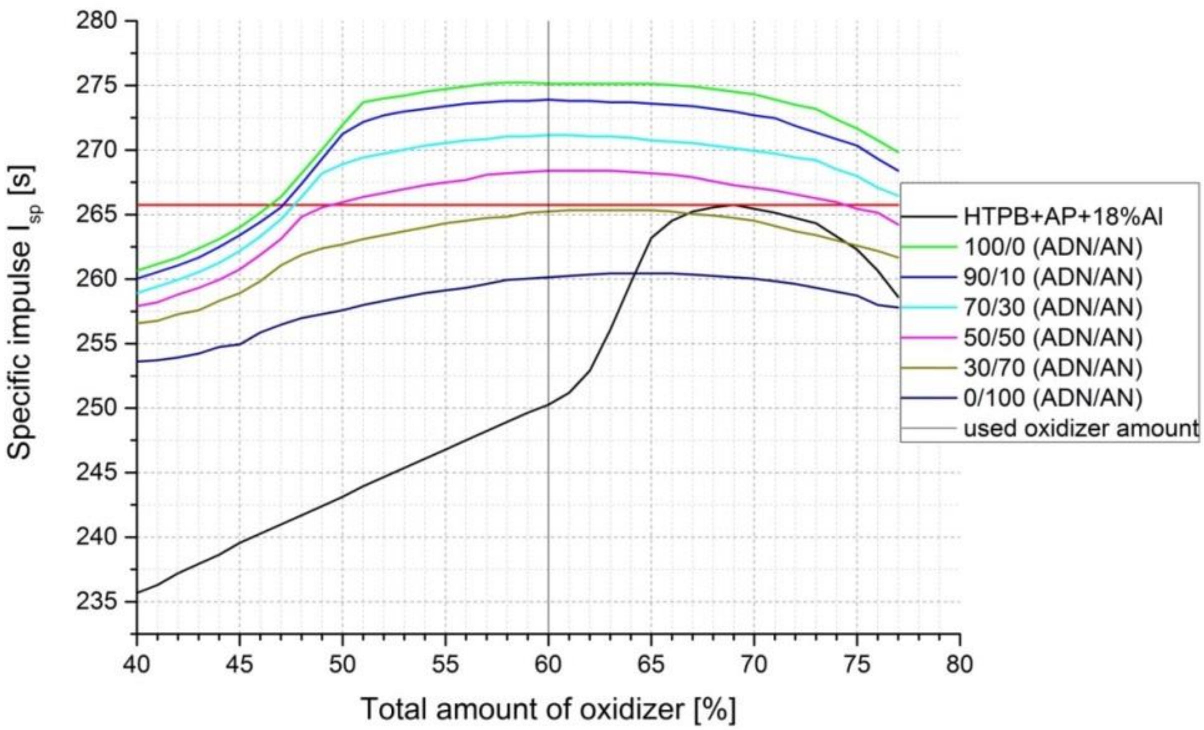

Figure 1. I_{sp} of ADN/AN/GAP/Al propellants with different amount and ratio of oxidizer

HTPB based aluminized ADN/AN Propellant

ADN/HTPB/Al propellant shows the highest theoretical specific impulse, even larger than energetic binder based propellants. Unfortunately, the top value is achieved at an oxidizer content of 72%, which leads to a total filler content of 90%. Such kinds of propellants are hardly to produce and to cast.

