New high energetic composite propellants for space applications : Refrigerated Solid Propellant (RSP)

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Abstract

Cryogenic solid propellants (CSP) are a new kind of chemical propellants that use frozen products to ensure the mechanical resistance of the grain. The objective is to combine the high performances of liquid propulsion and the simplicity of solid propulsion. The CSP concept has few disadvantages. Storability is limited by the need of permanent cooling between motor loading and firing. It needs insulations that increase the dry mass. It is possible to limit significantly these drawbacks by using a cooling temperature near the ambient one. It will permit to not change the motor materials and to minimize the supplementary dry mass due to insulator. The designation “Refrigerated Solid Propellants” is in that case more appropriate as “Cryogenic Solid Propellant”.

SNPE Matériaux Energétiques is developing new concept of composition with cooling temperature as near the ambient temperature as possible. They are homogeneous and the main ingredients are hydrogen peroxide, polymer and metal or metal hydride, they are called “Hydroxalane^{TM}”. This concept allows reaching high energy level. The expected specific impulse is between 355 s and 375 s against 315 s for HTPB / AP / Al composition. However the density is lower than for current propellants, between 1377 kg/m^3 and 1462 kg/m^3 compared to around 1800 kg/m^3. This is an handicap only for volume limited application. Works have been carried out at laboratory scale to define the quality of the raw materials and the manufacturing process to realize sample and small grain in a safer manner. To assess the process, a small grain with en internal bore had been realized with a composition based on Aluminium and water. This grain had shown very good quality, without any defect, and good bonding properties on the insulator.

Introduction

Advanced propulsion new energetic material for space application, referred hereafter as Refrigerated Solid Propellant (RSP), is presented in this paper. The compositions defining this concept are characterized by a high propulsive performance in term of specific impulse.

Cryogenic Solid Propellant (CSP), so named because of very low temperature, are widely reviewed in studies carried out by R. Lo and al. (e.g [1], [2]). In these works, CSP appears to be a promising new material for propulsion delivering a specific impulse higher than any traditional solid propellant (280s-450s vs. 220s-290s [2]). To illustrate CSP potential application, two designs are presented depending on the considered configurations (solid H_2O_2 locates between polymer modules or coherent propellant grain). Another interesting result of these studies is a first experimental demonstration of the feasibility of the concept considering H_2O_2/PE disk stack propellant. Extrapolation to large solid rocket boosters is developed in Ref. [3] by considering the case of Ariane 5 booster. It is shown that Solid H_2O_2/PE or Solid O_2/PE can advantageously be compared to HTPB/AP/Al propellant, despite a lower density compensated by an increase in performance.

RSP are reviewed and some energetic performances are given. A specific focus is done on the studies performed at SNPE on compositions having a freezing point not too far from room temperature (i.e. near 0°C). For this study, the presented composition consists in mixing oxidizer and fuel (typically aluminum powder which size spreads from 200 nm up to 5 µm). The solid structure is obtained by freezing the material. Security and feasibility aspects are presented and procedures are defined for the making of a refrigerated propellant grain. The last part is devoted to the ballistic characterization of RSP, motor test definition and experimental results obtained by firing a 600g grain.

I. Theoretical performance calculations

The aim of this previous study is to identify potential formulation for refrigerated composite propellants. This study is based on several thermodynamic calculations performed with the SNPE numerical code Ophelie. The composition is selected to reach a solidification point near 0°C. The considered oxidizers are as follows:

- Pure hydrogen peroxide (H_2O_2),
- Pure water (H_2O),
- Mixture H_2O_2/H_2O

The fuel materials are:

- Polymeric materials (polyethylene or polybutadiene),
- Aluminum.

Results are presented in the next figure. They are obtained by considering a *7 MPa* combustion pressure, vacuum condition and an expansion ratio of 40. For the purposes of comparison, theoretical specific impulses can be evaluated with regard to HTPB/AP/Al propellant (Butalane®) which delivered specific impulse is *315 s* for a density of *1758 kg/m*^{3}.

