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Performance of ADN/GAP Propellants Compared to Al/AP/HTPB

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Abstract

ADN/GAP propellants with or without metallic fuels are most likely candidates for a “green” alternative to AP/HTPB solid rocket propellants. These propellants are interesting not only in terms of environmental friendliness but also to overcome the intrinsic performance limitations of AP/HTPB. The paper focuses on burning tests of propellants in small scale motor testing. Different ADN/GAP based propellants were evaluated as a potential replacement of the smoky AP based composite propellants and low signature double base propellants. 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 propellant exceeds the non-metalized ones. 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. Basic investigations of the stability and prediction of the in-service time period show good opportunity for a future application.

Key words: composite propellants, small scale motor tests, specific impulse, ADN, GAP, FOX12, gap tests, stability

Introduction

Improvements in performance and signature, environmental considerations, and the reduction of the risks posed to service personnel call for the development of new composite propellants for tactical rocket motors. 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. Modern-day high-performance composite propellants generally consist of ammonium perchlorate, aluminium and a polyurethane binder. 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. Furthermore ammonium perchlorate and hydrochloric acid fumes have a negative impact in the environment and pose a health hazard to service personnel. 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. 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. For low-signature composite propellants AP must be replaces by a chlorine-free oxidizing agent. Energetic eco-friendly oxidizer, ammonium dinitramide (ADN), has entered the domain of advanced propellant systems [4, 7, 8, 9]. ADN has a dual advantage over the workhorse oxidizer of modern composite propellants, ammonium perchlorate (AP), in terms of clean combustion and superior heat of formation, resulting in environmental friendly, low-signature propellants with increased performance levels. Due to its lower oxygen balance of +25.8% instead of +34.04% of AP, an energetic binder like glycidyl azide polymer (GAP) is needed to compensate this drawback. In combination with an energy-rich binder, it is possible to formulate propellants, whose theoretical specific impulse (264s at a pressure ratio of 70:1) equals 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, compositions 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	---
FOX	---	---	---	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.

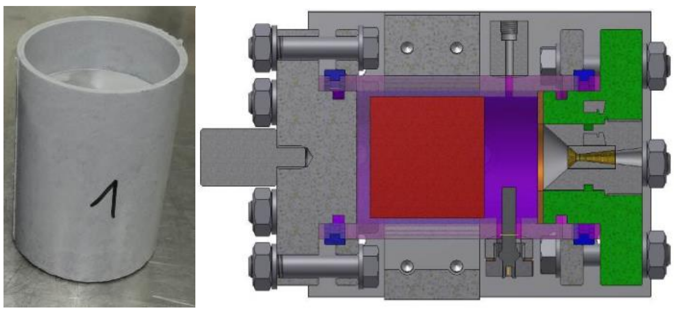

Figure 1. Grain with insulation and axial cross section of the combustion chamber with the nozzle pointing to the right.

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.

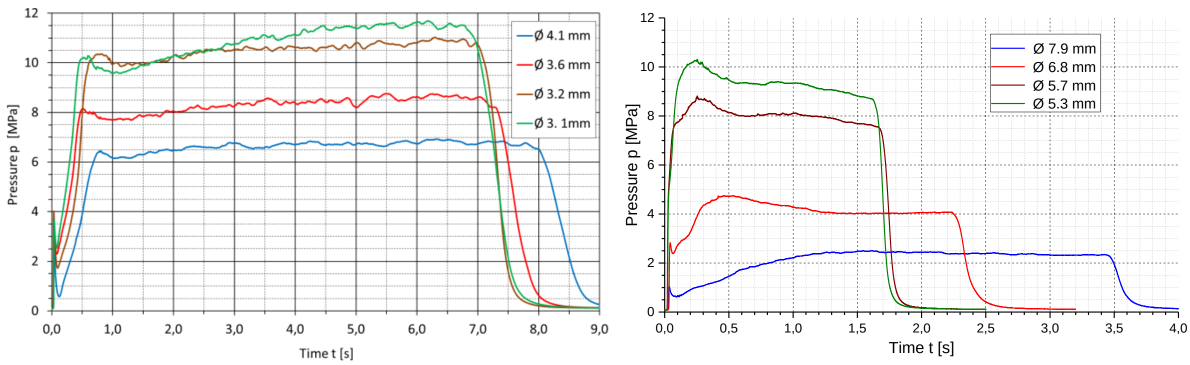

Figure 2. Measured chamber pressures versus time at different nozzle diameters of an Al/AP/HTPB (left) and Al/ADN/GAP (right) propellant