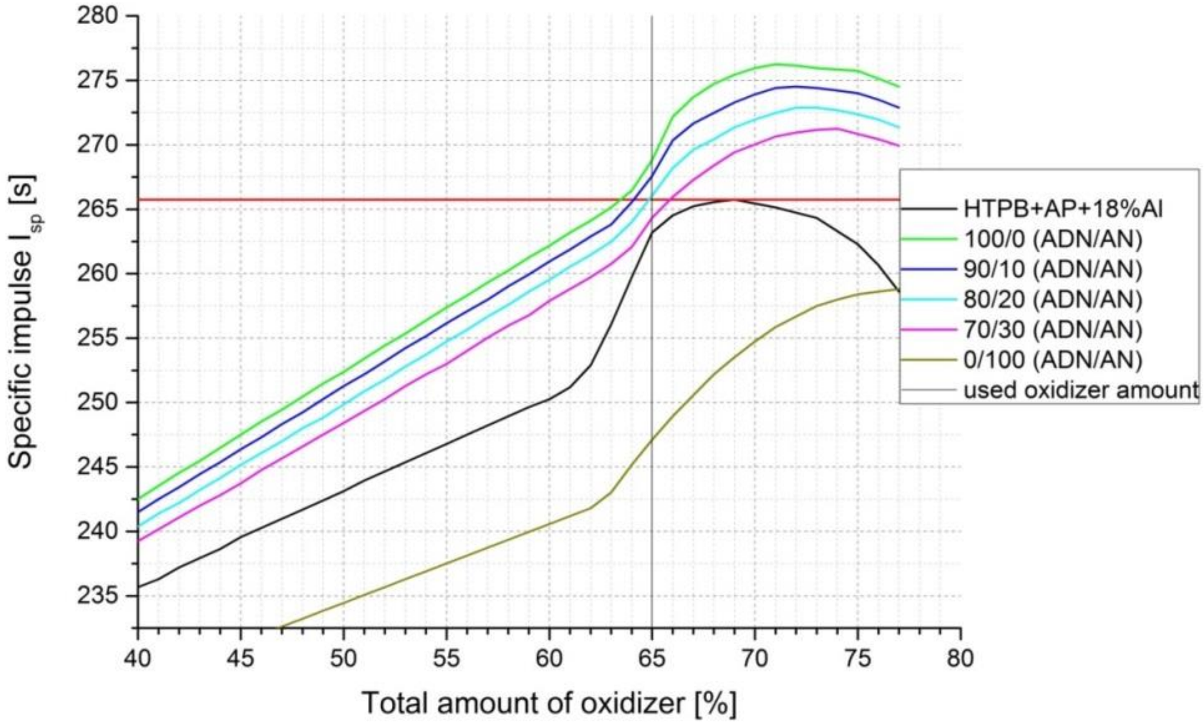

Figure 2. I_{sp} of ADN/AN/HTPB/Al propellants with different amount and ratio of oxidizer

Investigated propellants and burning rate assessment

For the selection of a formulation, it was tried to get as close as possible to the composition of the highest theoretical specific impulse but making sure that the slurries were easily cast-able into a mold. This leads to a different amount of oxidizer for GAP and HTPB based formulations. When a processable amount was found the ADN/AN ratio was varied by keeping constant the total amount of oxidizer and the ratio of coarse/fine particle distribution (70/30). The composition of the propellants is reported in the following tables (Table 2and Table 3).

GAP based aluminized ADN/AN Propellant

Table 2 summarizes the investigated propellant formulation with different ADN/AN ratios based on a GAP binder system.

Table 2. Compositions of GAP based propellants in mass-%

Label	ADAN52	ADAN53	ADAN54	ADAN55	ADAN56	ADAN50
ADN/AN ratio	100/0	90/10	70/30	50/50	30/70	0/100
GAP	16.13	16.13	16.13	16.13	16.13	16.13
E305	0.29	0.29	0.29	0.29	0.29	0.29
N100	2.28	2.28	2.28	2.28	2.28	2.28
BATEG	3.3	3.3	3.3	3.3	3.3	3.3
ADN	60	54	42	30	18	-
PSAN	-	6	18	30	42	60
Al	18	18	18	18	18	18

Increasing amounts of AN decrease the burning rate. For space application the desired burning rate should be in the range of 7 to 15 mm/s at 7 MPa. This can be reached with an ADN/AN ration between 30:70 and ~60:40. The pressure exponent exceeds the 0.5 level and should be adapted by a burning rate modifier.

