

SMALL SCALE MOTOR TESTS OF ADN/GAP BASED PROPELLANTS

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Abstract

Different ADN/GAP based propellants were evaluated as a potential replacement of the smoky AP based composite propellant and low signature double base propellants. The paper focuses on burning tests of propellants in a combustion chamber. The experimental results of an ADN/GAP, ADN/FOX12/GAP and Al/ADN/GAP propellant were compared with a standard Al/AP/HTPB propellant. In all cases the obtained experimental gravimetric specific impulse of the ADN/GAP based propellants were higher compared to the Al/AP/HTPB propellant. When it comes to the volumetric specific impulse the aluminized propellants exceed the non-metalized. But even in this case the aluminized ADN/GAP propellant outperforms the aluminized AP/HTPB. To achieve class 1.3 ADN was replaced by FOX 12 in parts.

Introduction

For military applications two different kinds of solid rocket propellants are used today. These are NC-based double base (DB) and elastomer-bonded composite propellants. The state-of-the-art composite propellant consists of ammonium perchlorate (AP), aluminum and a polymeric binder (HTPB). AP is an outstanding oxidizer but came under severe criticism over the past years due to environmental and health concerns [1-4]. The perchlorate ion is toxic for human beings and animals and contaminated groundwater. The disposal of AP based propellants, which were taken out of service is costly [5]. During combustion these propellants produce large, visible quantities of hydrochloric acid fumes and aluminium oxide dust, which hinder concealment and facilitate detection by hostile forces. If a low signature propellant is

needed for example for tactical rockets, double base propellants are the only option at time. Beside a couple of advantageous properties like a low pressure exponent, low temperature coefficient and plateau burning there are some disadvantages like low performance, high glass transition temperatures, low mechanical properties and detonable motors (class 1.1). Recently new problems arise by the European chemical directive REACH. Some of the burning rate modifier and plasticizer used in DB propellant are listed and must be replaced [6]. These make it necessary to refine the DB.

Tactical rockets are in need with a low-signature, high-performance composite propellant to replace smoky Al/AP/HTPB propellant and existing detonable double-base propellants. An alternative for DB propellant could be the development of low signature composite propellant. To ensure low signature a chlorine free oxidizer is needed which means that AP must be replaced.

Nowadays, developments focus on environmentally friendly high-performance propellants with low sensitivity, low signature, low vulnerability, temperature-independent combustion behavior, long-term storage stability and the replacement of toxic or ECHA (European Chemical Agency) listed ingredients.

A promising candidate for the replacement of AP is the new green high energy density oxidizer ammonium dinitramide (ADN) [4, 7, 8, 9]. In combination with an energetic binder (e.g. glycidyl azide polymer – GAP) it is possible to formulate smokeless and environmental friendly high energy propellants with a theoretical specific impulse of 267s at a pressure ratio of 70:1 which is equal or even exceeds that of current propellants [14]. Motor tests of an ADN/GAP propellant were published by FOI [10].

In the present paper experimental specific impulses of three different ADN/GAP propellant formulations were determined and compared.

Propellant formulation

Three different ADN/GAP based formulations [11, 12] were selected and compared to a standard Al/AP/HTPB propellant. The aluminized ADN/GAP propellant [13] allowed the direct comparison with the aluminized AP/HTPB reference propellant. The two non-aluminized composite propellants were chosen to compare the

performance of low signature propellants with the standard composite propellant. The ADN/HMX/GAP [14] represents a high performance propellant. The lack of fine ADN at that time made it necessary to use HMX as filler to improve the processing, mechanical properties and energy content. Double base propellants have a lower performance. This enables to replace part of the ADN by a less sensitive energetic material like FOX 12. The aim was to get a propellant with a similar Isp like double base but with a reduced sensitivity to shock. The propellant formulations are summarized in Table 1.