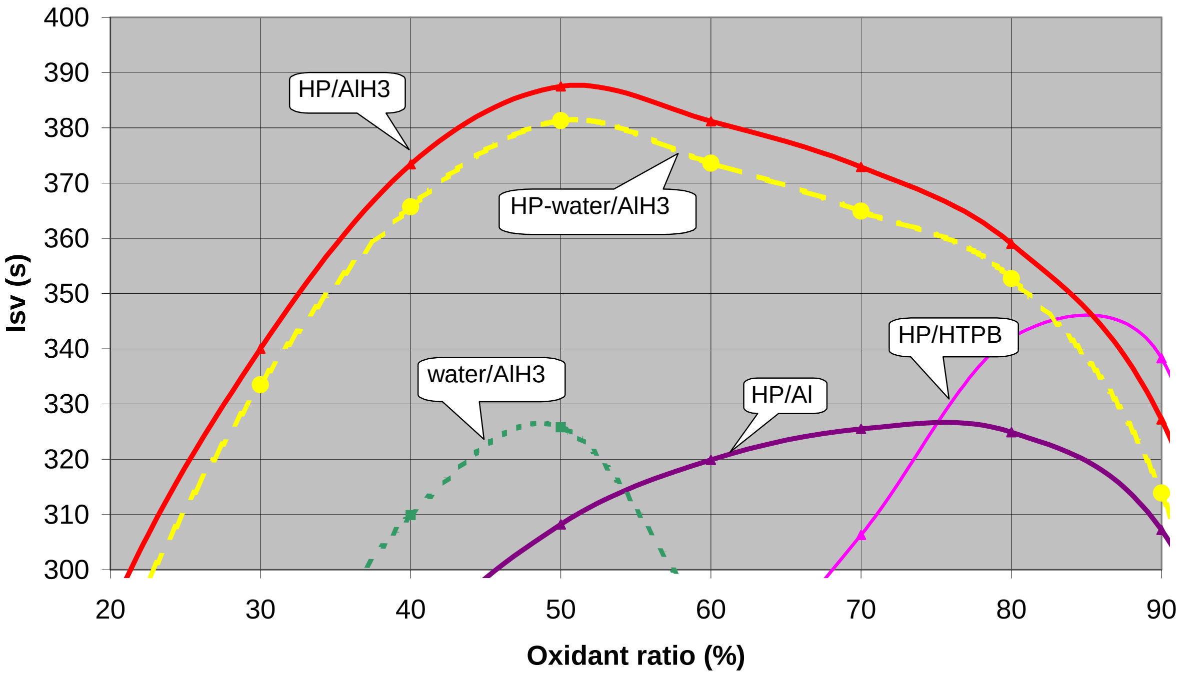

Figure 1 – Performance calculations

Considering the theoretical results shown in Figure 1, it appears that pure hydrogen peroxide is a good candidate due to its solidification temperature at 0°C and its large oxidizing properties. Advanced calculations were performed in order to determine the optimized formulation. The higher specific impulse is obtained with aluminum hydride in pure hydrogen peroxide (*387s*) although compositions with polymeric material or aluminum as fuel lead to lower values (respectively *342s* and *327s*). These values confirm the increase of the performance compared to the HTPB/AP/Al propellant. Practically, for reducing the two phases looses, the maximum of specific impulse (*373s*) was found for using a limited quantity of AlH_3 with addition of polyethylene in pure hydrogen peroxide. The same calculation performed with aluminum in replacement of AlH_3 shows a decrease in the performance which reaches the value of *355s*.

Study logic

However pure hydrogen peroxide can hardly be handled (due to its very high reactivity) and requires important cares and specific facilities to be produced and stored. Thus, dilute hydrogen peroxide in water was considered. It results in a decrease of the performance with the dilution of the hydrogen peroxide. The existence of an eutectic point for this mixture can be considered as an advantage. But the very low temperature of the solidification point can be seen as a limiting factor for potential applications.

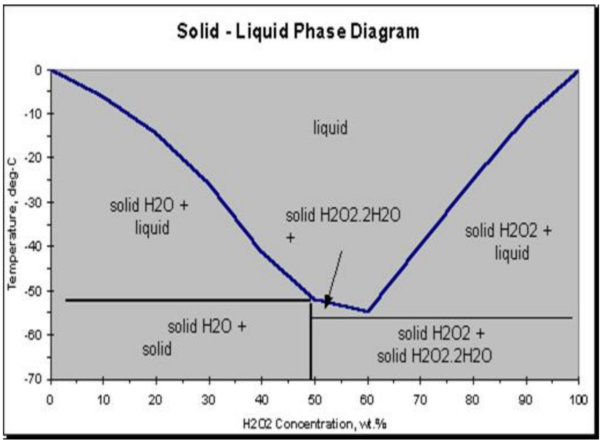

Figure 2 - Solid Liquid Phase Diagram of H_2O_2 and H_2O

To obtain a temperature near O°C for a solid propellant, high concentrated hydrogen peroxide aqueous solution (>90%) is not available in industrial application, therefore the use of pure crystal material is not reachable.