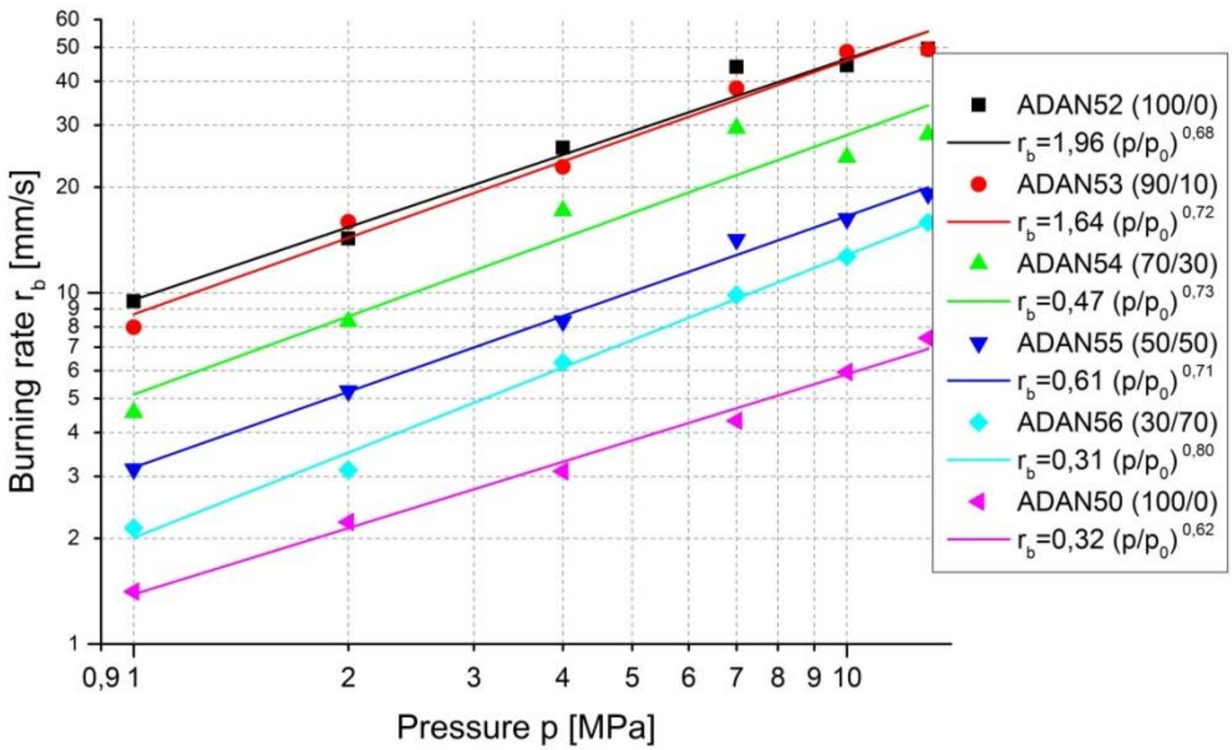

Figure 3. Burning behavior of ADN/AN/GAP/Al/BATEG propellants

HTPB based aluminized ADN/AN Propellant

Table 3 summarizes the investigated propellant formulation with different ADN/AN ratios based on a HTPB binder system.

Table 3. Compositions of HTPB based propellants in mass-%

Label	**ADAN74**	**ADAN75**	**ADAN76**	**ADAN77**	**ADAN78**	**ADAN79**
ADN/AN ratio	100/0	90/10	70/30	50/50	30/70	0/100
HTPB	13.23	13.23	13.23	13.23	13.23	13.23
IPDI	1.22	1.22	1.22	1.22	1.22	1.22
DOA	2.55	2.55	2.55	2.55	2.55	2.55
ADN	65	58.5	45.5	32.5	19.5	-
PSAN	-	6.5	19.5	32.5	45.5	65
Al	18	18	18	18	18	18

The burning behavior of propellant containing an oxidizer content of ADN more or equal of 50% of the total amount of oxidizer is dominated by the burning properties of ADN. The pressure exponent is considerably higher than 0.5 and reaches even values greater than 1. For the desired burning rate an ADN/AN ratio of 90:10 or higher is necessary, but the pressure exponent is completely inacceptable at this oxidizer ratio. On the other side the burning behavior change completely at an excess of AN in the oxidizer mixture and is dominated by the properties of AN. Low pressure exponents are achieved but at a very low burning rate.

The formulation with ADN as oxidizer only (ADAN74, Al/ADN/HTPB binder 18/65/17) can be compared to a similar propellant discussed by De Flon [10]. In this work the formulation Al/ADN/HTPB 15/60/25 showed a pressure exponent of 0.87 and a burning rate of 11.5 mm/s at 6 MPa. Considering the higher solid load of ADAN74 the achieved results ($n=1.01$, $r_b=13.8$ mm/s) can be considered consistent.

