High Performance Aluminized GAP-based Propellants – IM Results

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ABSTRACT

SNPE Matériaux Energétiques is carrying out studies on new high performance solid propellants based on GAP polymer (glycidyl azide polymer) and energetic plasticizers.

The challenge with the development of high performance propellants is to meet IM requirements. GAP-based compositions are a good answer to increase significantly energetic performances, with the additional energy given by the polymer. Meanwhile, safety and vulnerability characteristics of such propellants are not degraded. Indeed, aluminized GAP-based solid propellants have been developed to fulfil operational requirements, and tested up-to a 100 kg mock-up.

This paper is focused on risks associated with this kind of high energy propellants, and specifically on IM results. Among those, impact sensitivity data are obtained, as well as IM results to STANAG tests, like a type V reaction to bullet impact test (4241 STANAG).

CONTEXT AND INTRODUCTION

SNPE Matériaux Energétiques is carrying out studies on new high performance solid propellants for military needs based on GAP polymer (glycidyl azide polymer) and energetic plasticizers.

The challenge with the development of high performance propellants is to meet IM requirements. GAP-based compositions are a good answer to increase significantly energetic performances, with the additional energy given by the polymer. Meanwhile, safety and vulnerability characteristics of such propellants are not degraded. Indeed, aluminized GAP-based solid propellants have been developed to fulfil operational requirements, and tested up-to a 100 kg mock-up.

This paper describes in a first part aluminized GAP-based propellant main characteristics. In the second part, vulnerability tests and results are described, in the different fields of pyrotechnic safety, mechanical, thermal and finally a more specific and detailed focus on bullet impact threats.

PART I: ALUMINIZED GAP-BASED SOLID PROPELLANT CHARACTERISTICS

SME has chosen to develop GAP-based propellants named Azalane®. These propellants are based on fillers such as AP (Ammonium Perchlorate), nitramines and aluminum, and on crosslinked binders formulated with energetic plasticizers and with GAP (glycidyl azide polymer) as an energetic polymer. Indeed, GAP exhibits a high enthalpy of formation, which allows a significant increase in energetic performance with respect to currently operational propellants.

The requirements mainly relate to improvement in energetic performance and in IM behaviour. Other characteristics such as safety, ballistics, mechanics and ageing also have to be assessed. The optimization of the formulations has helped to develop propellants with the characteristics necessary for case-bonded grain configurations [1].

FORMULATION

Studies were carried out on compositions filled with AP, HMX and aluminum (Table 1). AP was used as a tool to adjust the burning rate to the needs.

Table 1 : Propellant formulations

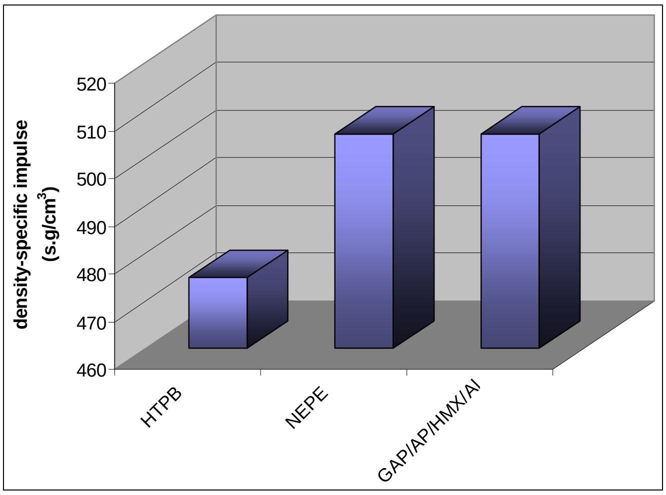
	Azalane®
Binder	GAP / TMETN / BTTN *
Fillers	AP, HMX, Al
Total solids	73%

** TMETN: Tri Methylol Ethane Tri Nitrate* *BTTN: Butane Triol Tri Nitrate*

PERFORMANCE

As GAP is an energetic polymer, this feature yields propellants with density-specific impulse higher than 88% total solids HTPB propellants by 4 to 10%. Energetic performance is similar to that of current NEPE propellants, but vulnerability behaviour is shown to be better, that is what will be demonstrated through this paper.