With pure water, performances are slightly decreased and, if AlH_3 provides the best result in this case, large formation of solid alumina are foreseen. The presence of that solid phase induces looses due to two phases phenomena. However, the density observed is relatively low. The presence of aluminum can reduce this effect.

In this way, the first step will consider the use of dilute solution which implies the presence of solid phase dispersed in a liquid solution.

From this first stage, it can be shown that:

- large specific impulses are available with such formulations,

- the best oxidizer is the hydrogen peroxide,
- for safety purposes dilution in pure water is to be considered.

II. Operating and definition of the firing composition

Safer process

The aim of this study is to ensure the possibility of mixing ingredients in a secure way. To achieve this goal, the following steps were defined:

1. Mix two ingredients at room temperature, in a porcelain vessel with very small quantities and remote-controlled,
2. Evaluate the thermal properties with Differential Scanning Calorimetry (DSC) analysis for a mixture representative of RSP composition,
3. Perform the classical safety tests required for the grain making.

This procedure was applied to several components in order to verify their compatibility and optimize the final composition. The main conclusions drawn from this safety study are synthesized in the following chart:

Test	Products	Results	
Porcelain Pot ***room temperature,*** ***Patm,*** ***200mg***	→ 110 tests with : • H_2O_2 at 30-50-60 and 75 % in water • Al powders from 300nm to 30µm • additive	The contact of these ingredients in binary mixture at this scale is not involving violent phenomena and the temperature increase of the mixture are lower than 2 degrees.	
Dynamic DSC ***20-500°C*** ***5°C/min***	H_2O/additive/Alu nano 79-1-20	$T_{onset\ dec}$ = 74 °C	Qdec # 2670 J/g
	H_2O_2 30%/additive 1/Alu nano 79-1-20	$T_{onset\ dec}$ = 104 °C	Qdec > 2100 J/g
	H_2O_2 30% only	$T_{onset\ dec}$ = 56 °C	Qdec # 370 J/g
ISI-ISF-ES	H_2O/additive/Alu nano 79-1-20 at -20°C	0 test positive over 30 performed tests	
	H_2O_2 30%/additive/Alu nano 79-1-20 **at 20°C**	0 test positive over 3 3.16J for ISI - 54.9N for ISF - 784mJ for ES	
	H_2O_2 30%/additive/Alu nano 79-1-20 **at -20°C**	0 test positive over 3 3.16J for ISI - 54.9N for ISF - 784mJ pour ES	

The thermal potential evaluated by DSC is important for a system containing H_2O_2 30% with nano aluminum powder for comparison with the results obtained with an only water system. It can be seen that the energy provided by the exothermal decomposition exhibits peaks which values are higher 2 000 J/g. Moreover, the temperature of this phenomenon seems compatible with a process at room temperature (T onset dec > 70°C). This test, used to evaluate thermal properties for a propellant composition, does not allow disqualifying this system.

For this system, no particular sensitivity has been demonstrated with the ISI, ISF and ES tests.

Additional tests at lower temperature allowed to determinate the process conditions to formulate homogenous propellant with water or an aqueous hydrogen peroxide solution (30%). However, composition with water and aluminium is chosen for ballistic characterisation and grain realization in order to provide a reference configuration.

Grain manufacturing

To make an homogenous propellant at cold temperature in acceptable chemical compatibility and thermal stability, we have imagined a process in three steps:

1. Mix the oxidizing solution with additives
2. Aluminum powder adding
3. Cooling the propellant in the motor configuration to obtain the adequate mechanical properties.