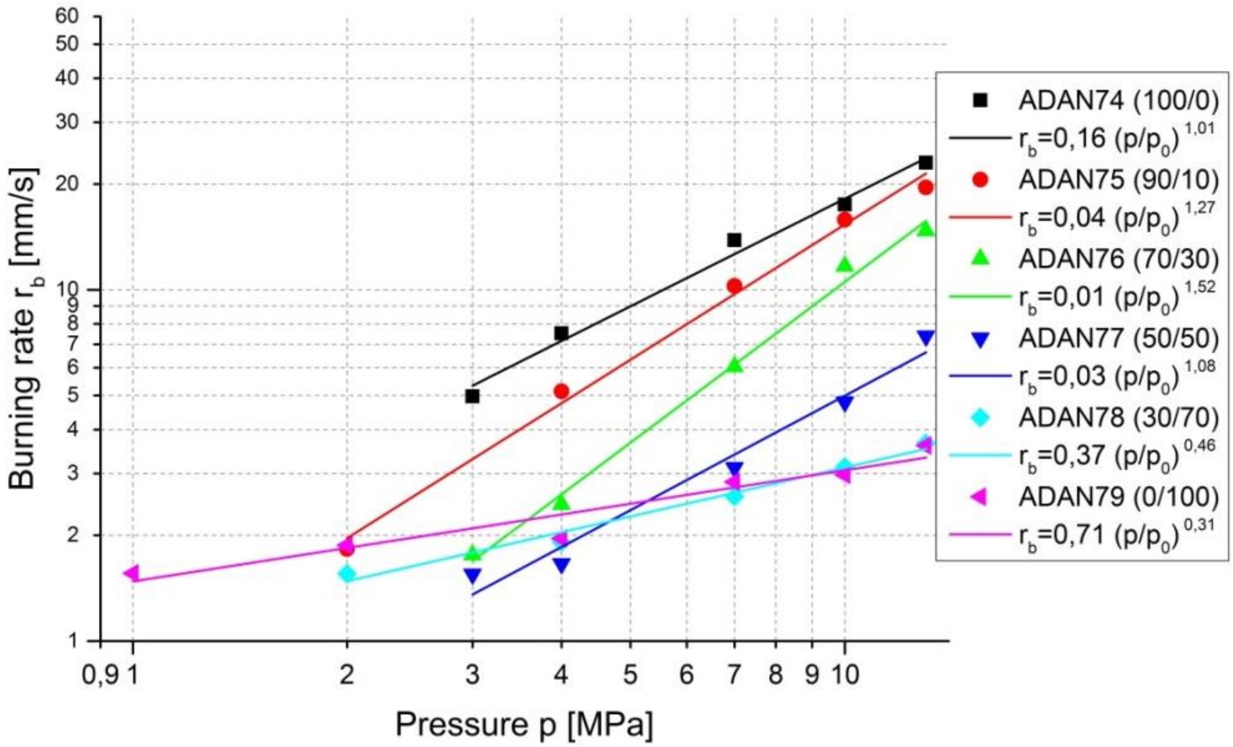

Figure 4. Burning behavior of ADN/AN/HTPB/Al/DOA propellants

Comparison between the investigated propellants

Oxidizer mixtures of ADN and AN allow to adapt the burning rate in a wide range especially in case of the energetic binder GAP (Figure 5). Propellant formulations with GAP binder outperform the specific impulse of an Al/AP/HTPB propellant in a wide range of ADN/AN ratios whereas HTPB formulations need high ADN/AN ratio or high oxidizer content (Figure 5).

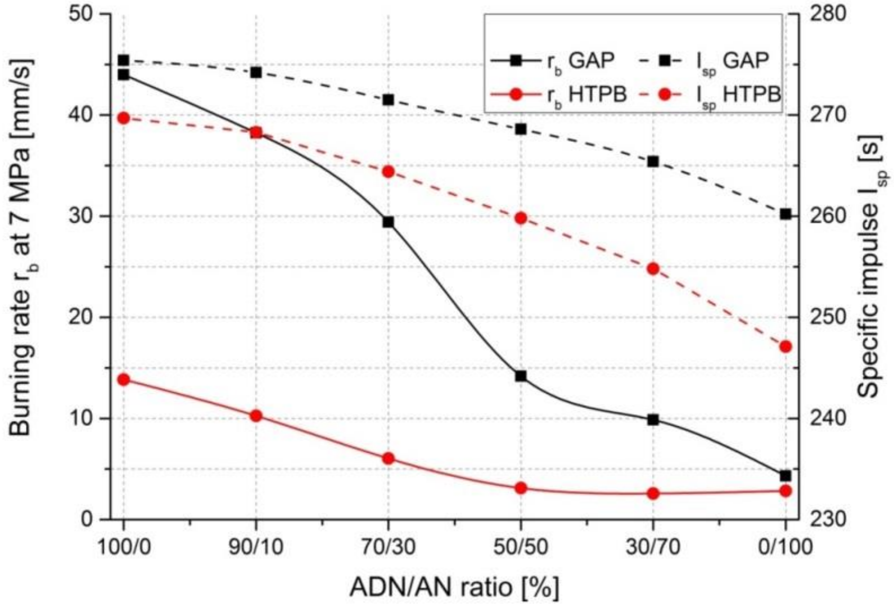

Figure 5. Burning rates (solid lines, left y-axis) and I_{sp} (dashed lines, right y-axis) at 7 MPa as a function of ADN/AN ratio for GAP and HTPB based propellants

The pressure exponent for aluminized ADN/AN propellant are totally different for inert and energetic binder. Whereas propellants with inert binder shows a strong dependence on the ADN/AN ratio, GAP based propellant are barely unaffected (Figure 6).