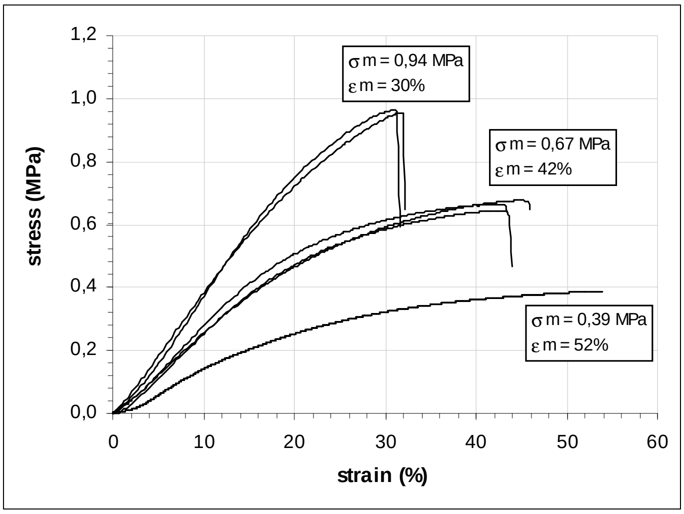
Figure 1 : Energetic performance



MECHANICAL PROPERTIES

The optimization of mechanical properties was obtained by controlling the formulation of the binder, the introduction of bonding agents and particle size distribution of the solids (Figure 2). This is a key point to ensure not only characteristics compatible with case-bonded grain configurations, but also satisfactory safety behaviour and a moderate response to external aggressions.

Figure 2 : Mechanical properties (+ 20°C, 50 mm/min)



PYROTECHNIC SAFETY CARACTERISTICS

Safety characteristics are shown in Table 2. One can note that, with respect to inert polymers, GAP does not bring any particular sensitivity.

Table 2 : Safety characteristics

Tests	Results
Friction sensitivity UN 3b)i)	76 N
Impact sensitivity UN 3a)ii)	22 J
Self ignition STANAG 4491 annex B2	172℃

PART II: VULNERABILITY REQUIREMENTS AND RESULTS

SAFETY CHARACTERISTICS IN DETONICS

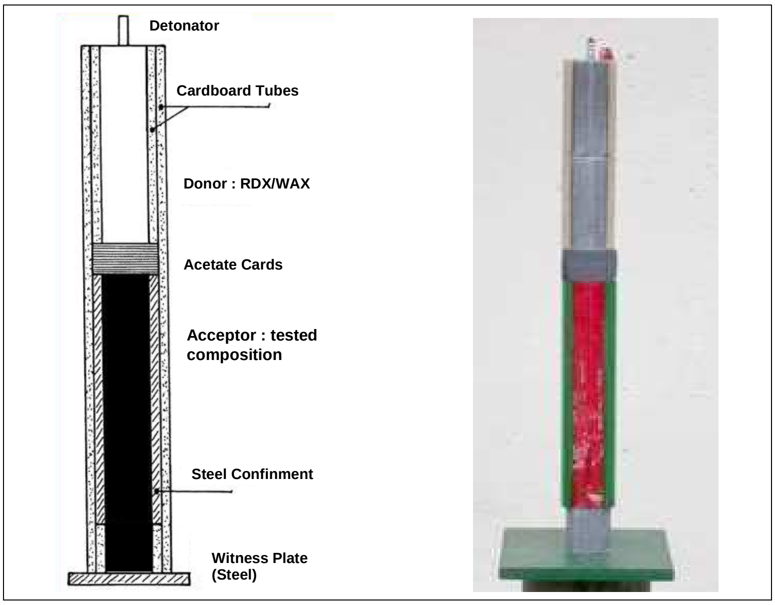
When dealing with high energetic material, containing energetic binder, plasticizer and nitramine, another important parameter to study is the critical diameter, which is the critical dimension under which no SDT can occur.

Thus, it has been measured on this composition: $2\text{ mm} < \varnothing c < 3\text{ mm}$

This result shows that specific studies on that type of composition has to be performed, in order to characterize properly their detonation ability, with a final objective of ensuring safety both in processes and handling. In the following, a focus is rather made on shock sensitivity given by LSGT results.