Table 1. Selected propellant formulations, composition in mass-%

Ingredient	Al/AP HTPB	Al/ADN GAP	ADN/HMX GAP	ADN/FOX12 GAP
Binder	9.55	24.0	25.5	25.6
Plasticizer	4.1	---	4.5	4.4
Additives	0.35	---	---	---
AP	68.0	---	--	---
ADN	---	60.0	58.5	50.0
HMX	---		11.5	---
FOX12	---	---	---	20.0
Al	18.0	16.0	---	---

Small scale motor testing

An end burning grain configuration (2.52 inches in diameter) with a neutral burning behaviour was chosen for the test in the combustion chamber. The 2.52 inch motor is shown in Figure 1. The insulated end burning grain (red section in Figure 1) is free to burn on one surface directed to the nozzle.

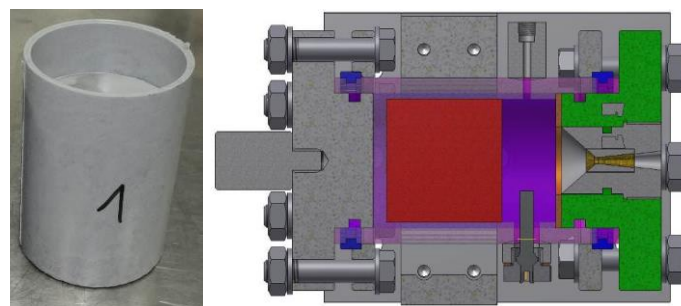


Figure 1. Grain with insulation and axial cross section of the combustion chamber with the nozzle pointing to the right

The pressure courses in the combustion chamber of the aluminized and non-aluminized propellants are presented in Figure 2 and 3. All of the ADN/GAP based propellant grains showed a steady combustion similar to the reference propellant grain based on Al/AP/HTPB.

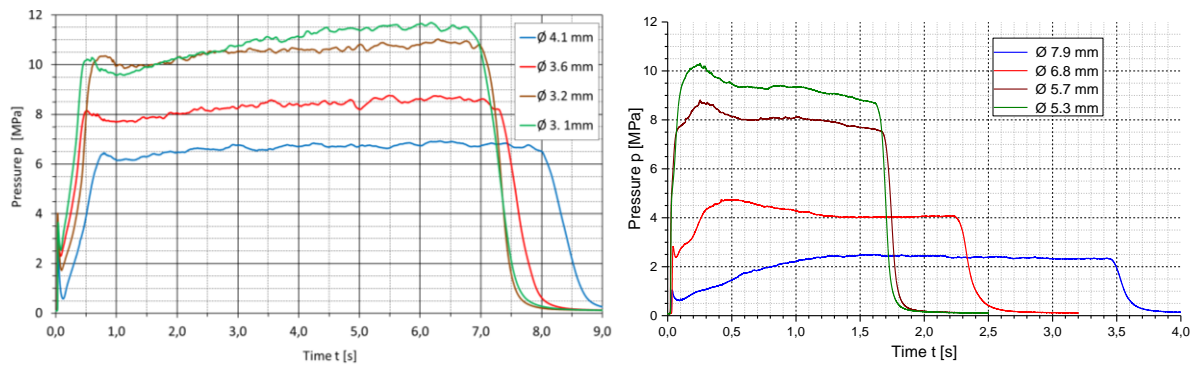


Figure 2. Measured chamber pressures versus time at different nozzle diameters of an Al/AP/HTPB (left) and Al/ADN/GAP (right) propellant