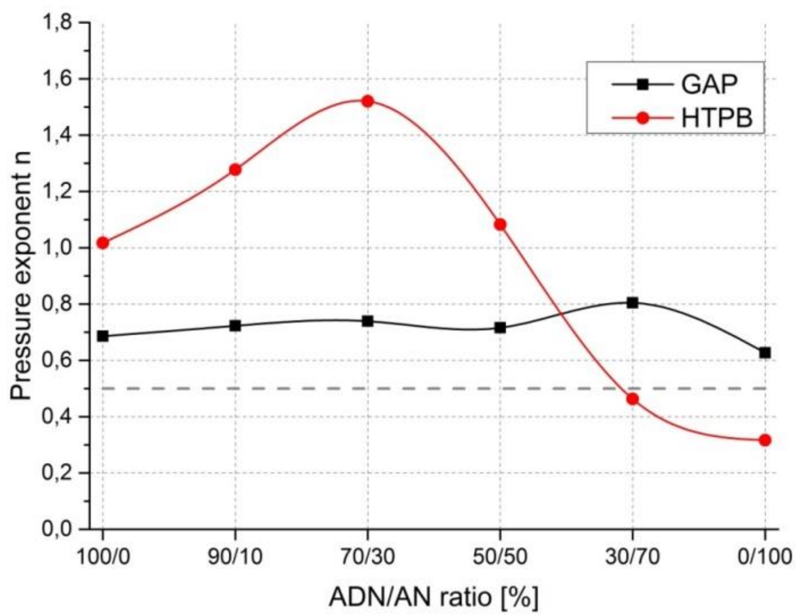

Figure 6. Pressure exponents as a function of ADN/AN ratio

Sensitivity assessment

The effect of different ADN/AN ratios on the friction and impact sensitivity of aluminized ADN/AN propellant is quite low and do not vary much in the presence of ADN. Insensitivity or reduced sensitivity can be obtained only with AN as oxidizer.

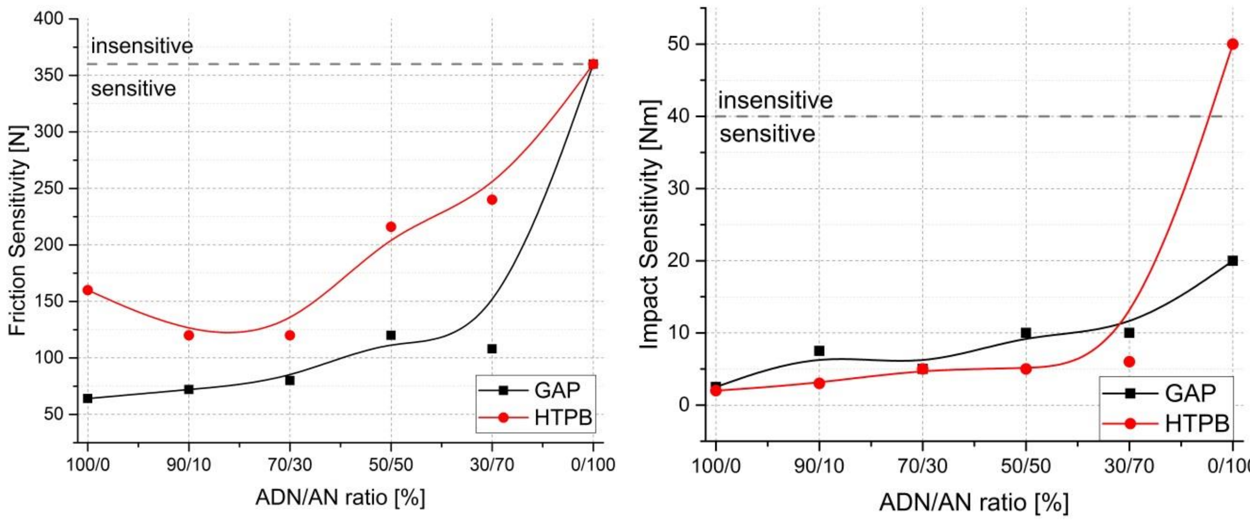

Figure 7 and Figure 8. Friction and impact sensitivity as a function of ADN/AN ratio

Compatibility

Vacuum stability tests of solid mixtures of ADN and PSAN showed no suspicious behavior in the case the phase stabilizer is selected carefully. PSAN stabilized with KNO_3 looks compatible with ADN whereas NiO as phase stabilizer causes a decomposition of ADN.