The shock sensitivity of Azalane® propellant was tested at Large Scale Gap Test (LSGT) according to STANAG 4488 annex B. The set up is presented in Figure 3. It consists in a RDX/wax donor that induces a shock wave to an acceptor (i.e the composition to evaluate) through a barrier made of acetate type material cards (0.19 mm thick). The acceptor sample diameter is 40 mm, its length 200 mm. The result is given by the minimum number of acetate cards which does not lead to the acceptor detonation (given at ± 5 cards). This diagnosis is assessed by the visual examination of the witness plate placed under the acceptor.

Figure 3 : Experimental set up for LSGT (∅ 40 mm, acetate cards 0.19 mm)



The Gap Test results on Azalane® propellant were the followings:

- 1 No Detonation and 1 Detonation at 140 cards
- 1 Detonation at 145 cards
- 3 No Detonation at 150 cards

The threshold value in terms of number of cards can reasonably be estimated around 150 cards for this type of propellant. This value corresponds to a barrier thickness of 28.5 mm, that is to say a pressure level of 48 kbar delivered by barrier. These values have been compared to the ones obtained with former NGL based high energetic NEPE propellant and a classic PBX, see Table 3.

Table 3 : LSGT results of Azalane®, compared with NEPE propellant and I-PBXN-109

	Azalane®	NEPE propellant	I-PBXN-109
Simplified composition	GAP/BTTN/TMETN AP HMX Aluminum	PGA*/NGL/BTTN AP HMX Aluminum	HTPB Aluminum I-RDX®
LSGT Result (Nb of acetate cards)	150	200	140
Pressure in acetate (kbar)	48	25	53

** Polyglycidyl adipate*

From these results, one can assess that this type of high energetic propellant is at least as little sensitive to SDT as "good" insensitive explosives, such as the I-PBXN-109. One can also deduce that this propellant is likely to initiate in detonation, like for instance to shaped charge type threat.

Thus, all safety characteristics allow a hazard classification 1.3c, both for manufacturing and storage, (according to French regulations) as well as transportation (according to UN Recommendations on the Transport of Dangerous Goods).

RESPONSE TO SLOW HEATING

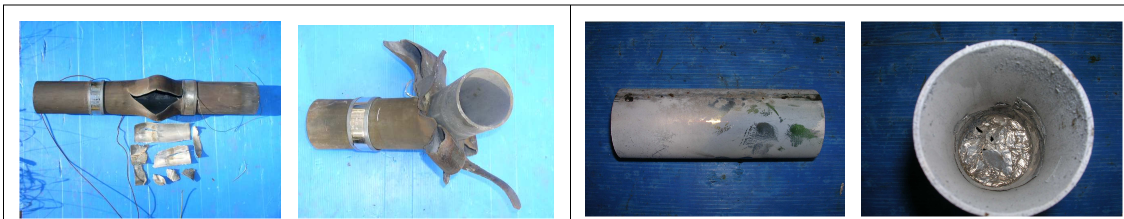
Propellant response to thermal threat is another important field of investigation for IM final assessment, especially under slow heating conditions. Two kinds of small scale tests are performed, with isothermal conditioning or with slow heating rate.

The unconfined thermo-ignition critical temperature test (SNPE #41) [2] brings input data for numerical simulations, (Arrhenius law parameters).The sample is heated by exposition to a constant external temperature. A test involves 10 samples (at least) to be tested at different temperature inside thin aluminium cup (samples can be considered as unconfined). Samples are cylinders (50mm in height – 50 mm in diameter).

Small scale slow heating tests are performed on same sample geometry. Various confinement devices are used. The sample in its cup is put inside a steel oven heated by electrical resistances. From each trial, the sample temperature history, violence of reaction and time-to-reaction are assessed data.

As a preliminary assessment, these sub scale tests have been performed on Azalane®. The main information obtained from all those tests is that GAP-based propellant such as Azalane® exhibits moderate responses compared to classical HTPB propellants, like exposed on pictures in next figure.

Figure 4 : Pictures of HTPB based and GAP based propellant after isothermal small scale tests



Vessel and oven after HTPB propellant small scale isothermal test	Vessel after Azalane® propellant small scale isothermal test

Further tests including slow heating standard tests will have to be performed in order to achieving IMness for rocket motors made of alumized GAP based propellant.

ELECTROSTATIC SENSITIVITY

Sensitivity of solid propellants to electrostatic discharges was mainly investigated in the late 80's and beginning of the 90's. Indeed, several incidents and/or accidents had occurred during this period, in propellant manufacturing plants, but as well on full scale rocket motors in military storage or operational area.