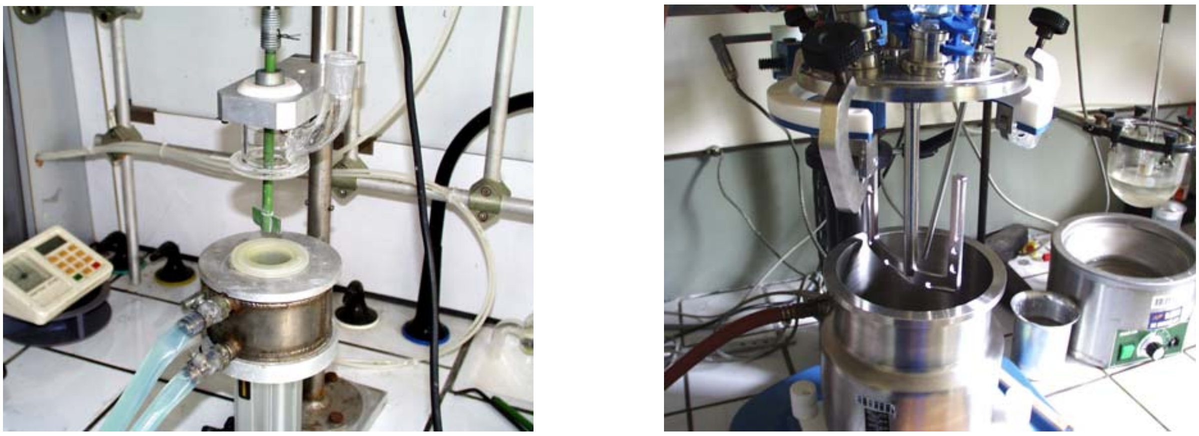

Figure 3 - experimental making of the grains

In these conditions, we can make cold solid propellant with a 30% aqueous hydrogen peroxide solutions with aluminum powder. The temperature of the storage grain is comprised between -35°C to -30°C for obtaining a good solidification.

We had conducted several experiments in order to assess the principal characteristics (stirring speed, temperature of the vessel, and amount of aluminum powder…) in experimental conditions compatible with the scaling up.

Formulation had been optimized to obtain propellant of good quality, without appearing defaults such cracks at refrigerating the sample of propellant, for example, composition 2 is more homogeneous than composition 1 for which some default appearing at low temperature.

Composition 1
H_2O_2 30% + additive 1 + aluminum (79-1-20)

Composition 2
H_2O_2 30% + additive 2 + aluminum (79-1-20)

Figure 4 - ***RSP visualization***

III. Small scale firing test

The proposed formulations are evaluated at small scale setup in order to characterize their burning rate. For a composition close to the ones presented in this study, a stable end-to-end combustion was observed in Ref. [4].

Experimental setup used for small scale tests

One of the main unknown is the burning rate of such compositions. These data are essential for dimensioning the test motor configuration (i.e. throat area with regard to the burning surface and burning rate). For these purposes, two types of tests are imagined.

The first experimental setup was developed at ICARE laboratory. It considers a pipe full with Refrigerated Solid Propellant which is placed in a closed bomb in order to evaluate the influence of the pressure on the burning rate. Specific windows dimensioned to support the pressure up to 20 MPa, allow visualizing the combustion progression in the pipe as it can be observed on Figure 5. The pressurization is ensured by inert gas such as argon to prevent any post combustion with hydrogen generated during the test. The RSP mixture is ignited by a hot wire at the top end and the bottom end is closed by a small plane of glass. These *1cm* diameter pipes are made of glass, so the combustion localization can be visualized and recorded with a high speed camera (Phantom V5 with a speed of 1000 pictures per second). The burning rate is obtained by derivation of the reactive zone position.