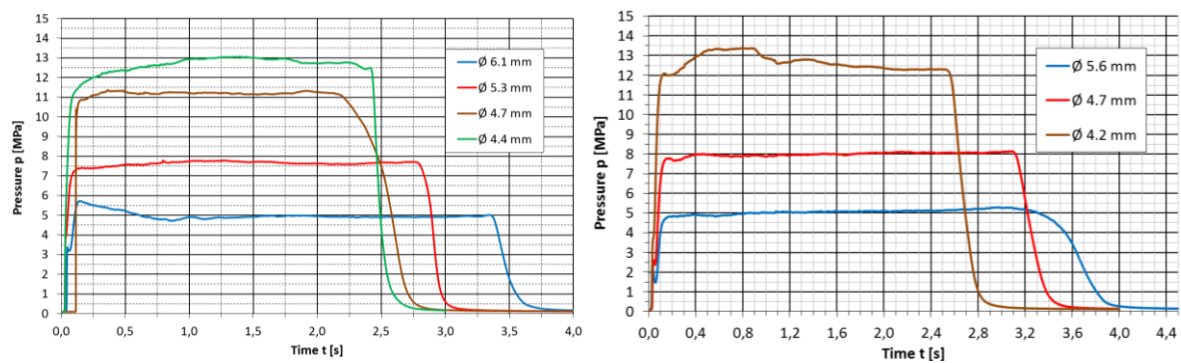


Figure 3. Measured chamber pressures versus time at different nozzle diameters of an ADN/HMX/GAP (left) and ADN/FOX12/GAP (right) propellant

The Al/AP/HTPB propellant produced a lot of smoke during combustion (AGARD class: CC^{*}). The aluminized ADN/GAP propellant has no secondary signature (AGARD class: CA^{*}) and the two non-aluminized propellant showed no visible signature (AGARD class: AA^{*}).

The results of the test firings are summarized in Table 2 and calculated from the pressure and thrust recordings and by use of the ICT Code [16] using equilibrium flow condition.

The densities as well as the chamber temperatures of the non-aluminized propellants are lower as the reference propellant. Thermodynamic calculations showed that the

^{*} The exhaust plume smoke characteristic is estimated by the author

molar number of gases are higher and the mean molecular masses of the gaseous reaction products are lower. Both have a positive effect on I_{sp} and the constant C^* .

In Table 2 the calculated and experimental delivered gravimetric specific impulses (I_{sp}) are compared at a chamber pressure around 7 MPa. Despite the higher theoretical I_{sp} of the metallized propellant, the I_{sp} calculated from experimental data are similar to the non-aluminized. Surprisingly the $I_{sp_{exp}}$ of Al/AP/HTPB is the lowest at this chamber pressure and even lower than the FOX12 containing propellant. The reasons might be the two-phase losses and not complete combustion of the aluminium which is evidenced by the lower C^* efficiency.

Table 2. Results of the propellant tests (blue fonts represents experimental data) for an calculated chamber pressure of 7 MPa (pressure ratio of 70:1)

Propellant	Al/AP HTPB	Al/ADN GAP	ADN/HMX GAP	ADN/FOX12 GAP
Density [g/cm ³]	1.759	1.713	1.584	1.577
Oxygen balance [%]	-33.61	-30.23	-26.17	-29.71
Chamber temperature T_c [K]	3455	3518	2765	2458
Total molar number [mol/kg]	37.6	39.9	45.6	46.8
Mean mol. mass of gas [g/mol]	29.2	27.0	21.9	21.4
Chamber pressure $p_{theor.}$ [MPa]	7	7	7	7
Chamber pressure p_{exp} [MPa]	8.2	7.9	7.6	7.9
Burning rate r_{exp} [mm/s]	8.2	24.1	21.1	19.0
$I_{sp_{ICT\ Code}}$ [Ns/kg]	2600	2698	2462	2335
$I_{sp_{exp}}$ [Ns/kg]	2070	2247	2237	2099
$I_{sp_{exp}}/I_{sp_{ICT\ Code}}$ [%]	80	83	91	90
Vol. $I_{sp_{exp}}$ [Ns/dm ³]	3632	3840	3546	3305
$c^*_{ICT\ Code}$ [m/s]	1523	1596	1561	1486
c^*_{exp} [m/s]	1231	1346	1426	1341
η_{C^*} (c^* efficiency)	0.81	0.84	0.91	0.90

Figure 4 and 5 compared the experimental investigated specific impulses. In the case of the gravimetric specific impulses the ADN/HMX/GAP propellant outperforms the

Al/AP/HTPB propellant in the entire pressure range. Even ADN/FOX12/GAP propellant with the lower performance beats the Al/AP/HTPB in the lower pressure range.