Based on SNPE large experience [3] in this field, the two first electrical properties to be characterized on a new Energetic Material are:

- Its classification as "conductive" or "insulating" in accordance to electrostatic phenomena with a threshold value at around 10^9 Ω.m. This value is intrinsic for each formulation and gives a first and simple criterion for electrostatic discharge response assessment. Conductive propellants are not able to accumulate electrostatic charges. Thus, these are intrinsically unable to induce electrostatic discharges in accidental scenario.
- Its classification as "sensitive" or "no-sensitive" substance when submitted to large scale electrostatic discharge sensitivity test through STANAG 4490 annex B (SNPE #37A) .This test is considered to be the reference for electrostatic discharges behaviour detection.

The next table gives ES tests results for Azalane®, and a comparison with HTPB based propellants.

Table 4 : ES tests results for Azalane®, compared with HTPB based propellant

Test	HTPB / AP / Al based propellant *	Azalane® propellant
Volumic electrostatic resistivity (Ω.m)	10^{+10}	10^{+05}
Intrinsic characteristic	INSULATING	CONDUCTIVE
Large scale test STANAG 4490 annex B	SENSITIVE TO ES DISCHARGES	NO-SENSITIVE TO ES DISCHARGES

** HTPB based propellant with Al content mass over than 17% are concerned by these ES values.*

Indeed, it is obvious that this new type of propellant has a different behaviour when submitted to ES discharges, leading us to the very interesting and promising conclusion that no such ES accident can occur with this new type of aluminized GAP based propellant.

BULLET IMPACT AND NO-DETONATIVE SHOCKS RESPONSES

To assess propellant sensitivity and violence of reaction, to bullet impact, friability test and closed vessel combustion test are commonly used as screening characterizations.

a/ Friability Critical Impact Velocity test

The Friability test UN 7 c) ii) is used to determine the response to bullet impact and fragmentation effects of mechanical shocks on EM grains [4]. Indeed, based on this trial, a first estimation of sensitivity to no-detonative shocks can be given, from an expert point of view.

This test consists in:

- Projecting a test sample of 9 g, against a wall (steel plate), at a specified velocity (typically in a range of 100 to 250 m/s);
- Collecting the fragments;
- Burning them into a closed vessel. The pressure signal P(t) in the vessel, is recorded during the combustion process. It is directly related to the specific surface that is generated at impact within the tested sample: assuming the material burning rate law $r_b(P)$, the combustion surface evolution can be deduced.
- The maximum pressure rate is also deduced from the pressure curve and currently analyzed: $(dP/dt)_{max}$

Several shots are performed, at different impact velocities. At last, the tested material is characterized by the plot of its maximum pressure rate value (dP/dt)max versus the impact velocity.

These results are commonly synthesized as the maximum pressure rate $(dP/dt)_{max}$ at a 150 m/s impact velocity. This value is considered for EIDS (Extremely Insensitive Detonable Substances) assessment, with a threshold value of $(dP/dt)_{max}$ = 18 MPa/ms.

For expert analysis, results are analysed trough Critical Impact Velocity. This CIV is the velocity outcoming derivative pressure equal to 18 MPa/ms, This velocity has to be higher than 150 m/s.

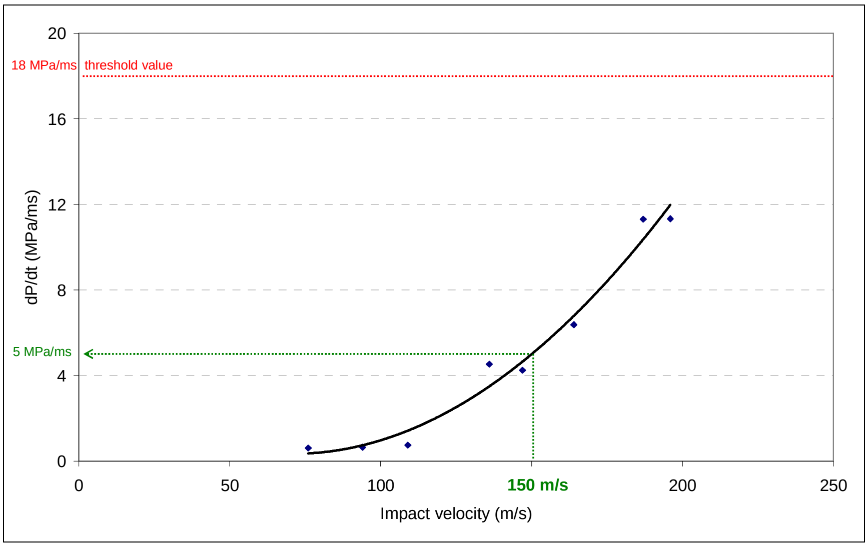
Series of tests have been performed on Azalane® propellant samples, from 70 m/s up to 200 m/s impact velocities. From these trials, the following main parameters are deduced:

$(dP/dt)_{max}$ = 5 MPa/ms @ 150 m/s

and $(dP/dt)_{max}$ = 18 MPa/ms has not been reached, thus, **Critical Impact Velocity > 196 m/s**

This composition exhibits a very smooth high pressure rate $(dp/dt)_{max}$ increase with impact velocity: this allows us to assess the maximum pressure rate at 150 m/s for this composition. A common representation of these results is given in next plot.

Figure 5 : Friability results – $(dP/dt)_{max}$ curves for Azalane® propellant



Due to its good mechanical properties, the threshold value of $(dP/dt)_{max}$ = 18 MPa/ms, is reached beyond impact velocities that have been tested. Moreover, this impact velocity is considered as a key value, and thus exhibits great margins, when compared to the common reference value defined at 150 m/s. Classical HTPB composite propellant exhibit very similar impact velocity when $(dP/dt)_{max}$ reaches 18 MPa/ms.

b/ <u>Closed Vessel burning test</u>

The burning properties of high energetic materials are also usually investigated in closed vessel, up to 700 MPa [5]. This test allows determining maximum pressure for nominal combustion regime known as "layer by layer combustion". Beyond this pressure, cracking combustion regime occurs with catastrophic combustion surface increasing which outcomes deflagration or detonation response.

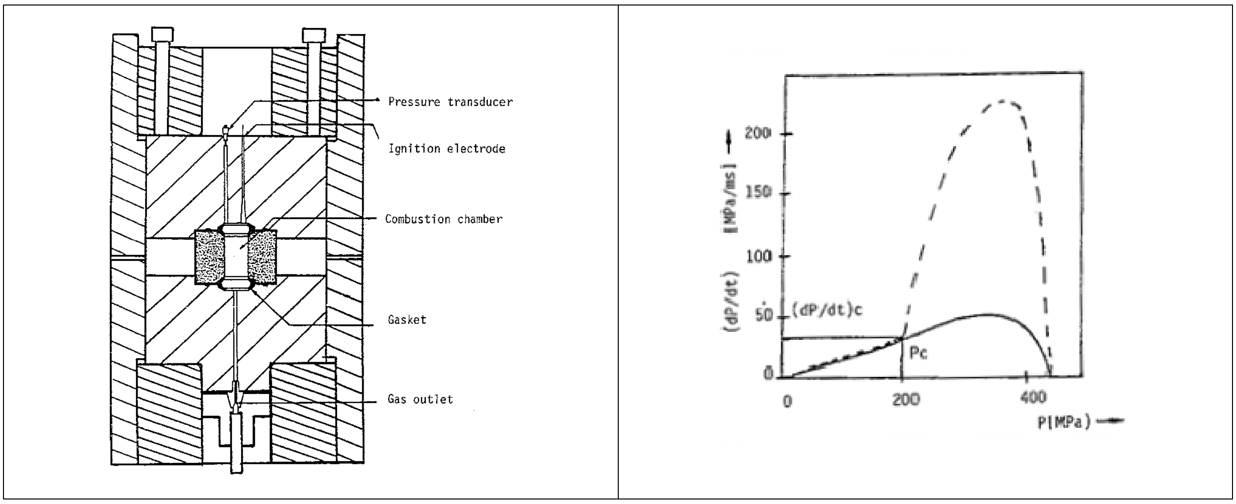
In this test, the loading density is close to 400 kg/m3 and the samples have a parallelepiped shape. In such a test, a first insight on the material burning process is given by the dp/dt curve, obtained after pressure data processing.

Depending on the pressure curve shape, two kinds of mechanisms may appear, as shown with the examples in Figure 6:

- A classical burning process, as a layer by layer combustion propagation, with both monotonic pressure and dp/dt - time history.
- A more violent burning process, or cracking combustion, characterized by a sharp change of slope at a critical value P_c (cracking pressure) associated with $(dp/dt)_c$. This critical point is typical of a sudden increase in gas production during material combustion, which can be related to a deflagration-to-detonation transition ability of the material.