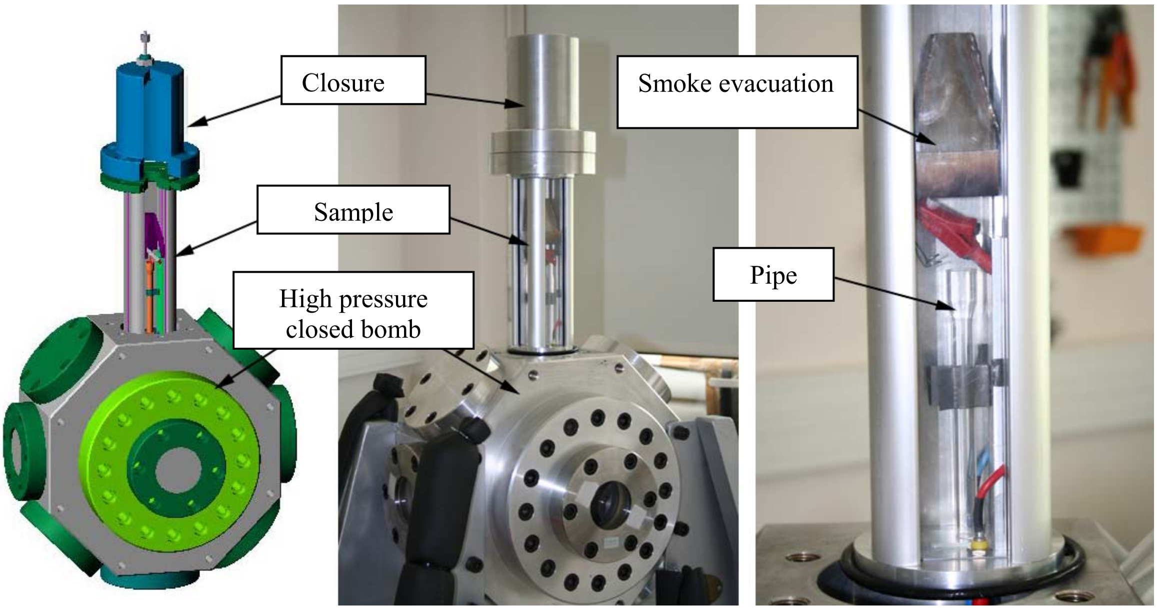

Figure 5 - Experimental setup developed at ICARE laboratory (ICARE Picture)

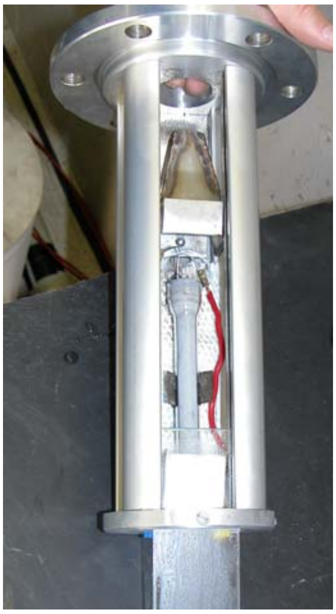

Figure 6 - Experimental pipe filled with refrigerated solid propellant (ICARE Picture)

The second experimental test is devoted to small BATES grains. The aim of this test setup is to validate the ignition and the combustion of the RSP in such a configuration. An ignition pellet is place at the bottom of the tube and the grain presents a cylindrical geometry with a central bore (see Figure 7). This configuration allows the hot gas generated by the ignition pellet and combustion products to be expulsed. For this test, firings are performed at atmospheric pressure.

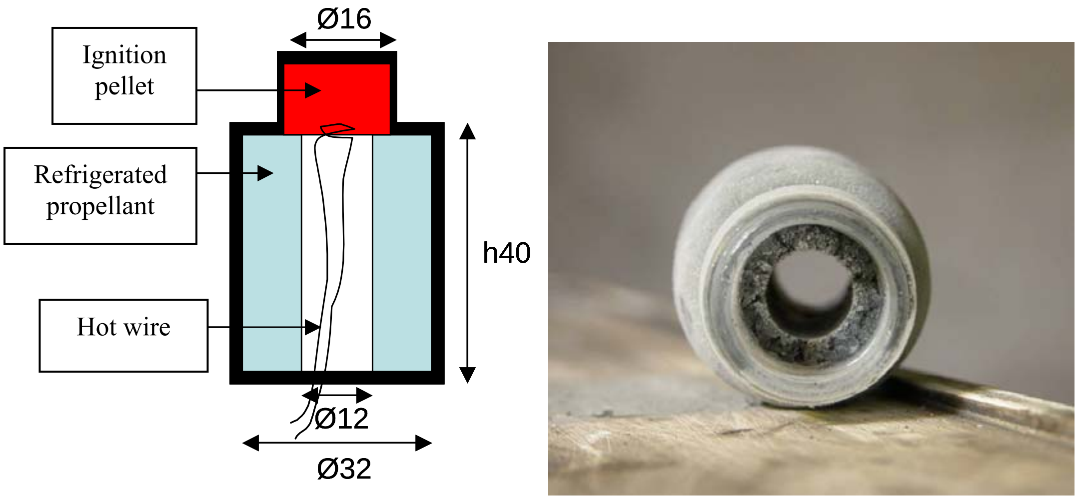

Figure 7 - Schematic view of the mini-BATES setup and RSP material before placing the ignition pellet

Small scale results

The results obtained with small scale tests deal with:

- Compositions ignition
- Ballistic data acquisition

Composition formulations

The tested compositions are presented at the Table 1. The five compositions vary by the nature of the oxidizer or the size of the aluminum powder. Typically micrometric particles are *5 µm* in diameter whereas nanometric aluminum is characterized by an average diameter of *200 nm*. The protective layer of *3-5 nm* thickness is composed by alumina without any other specific coating as it is often found for nanometric aluminum powders.