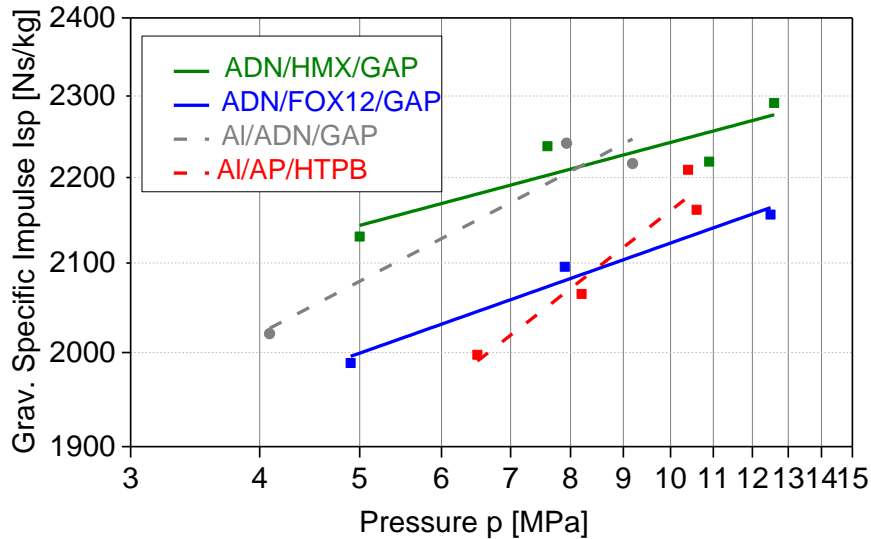


Figure 4. Experimental determined gravimetric specific impulses at different pressures

When one considers the volumetric specific impulses the aluminized propellants are the winner, as usual. But up to 10 MPa the Al/ADN/GAP propellant performed better as the Al/AP/HTPB propellant.

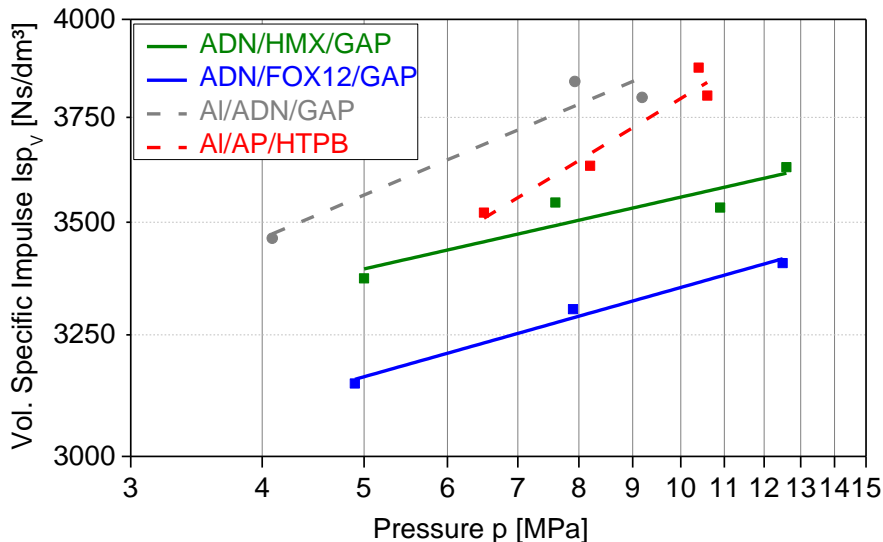


Figure 5. Volumetric specific impulses at different pressures calculated from experimental gravimetric Isp and the density of the propellants

The burning rates of the ADN/GAP propellants are at least double of the AP/HTPB one. Experimental determined pressure exponents from the test in the combustion

chamber are in the most cases lower compared to Crawford measurements (Figure 6).