The codification of results is given by indicating the measured maximum pressure, the pressure P_c at the change of slope, and possibly the number of breaks observed on these curves.

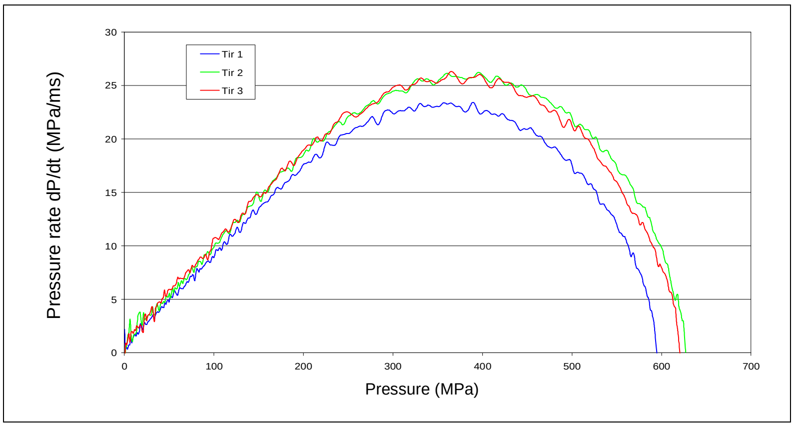
Figure 6 : High pressure closed vessel device



This test is one of the most pertinent way to quantify the damage through the specific surface, induced by a mechanical loading. It gives a relation between mechanical loading and reactivity, in other words violence of reaction. Indeed, it allows quantifying the specific surface in the sense of the violence of reaction.

Three trials have been performed with Azalane samples, none exhibits a cracking pressure during test, up to the maximum operating pressure (>627 MPa), as shown on Figure 7. This result is in accordance with the good mechanical properties of this propellant, as well as its good friability level.

Figure 7 : *dP/dt=f(P) curves under high pressure combustion for* Azalane® propellant



Analyzing these results (friability and high pressure combustion test), one can assess that this composition have a great potential for no violent reaction when submitted to bullet impact threat. Indeed, bullet impact trials have been performed to confirm this point.

c/ Bullet Impact trials

Beside small scale characterizations, monitored bullet impacts on test vehicle have to be performed, for preliminary IM assessment of the propellant to bullet impacts. This kind of experiments on mock-ups are more representative of warheads showing similar geometry (calibre, case thickness,…) and gaps volumes. They can even constitute an ultimate validation step.