Table 4. Vacuum stability test (VST) @ 80°C, 279 h, 1:1 mixture

	Prilled ADN	Coated ADN prills
KNO_3-PSAN	√	√
Coated KNO_3-PSAN	√	√
NiO-PSAN	Not compatible	Not compatible

Despite the good results of the VST, a mixture of the oxidizer used in a propellant formulation leads to a decreasing and broadening of the endothermic melting peak of ADN (Figure

10) in DSC measurements. The reason for this behavior might be the formation of an eutectic mixture [11][12].

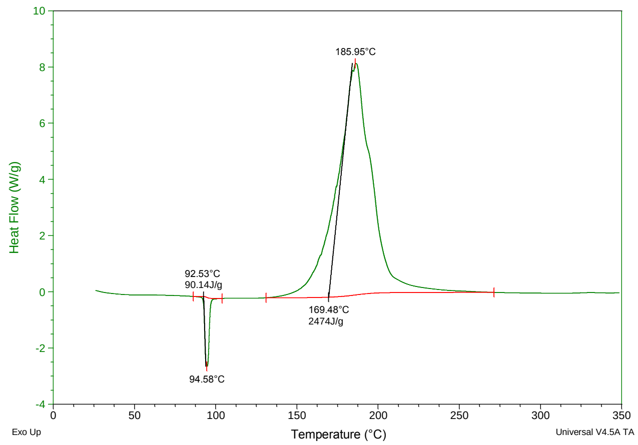

Figure 9. ADN based propellant

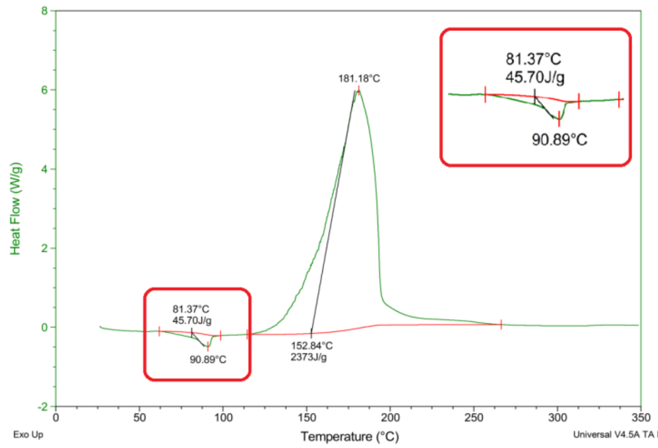

Figure 10. ADN/PSAN propellant

An additional indication for the formation of an eutectic is the increasing peak at around 60°C by repeating the DSC measurement in a temperature range between 2 and 71°C (Figure 11, left diagram). The impact on the stability is not yet investigated but regarding to Nazin et al. [12] the decomposition of ADN is increased which is problematic with regard to propellant stability.

To avoid the formation of an eutectic, ADN and PSAN prills have to be separated from each other. One approach is to apply a coating on the prills. In an ideal situation, this can avoid the peak at 60°C (Figure 11, right diagram). Further investigations have to be carried out to prove this concept.

For HTPB a detailed analysis was made and it is shown graphically in Figure 12. The VST measurements of HTPB at 80°C and in mixture with ADN showed good behaviour, means the assessment is stable for the individual components and for the 1:1 mixture per mass.