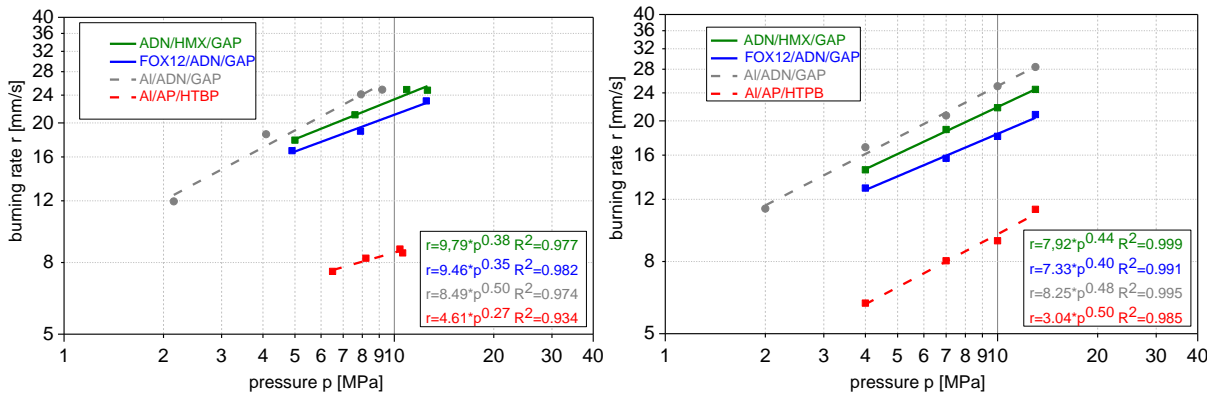


Figure 6. Burning rates at different pressures in the burning chamber (left) and Crawford bomb (right)

For an application the ability of the propellant to propagate a detonation is of importance. For a propellant class 1.3 or better is a fundamental objective. The gap test with 21 mm in charge diameter (ICT small scale gap test) was performed to determine the possible class. FOX12 reduced the sensitivity in the ADN/GAP formulations and this is most probably classified as 1.3. In the case of the other ADN/GAP based propellants without FOX12 it has not yet been finally clarified if they are class 1.3. With ICT 21mm gap test some uncertainties due to the calibration are still of concern. Maybe a larger diameter has to be taken also.

Table 3. Results of the 21mm gap test (ICT standard)

	Al/AP HTPB	Al/ADN GAP	ADN/HMX GAP	ADN/FOX12 GAP
PMMA [mm]	0	4	4	1
Initiation pressure [kbar]	~83	~62	~62	~77
Class	> 1.3	Probable 1.3*	Probable 1.3*	1.3

*not clear. A 50mm gap test is probable necessary

The ADN/GAP propellants are sensitive against friction (70-160N) and some formulations are very sensitive to impact (2-5 Nm) [15]. In comparison to the widespread Al/AP/HTPB and DB propellant the sensitivities are in similar order.

Table 4. Friction and impact sensitivities of different propellants

	Al/AP HTPB	Al/ADN GAP	ADN/HMX GAP	ADN/FOX12 GAP
Friction sensitivity [N]	120	144	72	108
Impact sensitivity [Nm]	6	5	3	6

Double base: FS ~120N, IS ~5Nm; Al/AP/HTPB: FS 60-120N, IS 5-8Nm; AP/HTPB FS 30-120N, IS 3-4Nm [15]

Conclusion

The experimental investigations in the combustion chamber showed that ADN/GAP based propellants have the potential to act as a high energy and low signature propellant in future application. They can replace the smoky high performance Al/AP/HTPB composite propellant to avoid the AP which has been under increased criticism in the last few years. The lack of alternatives for the low signature double base propellants for tactical rockets might be another area of application. In combination with less sensitive energetic materials like FOX 12 it is possible to develop low signature composite propellants with similar specific impulse but lower sensitivity.

Acknowledgment

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Abbreviations

ADN	ammonium dinitramide
Al	aluminum
AP	ammonium perchlorate
c*	characteristic velocity
exp.	experimental
GAP	glycidyl azide polymer
FOX12	guanylurea dinitramide, GUDN
FS	friction sensitivity
HMX	cyclotetramethylene tetranitramine, octogene
HTPB	hydroxyl terminated polybutadiene
ICT Code	thermodynamic code from Fraunhofer ICT
IS	impact sensitivity
Isp	specific impulse
NC	nitrocellulose
Vol. Isp	volumetric specific impulse
n	pressure exponent
r	burning rate
T _c	chamber temperature
wt	weight percentage
η_{c^*}	C* efficiency
\varnothing	diameter