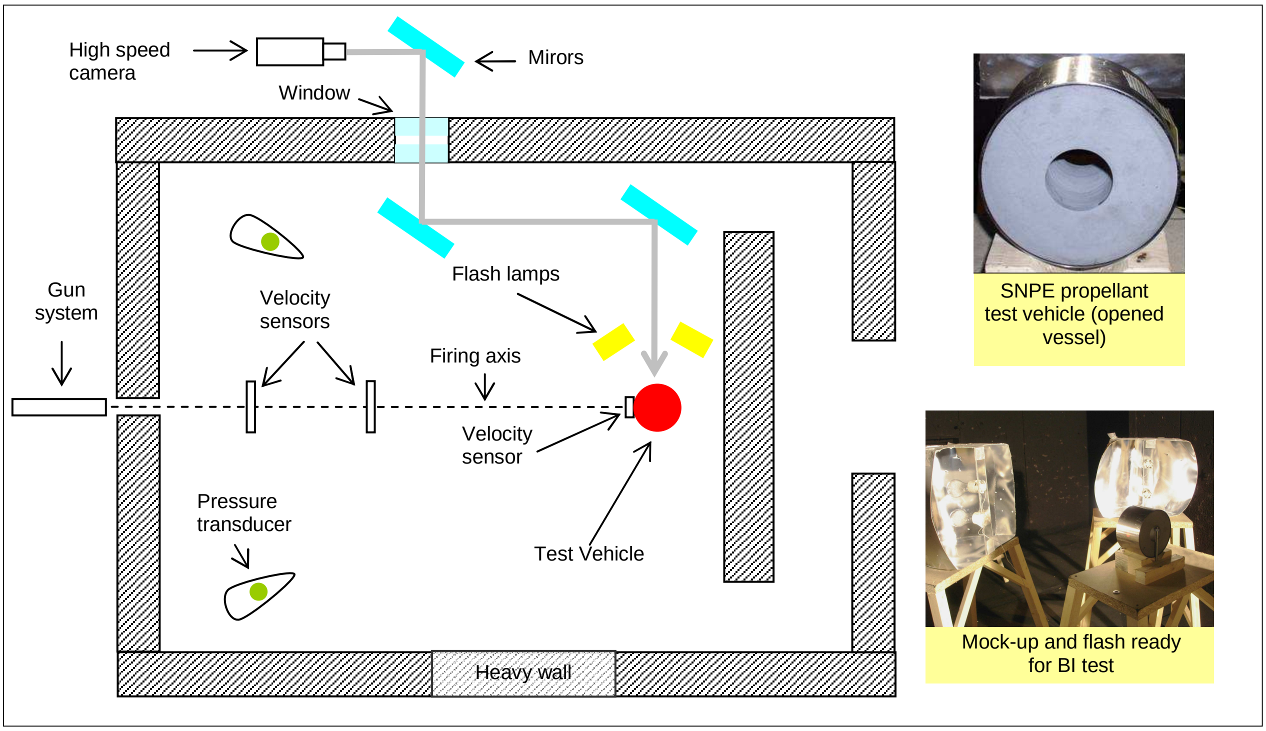
Various types of guns are available at SNPE for different kinds of testing. In order to test Azalane® propellant, the STANAG 4241, edition 2 procedure [6] is applied: calibre 0.5" armour-piercing bullet (12,7 mm) firing test, launched from a rigidly mounted gun, with an impact velocity adjusted to 850 m/s.

For accurate data acquisition, these bullet impact tests are equipped with various monitoring techniques, such as:

- Digital high speed framing camera, very useful to describe as precisely as possible the trials and the phenomena encountered, with 100.000 frames per second (average rate). Flash bulbs are used, for events back-light.
- Projectile velocity measurement (sensors),
- Transducer for blast overpressure measurement,
- Internal pressure sensor in gaps volume for propellant test vehicle (closed vessel)…

At SNPE Le Bouchet Research Centre, it has to be noticed that bullet impact tests are performed in a detonation chamber. The test configuration is given in next figure, with test vehicle and instruments positions.

Figure 8 : Impact test configuration, in SNPE Research Centre



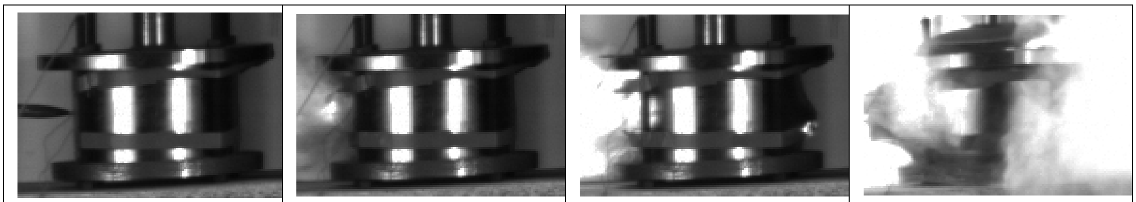
The standard SNPE test vehicle, specially designed for rocket propellant testing is there used. A picture is shown on previous figure. The structure is constituted of a cylinder (Inner diameter: 158mm – Length: 100mm), with two 5 mm thick lid, closed with tie rods, made of standard stainless steel. The mock-up is filled with the propellant to be tested which has a cylinder central bore of 52 mm diameter, and a thin slice of liner is added between propellant and the metallic case to be more representative of a rocket motor.

Two different firing tests are performed: one first firing test in standard configuration, thus in a closed vessel, for reaction violence assessment and a second one in an open vessel, in order to identify the ignition scenario, mainly based on high video images. Tests vehicles are impacted on the side so that the bullet crosses the bore area.

❖ ***<u>Bullet impact test #1, in closed vessel, fired @ 850m/s</u>***

The bullet velocity is measured at 869 m/s. Thanks to high speed camera images, in Figure 9, an accurate scenario of reaction can been expressed.