The first two cases (#7 and #8) are considered in order to characterize the influence of oxidizer. Considering the stability study results, the *5µm* powder is used with H_2O_2. The #9 test tried to optimize the ignition of #8 with adding a small amount of nanometric aluminum in contact with the hot wire. A first *1 cm* thick zone containing nanoaluminium is supposed to be ignited and then to propagate the combustion to the composition containing micrometric sized aluminum. The two last cases are devoted to compositions mixing nanometric and micrometric powders. The total amount of aluminum was increased in order to ensure the combustion propagation by increasing the temperature (the stoechiometric ratio is nearly for 1:1 proportion).

		# 7	# 8	# 9		# 10	# 11
Oxidizer	H_2O_2 30%		70				
	H_2O	70		(10cm) 70	(1cm) 60	60	60
Al powder	Alu 5µm		30	30		20	10
	Alu nano	30			40	20	30

Table 1 – Compositions tested in small scale tests

Ignition

For pipe tests, the ignition is ensured by a hot wire. The tested compositions presented in the Table 1 gave the following results:

- Composition #7 ignited and completely burned.
- Composition #8 ignited but the combustion stooped at *1 cm* from the initial surface.
- Composition #9 was a test to improve the ignition. It appears that combustion propagating strategy from nanometric to micrometric composition failed: the combustion stopped near the transition region. The lower ignition temperature for nanometric *vs.* micrometric sized aluminum powders may be possible explanation.
- Compositions #10 and #11 are mixture of nanometric and micrometric powders. Composition #10 exhibited uncontrolled behavior with stops or normal combustion whereas composition #11 completely burned.

Mini-BATES grains are ignited by hot gases generated by a propellant pellets. Several ignition compositions were tested to determine the most efficient one, but only HTBP/AP/Al propellant successfully achieved the ignition of the refrigerated composition. With TGS and HTPB/AP propellants, a dry material was found in the pipe and no combustion was observed. Another interesting result was the time required to ensure the complete ignition followed by combustion of the energetic material. It appears that ignition needs quite a long time of 4 s. Figure 8 shows the combustion of a composition similar to #11. Large residues ejected from the burning surface can be observed, as well as a post combustion flame resulting from the reaction of generated H_2 with oxygen of ambient air. These results are of practical interest to choose the composition for the making the BATES grain, considering their ability to sustain a self combustion.

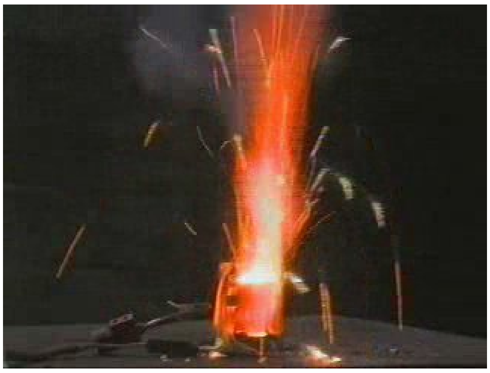

Figure 8 - Combustion of Mini-BATES grain at atmospheric pressure

Ballistics

When combustion is completed, the burning rates are presented hereafter in Table 2. A traditional Vieille law $r_b = aP^n$ is used for modeling this burning rate (r_b in mm/s and P in MPa).

composition	a	n
H_2O/Nano (60/40)	1.57	0.36
#10 H_2O /Nano/Micro (60/20/20)	0.87	0.12
#11 H_2O /Nano/Micro (60/30/10)	3.08	0.3

Table 2 – Ballistic results for the different tested compositions

IV. BATES firing

To conclude the proposed approach, the preliminary firing of a consequent grain raised as a challenge. It was not obvious that the behaviour observed at small scale were the same at a larger scale. It is to be clearly noted that the next section aims to demonstrate the validity of the procedure to achieve and fire such a grain.

The making procedure was adapted to the specificity of the material, especially to take into account of the thermal expansion occurring during the freezing phase. The making of an inert grain (i.e. aluminum was replaced by silica particles) confirmed that the thermal insulation was not damaged by the dilatation of the RSP. Moreover, this grain was conserved several months in a refrigerated room. No evolution of the geometry was observed and the RSP adhesion to insulation material seemed to remain of excellent quality.