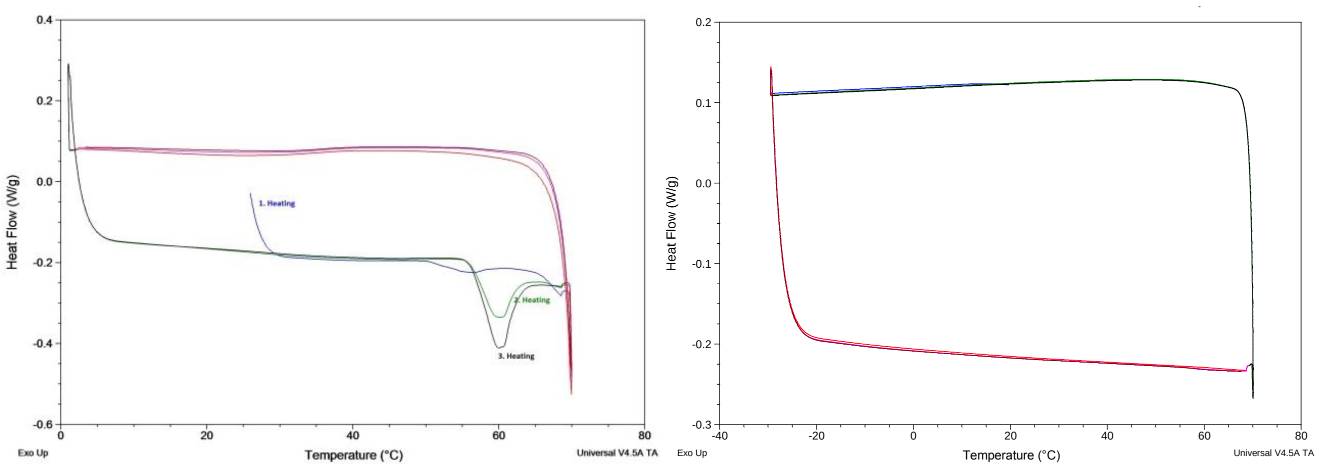

Figure 11. Three runs of DSC measurements of propellant with uncoated oxidizers (left) and coated ADN and coated PSAN (right)

The course of the curve of the reactivity calculated for the condition of 100°C and 40h test time along the actual measurement time at actual 80°C test temperature (red dashed line and right y-axis of 12) reveal a strong reactivity (R) between HTPB and ADN at the beginning of the measurements. The reaction can be interpreted as a strong inter-reaction of HTPB surrounding the ADN particles. This means strong changes in the HTPB shell of the particles and the question arise if the contact between binder and ADN particles is sufficient in terms of good mechanical behaviour. The reactivity limits (for 100°C, 40h) are indicated with two horizontal lines with magenta colour. One can see that the reactivity curve $R_{G,0}$ for 100°C, 40h (dashed red line) is just on the limit. Values of $R_{G,0}$ essentially below –1 ml/g indicate incompatibility, as well as values above +1 ml/g. The two blue lines correspond to the left y-axis. They describe stability with the normalized gas generation $V_{G,0}$ at 80°C (solid blue line) and calculated for 100°C and 40h (dashed blue line). The dashed blue line is always above the stability limit of ≤ 2ml/g for test condition 100°C, 40h. But especially at the begin of testing, high instability is indicated, see dashed blue line. Also the reactivity (dashed red line) is high at the beginning. This is also expressed in Figure 13, which shows the course of gas generation $V_{G,0}$ at 80°C and its time derivative $dV_{G,0}/dt$. In the first 30 to 60 hours, one has a high reactivity between the two components.