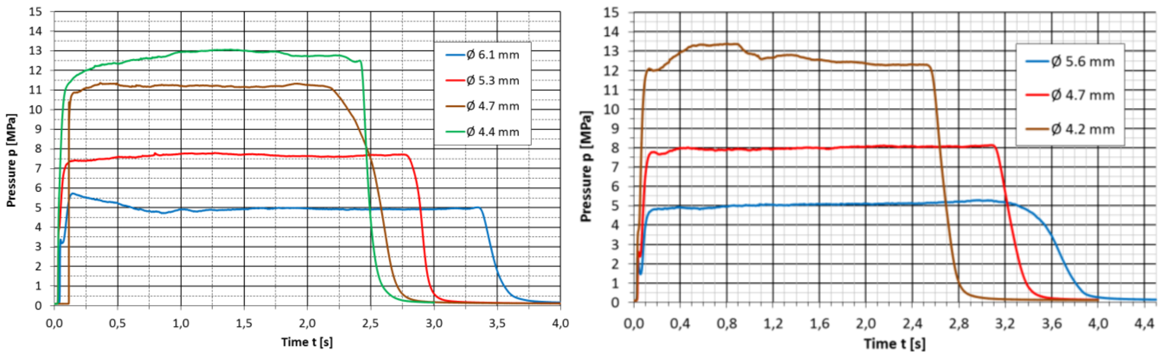

Figure 3. Measured chamber pressures versus time at different nozzle diameters of an ADN/HMX/GAP (left) and ADN/FOX12/GAP (right) propellant

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 [17] 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 molar number of gases are higher and the mean molecular masses of the gaseous reaction products are lower. Both have a positive effect on Isp and the constant C*.

In Table 2 the calculated and experimental delivered gravimetric specific impulses (Isp) are compared at a chamber pressure around 7 MPa. Despite the higher theoretical Isp of the metallized propellant, the Isp calculated from experimental data are similar to the non-aluminized. Surprisingly the Isp_{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 loses and not complete combustion of the aluminium which is evidenced by the lower C* efficiency.

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.

* The exhaust plume smoke characteristic is estimated by the author

Table 2. Results of the propellant tests (blue fonts represent 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
$Isp_{ICT\ Code}$ [Ns/kg]	2600	2698	2462	2335
Isp_{exp} [Ns/kg]	**2070**	**2247**	**2237**	**2099**
$Isp_{exp}/Isp_{ICT\ Code}$ [%]	80	83	91	90
Vol. Isp_{exp} [Ns/dm³]	**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

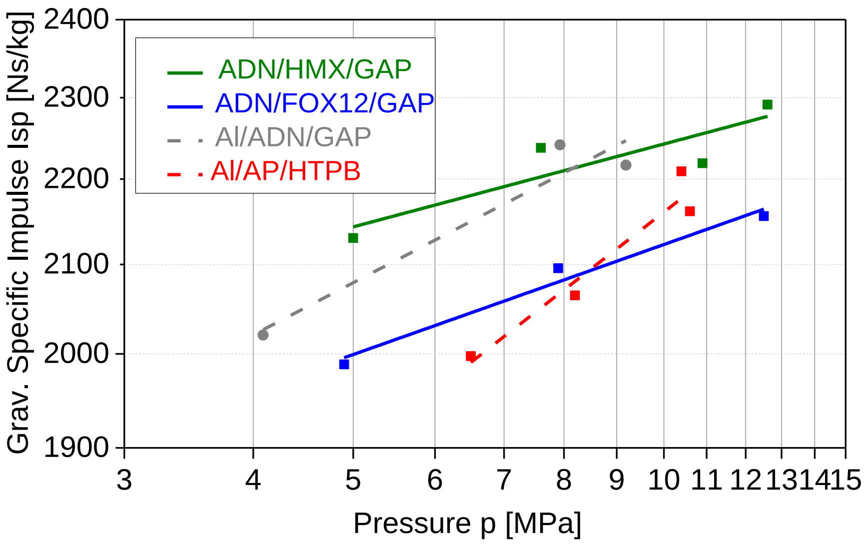

Figure 4. Experimental determined gravimetric specific impulses at different pressures

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.

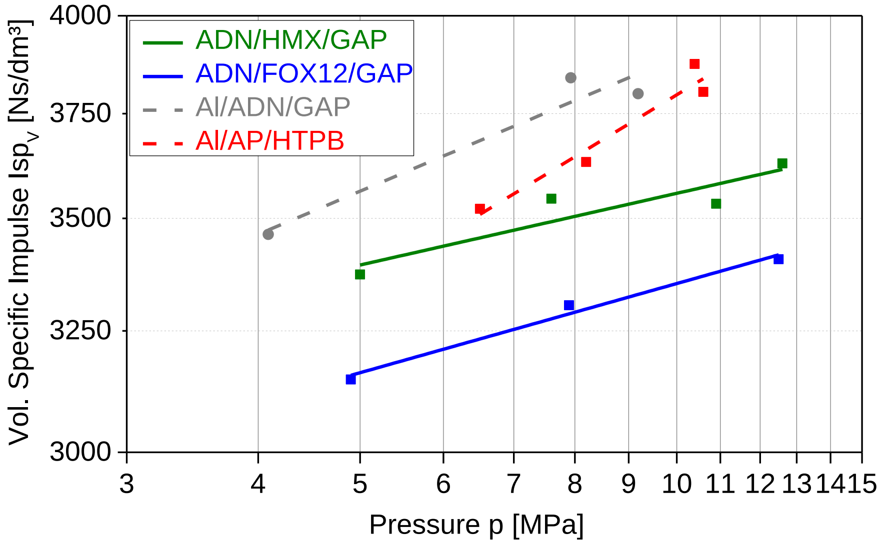

Figure 5. Volumetric specific impulses at different pressures calculated from experimental gravimetric Isp and the densities of the propellants.