References

- [1] A. M. Popescu, J. R. Collins: *Perchlorate Contamination and Health Issues*, Nova science publisher, New Jersey, 2011.
- [2] K. Sellers, K. Weeks, W.R. Alsop, S.R. Clough, M. Hoyt, B. Pugh, J. Robb: *Perchlorate: Environmental Problems and Solutions*, CRC Press, 2006.
- [3] B. Gu, J.D. Coates: *Perchlorate – Environmental Occurrence and Treatment*, Springer, New York, 2006.
- [4] Eurenco: Dinitramide News, October 2004. Available from https://uppsagd.files.wordpress.com/2012/03/ammoniumdinitramide_news_oct_2004_eurenco.pdf (last accessed on March 30, 2015)
- [5] C. Marraud, A. Schyns, A. Mano: Advanced biological treatment for solid propulsion; *10th International Symposium on Special Topics in Chemical Propulsion & Energetic Materials (10-ISICP)*, 2-6 June 2014, Poitiers, France.
- [6] J. Fleming, S. Bullock, M. Sloan: The REACH regulation and implication for a rocket motor manufacturer; *10th International Symposium on Special Topics in Chemical Propulsion & Energetic Materials (10-ISICP)*, 2-6 June 2014, Poitiers, France.
- [7] M.Y. Nagamachi, J.I.S. Oliveira, A.M. Kawamoto, R.L. Dutra: ADN – The new oxidizer around the corner for an environmental friendly smokeless propellant, *Journal of Aerospace Technology and Management*, 1 (2009), 153-160.
- [8] A. Larsson, N. Wingborg: Green Propellants Based on Ammonium Dinitramide (ADN), *Advances in Spacecraft Technologies*, Dr. J. Hall (Ed.), InTech, 2011, 139-156.
- [9] G. Da Silva, S.C. Rufino, K. Iha: Green Propellants: Oxidizer, *Journal of Aerospace Technology and Management*, 2013, 5.2.

- [10] N. Wingborg, S. Andreasson, J. de Flon, M. Johnsson, M. Liljedahl, C. Oscarsson, Å. Petterssons, M. Wanhatalo: Development of ADN-based Minimum Smoke Propellants, *AIAA Paper 2010-6586*.
- [11] V. Gettwert, A. Franzin, M. A. Bohn, L. T. DeLuca, T. Heintz, V. Weiser: ADN/GAP Composite Propellants with and without Metallic Fuels; *10th International Symposium on Special Topics in Chemical Propulsion & Energetic Materials (10-ISICP)*, 2-6 June 2014, Poitiers, France.
- [12] L. T. DeLuca, I. Palmucci, A. Franzin, V. Weiser, V. Gettwert, N. Wingborg, and M. Sjöblom: New Energetic Ingredients for Solid Rocket Propulsion, *9th International High Energy Materials Conference and Exhibit (HEMCE)*; February 13-15, 2014; Thiruvananthapuram, Kerala, India
- [13] Gettwert, V.; Fischer, S.; Menke, K.: „Aluminized ADN/GAP Propellants – Formulation and Properties, Proceedings: *44th International Annual Conference of Fraunhofer ICT “Energetic Materials” – Characterisation and Modeling of Ignition Process, Reaction Behavior and Performance*, June 25 – 28, 2013, Karlsruhe, Germany, P57.
- [14] K. Menke, T. Heintz, W. Schweikert, T. Keicher, H. Krause: Formulation and Properties of ADN/GAP Propellants, *Propellants Explos. Pyrotech.* **34** (2009), 218-230.
- [15] E. Landsem, T.L. Jensen, T.E. Kristensen, F.K. Hansen, T. Benneche, E. Unneberg: Isocyanate-Free and Dual Curing of Smokeless Composite Rocket Propellants, *Propellants Explos. Pyrotech.*, **38** (2013), 75-86.
- [16] F. Volk, H. Bathelt, User's Manual for the ICT-Thermodynamic Code, Volume 1, ICT-Bericht 14/88, T/RF 11/I 0001/I 1100, Pfinztal, Germany, 1988.