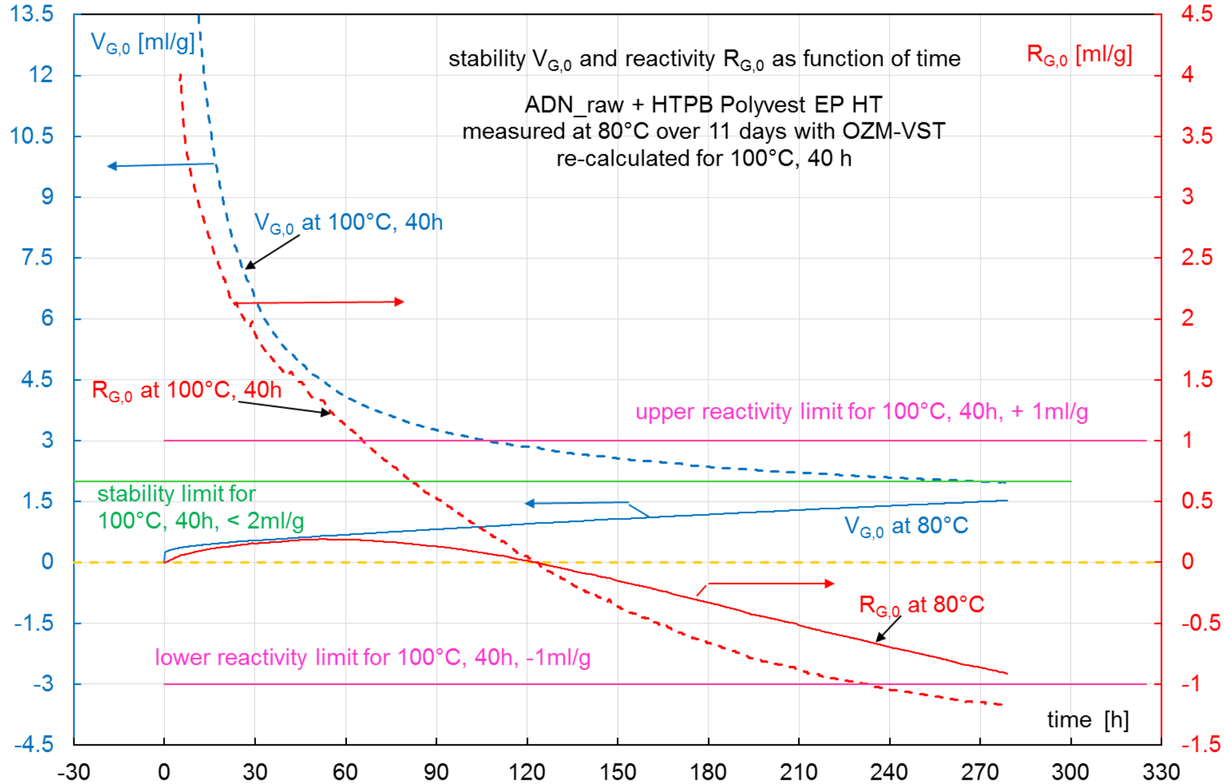

Figure 12. VST measurements of HTPB and ADN for the determination of the stability (blue solid line @80°C; dashed line @ 100°C, 40h) and reactivity (red solid line @ 80°C; red dashed line @ 100°C, 40h)

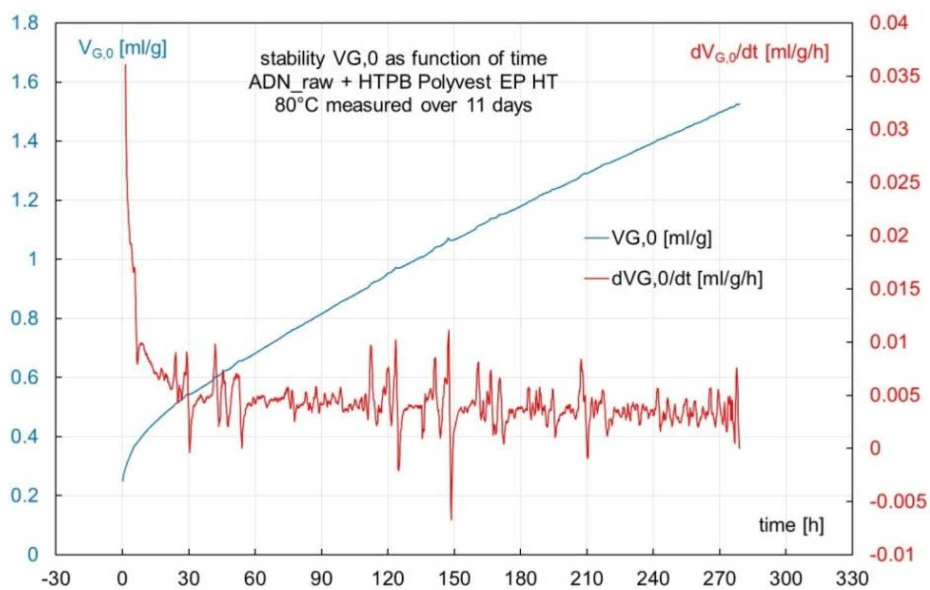

Figure 13. Normalized gas generation $V_{G,0}$ (indicating stability) of the 1:1 mixture (blue solid line) per mass of ADN and HTPB Polyvest at 80°C measured over somewhat more than 11 days and the time derivative of $V_{G,0}$. This indicates a high reactivity between ADN and Polyvest at the beginning means for the 30 to 60 hours.

Conclusions

Varying the ratio of the ADN/AN oxidizer mixture, it is possible to tune the burning rate of aluminized ADN/AN propellants. For GAP based propellants an increasing AN content is decreasing the burning rate and impact sensitivity. In case of the inert binder HTPB, AN is increasing the pressure exponent to completely unacceptable values for formulations with desired burning rate and specific impulse. Requirements are in competition to each other especially in the case of propellant with inert binder. To achieve the right burning rate and wished I_{sp} values, high amounts of ADN are required, whereas the pressure exponent and the sensitivity require high amounts of AN. Compatibility issues between ADN/AN and ADN/binders have to be solved and an ADN compatible inert binder has to be found. The replacement of ammonium perchlorate (AP) by a mixture of ammonium dinitramide (ADN) and ammonium nitrate (AN) in propellant formulations is still a challenge. Upcoming work will show if it is possible to find a formulation which has the desired properties.

Acknowledgement

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