Two axi-symmetrical RSP grains were performed following that procedure and the formulation recommendations given in section II. The grains visual aspect seemed to be correct, without any particular defect.

Cylindrical BATES and half-BATES grains were fired at CRB – SNPE Matériaux Energétiques Rechearch Center at the end of 2006. The dimensions for the BATES configuration are as follows: outer diameter of *86 mm*, inner diameter of *60 mm* for a total length of *157 mm*. The next figure shows a picture of the grain which total mass is *550 g (220 g for the half-BATES)*. They are made of the #11 composition (H_2O and a mixture of micrometric/nanometric aluminum powders) and were stored at *–30°C* during one day before firing. The grains do not show any defect, such as crack. During this period, no deformation of the geometry (i.e. no thermal dilatation) was measured before introducing in the study motor (see Figure 9). With regard to ballistic results, the nozzle throat was dimensioned to obtain combustion at *2* and *3 MPa* respectively for the half-BATES grain and the BATES grain. The ignition is ensured by a HTPB/AP/Al propellant chosen for the hot temperature of the provided gases and its ability to ignite such a composition. The web thickness of the igniter is dimensioned for a 4 s burning. Its geometry is a ring inhibited on its lateral surfaces. The *4 s* time was considered long enough to allow the ignition of the refrigerated composition at BATES scale.

Figure 9 – BATES grain after storage

The next figure shows a visualization of the plume resulting of the refrigerated solid propellant combustion. The presented moment corresponds to few milliseconds after the end of combustion of the ignition bloc. At that time, the RSP burns on its own as it was observed during small scale test. The very luminous flame is generated by the post combustion of the hydrogen released by the decomposition of the refrigerated solid propellant and the ambient air oxygen.

Figure 10 – Firing visualization

The combustion chamber was equipped of pressure transducers. The pressure evolutions correspond to the following firings:

- Igniter alone,
- Half-BATES grain,
- BATES grain.

Considering the igniter, it was observed that the performing time corresponds to the desired value of *4s.* and the pressure maximum measured is *1.6 MPa*. The BATES and half-BATES pressure evolution curves indicate that the grain ignition occurs at the beginning of the firing. For this reason, an important ignition peak is observed and the higher pressure evolution reduces the performing time of the igniter. From the analysis of this stage, it can be deduced that the grain ignition is not homogenous on the whole surface. The BATES surface offered to the hot gases is quite twice the one of the half-BATES grain. With the hypothesis of an homogenous ignition, the two configurations cannot present the same pressure levels as it is measured for more than *1s*. This phenomenon is also confirmed by the very long end of combustion. However, a regular combustion is observed after this ignition phase.

An important amount of solid residue was found the combustion chambers for both half-BATES and BATES firings. Performed analyses revealed that a small proportion of unburned aluminum is present in these residues. The mass fraction (around *13 %* of the residue) allows an estimation of *17%* of initial aluminum which does not participate to the combustion and as consequence to the performance. This result may explain the lower pressure measured (*2 MPa vs. 3MPa* expected for BATES configuration).

Conclusion

The Refrigerated Solid Propellant concept offers the possibility to significantly increase energy performance levels of solid propellants.
SNPE Matériaux Energétiques is developing new formulations called "Hydroxalane^{TM}" with a storage temperature as near as possible at room temperature, the range 0°C to minus 20°C seems accessible, to limit to the maximum the drawback induced by the need for cooling the grain. These compositions are homogeneous and the main ingredients are hydrogen peroxide, polymer and metal or metal hydride. The expected specific impulse is between 355 s and 375 s against 315 s for HTPB / AP / Al composition. However the density is lower than for current propellants, between 1377 kg/m^3 and 1462 kg/m^3 compared to around 1800 kg/m^3. This is a disadvantage for volume limited application.
The manufacturing process of the propellants and the selection of raw materials showing good chemical compatibility with hydrogen peroxide had been assessed by laboratory tests. To assess the manufacturing process, a grain (550g) with an internal bore had been realized with a composition based on aluminium and water. This grain had shown very good quality, without any defect, and good bonding properties on the insulator. The combustion properties of this composition had been assessed by firing small grains ($\Phi = 32$ mm, H=40 mn). When one part of the aluminium is nanosized, the grains burn well with a low pressure exponent.

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