The burning rates of the ADN/GAP propellants are at least double of the AP/HTPB one. Experimental determined pressure exponents from the motor test are in the most cases lower compared to Crawford measurements (Figure 6).

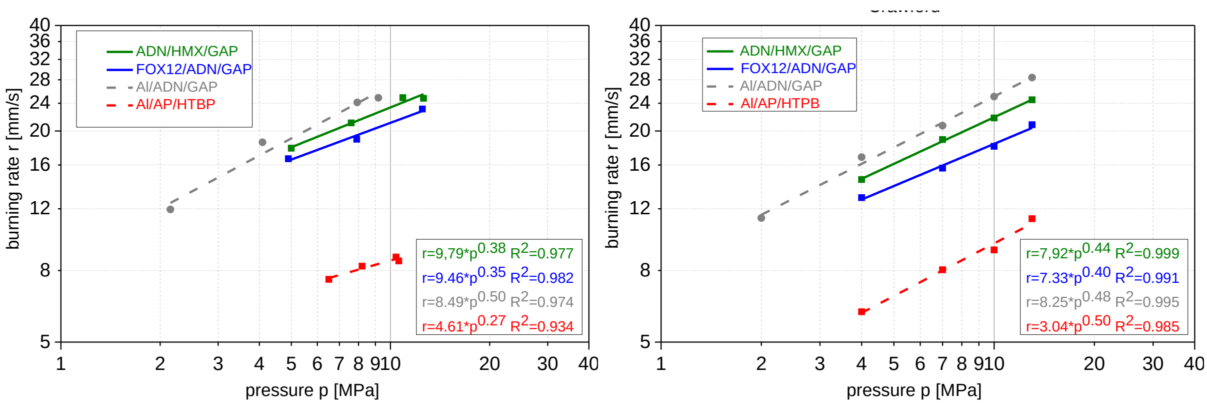

Figure 6. Burning rates at different pressures from the motor test (left) and Crawford bomb (right)

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)

Propellant	**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 probably 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

Propellant	**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]

Chemical stability

The stability of ADN/GAP based propellants are described using the example of an Al/ADN/GAP formulation. A general way for the evaluation of the stability is the determination of the heat loss which should be less than 5% of the total energetic content. The heat losses in air and argon were measured by heat flow microcalorimetry (HFMC). The energy losses after 15 days are strikingly lower than the 5% value of the heat of explosion.

Table 5. Energy loss of Al/ADN/GAP propellant

Atmosphere	Found loss after 15d [J/g]	Heat of explosion Q_{EX} / Q_{EX} (water gaseous) [J/g]*	5% of Q_{EX} / Q_{EX} (water gaseous) [J/g]
Air	15	7025.5	351
Argon	7	6814.2	341

* calculated by ICT Code with loading density of 0.1g/cm^3

In the case of the vacuum stability nothing noticeable was observed at 80°C for 144h. The data were formally converted to 100°C for 40h according to the generalized van't Hoff rule [16]. The calculated gas formation was 1.40 ml/g at 100°C. STANAG 4556 consider a sample as stable if the gas evolution from 1 gram of test substance is less or equal than 2 ml. According to this definition the propellant is stable.

Due to ADN the Dutch mass loss test was performed at 80°C instead of 105°C , but with the standard test times and standard procedure .The results were formally converted to 105°C again according to the generalized van't Hoff rule [16].

Table 6. Results of the Dutch mass loss test

Test times [h]	Measured mass loss at 80°C [%]	Formal mass loss at 105°C [%]
0-8	0.35	5.45
0-72	0.43	6.70
8-72	0.08	1.25

The Dutch mass loss test is formally fulfilled, because the limit value of 2% at 105°C for the test time period 8 to 72 h is not surpassed. But in the first 8 hours the mass loss has high values which are considered somewhat to high. Additional mass loss measurements at 70, 75, 80, and 85°C for 30 days allowed the prediction of the in-service time period by an Arrhenius parameterization. If a mass loss of 0.5% is assumed the in-service time could be 36 years at a storage temperature of 50°C and 12 years at 55°C.

The thermal stability determined by self-ignition temperature (SET: 156.5°C at 5°C/min) and adiabatic self-heating rate (SHR: onset 124°C, deflagration 156°C) are dominated by the SET and SHR of ADN.

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 shock sensitivity. The stability of the propellants is sufficient for application.

Acknowlegment

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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
mass-%	mass percentage
η_{c^*}	C* efficiency
∅	diameter

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