Figure 9 : Kinematics of bullet test #1 in closed mock-up (high speed video images)



T0 : impact on vehicle (left side)	T0+210 µs : combustion begins	T0+263 µs : bullet out of the mock-up (right side)	T0+599 µs : cover rupture

Just after impact on the mock-up, combustion (lights on high speed camera pictures) is observed, before the bullet gets out of the vehicle. Then, the up lid opens; with pressure increase in the bore area up to a few tens of bars is measured just before opening. Then, the next step is the mock-up pneumatic explosion.

After firing, the test mock-up metallic cylinder is recovered, cut in two parts. Some residual unburned propellant pieces are recovered in the test chamber, as shown in next picture.

Figure 10 : Pictures after bullet impact test #1 in closed vessel

Almost 40 % (in mass) of the tested EM was recovered unburned (which is a necessary under estimated value, given as a slight indication). Neither metallic fragments nor blast overpressure was generated (no peak on pressure signal), which is another proof of moderate reactivity level of the Azalane® propellant.

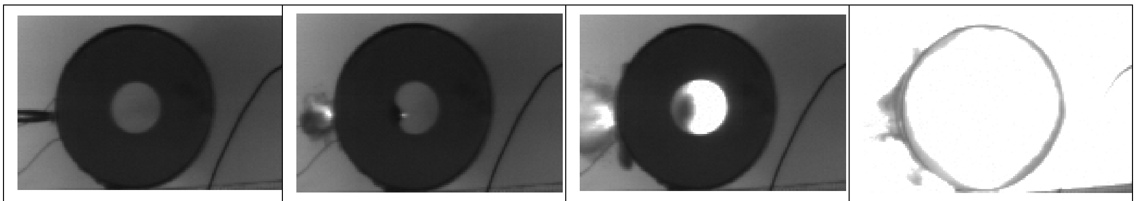
This reaction level is comparable to a **type V reaction**, according to STANAG 4439 / AOP39.

❖ ***<u>Bullet impact test #2, in opened vessel, fired @ 850m/s</u>***

The second test is performed in an open vessel, in order to identify the ignition scenario and reaction of the EM when impacted by a bullet. The bullet velocity is measured at 864 m/s.

As shown on Figure 11, the propellant is ignited by friction of the bullet on the propellant. Then, a slow combustion of the EM begins and the bullet crosses through the mock-up, damaging the metallic vessel. The combustion expands into central bore area, but without violence reaction.

Figure 11 : Kinematics of bullet test #2 in open mock-up (high speed video images)



T0 : impact on vehicle (left side)	T0+84 µs : bullet in central bore	T0+136 µs : combustion in central bore (light)	T0+210 µs

Like for the previous test, neither metallic fragments are generated nor blast overpressure is measured.

Figure 12 : Pictures after bullet impact test #2 in open mock-up

In this case, the vehicle cylinder is found after firing, in two pieces (except for the lid or the aft-end), with the exact print of the bullet getting in and out of the mock up. Most of the EM sample is found unburned on the ground after test, crushed in small pieces (like shown on the second picture). It represents more than 90 % (in mass) of the initial tested EM (necessary under estimated value, given as a slight indication). That makes us think that the combustion no longer goes on right after the metallic cylinder opens on its side, once the bullet gets out: the combustion process just stops.

Indeed, Azalane® propellants exhibit a satisfactory behaviour in the standard configuration at 0.5'' bullet firing threat.

SYNTHESIS

As a synthesis of all these IM characteristics, previously described and discussed are summarized in Table 5.

Table 5 : Azalane® IM characteristics

Tests	Results
Slow-Cook-Off (Small scale)	Non violent reaction (Combustion)
Large Scale Gap Test	150 cards (~ 50 kbars)
Critical Impact Velocity	> 196 m/s
Closed vessel burning test	No cracking combustion up to 627 MPa
Bullet impact test	Type V reaction

CONCLUSION

These tests results show that high energetic performance and IM behaviour are not intrinsically incompatible. Azalane® solid propellant exhibits satisfactory behaviour to small scale test assessment: slow heating threats, to electrostatic phenomena, to bullet impact test and mechanical shocks.

Azalane® responses are equivalent or even better than for HTPB propellants. That makes possible to expect rocket motors filled with Azalane® propellant with attractive IM signature.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the French Ministry of Defence (DSP/Num), for their financial support on this study. They are also thankful to SNPE Le Bouchet Research Centre teams, strongly involved and concerned on this study.

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