Metallized Solid Rocket Propellants Based on AN/AP and PSAN/AP for Access to Space

S. Levi, D. Signoriello*, A. Gabardi*, M. Molinari*, L. Galfetti*, L.T. DeLuca*, S. Cianfanelli** , and G.F. Klyakin****

**SPLab, Dipartimento di Energetica, Politecnico di Milano, I-20156 Milan, Italy*

***Avio S.p.A., Colleferro, I-00034 Rome, Italy*

****South-Russia Technical University, 346428 Novocherkassk, Russia*

Abstract

Solid rocket propellants based on dual mixes of inorganic crystalline oxidizers (Ammonium Nitrate, AN and Ammonium Perchlorate, AP) with binder and a mixture of micrometric-nanometric Aluminum were investigated. Ammonium Nitrate is a low-cost oxidizer, producing environment friendly combustion products but with less specific impulse compared to Ammonium Perchlorate. The better performance obtained with AP and the low quantity of toxic emissions derived by using AN have induced to a good compromise characterized by a mixture of both salts. To improve the thermal response of raw AN, different types of Phase Stabilized Ammonium Nitrate, PSAN and AN/AP co-crystals were investigated.

1. Background

Ammonium Nitrate (AN), an inorganic solid oxidizer already used in rocket propulsion years ago, is still a widely employed oxidizer yielding, with common organic fuels and under thermochemical equilibrium, combustion products with no environmentally harmful constituents. Its relatively low enthalpy of formation is balanced by the low cost of the commercial grade product. Another advantage of AN-based compositions consists in comparatively low sensitivity to mechanical stimuli. Nevertheless, at this stage of development of reduced cost space launchers, all available information concerning the fundamental performance of AN-based energetic materials should be reviewed, with particular attention to their ballistic properties and the actually delivered performance.

Solid rocket propellants presently used in space launchers release, after combustion, a large amount of substances toxic for people and polluting for the environment (HCl, notably). Indeed, current compositions use as oxidizer Ammonium Perchlorate (AP), an inorganic ammonium salt capable of an elevated oxidizing power and thus satisfactory specific impulse. However, in its decomposition mechanism, every mole of AP produces 2 moles of oxygen and also 1/2 mole of chlorine[1]

$$NH_4ClO_4 \rightarrow \frac{1}{2}N_2 + \frac{1}{2}Cl_2 + 2O_2 + 2H_2 \quad \textbf{(1)}$$

Successively, chlorine reacts with other elements released during combustion and generates several polluting substances.

In this work, new propellants aiming at space access and environmental protection are studied. Use of AP was minimized and its presence replaced, partially or totally, by AN. The AN molecule generates non-polluting combustion products and thus can virtually be considered a green oxidizer; besides, raw AN costs about one tenth of AP. Both reasons make AN an attractive option for solid rocket propellant formulation. Nevertheless, employment of AN in space propulsion is not recommended due to a series of negative facts with respect to AP:

- High hygroscopicity: AN crystals easily absorb humidity and expand thus suffering a decrease of density, volumetric specific impulse, and mechanical properties.
- Low density: 1.73 g/cm^3 for AN and 1.95 g/cm^3 for AP.
- Limited oxidation capacity: lower oxygen percentage and decomposition are characterized by a lower monopropellant flame temperature (@ 70 bar 1247 K for AN and 1405 K for AP).
- Several polymorphic phase transitions occurring at -16.9 °C, +32.3 °C, +84.2 °C, +125 °C. The subsequent volumetric changes create mechanical strains that may damage the propellant grain under cyclic variations of temperature. The most disturbing transition is at +32.3 °C, involving a volumetric variation of about 6% at a temperature level easily reached during storage.

- A liquid melting layer accompanies AN combustion.
- Difficult burning in the absence of catalysts.

All of these facts lead in general to inferior ballistic performance of AN-based propellants with respect to AP-based propellants, and underline:

- Relatively low volumetric and weight specific impulses.
- Low burning rate, little affected by particle size but strongly sensitive to pressure and initial temperature.
- Low quality of combustion, with high values of PDL (Pressure Deflagration Limit) and low reactivity at low pressures.

To be technically competitive, AN-based propellants should match the following requirements :

- energy characteristics close to those of the current AP-based propellants;
- absence of AN polymorphic transformations at the expected operating temperatures;
- a satisfactory steady burning rate law (level and sensitivity);
- modest level of specific impulse losses.

For the above reasons, AN applications in space propulsion require additives able to improve the ballistic performance. They should be, at the same time, low-cost and environmentally compatible. Considering the good propulsive performance of the relatively expensive AP and the low environmental impact of the low-cost AN, use of dual-oxidizer AN+AP compositions, with prevalence of AN, seem a good compromise between the two options.

To improve the ballistic performance, metallic additives were investigated. In particular, bimodal micrometric-nanometric Aluminum mixtures were tested. As well known in the literature[2,3,4], the introduction of nanometric Al (nano-Al) powders increases steady burning rates and reduces the size of condensed combustion products. On the other hand, nano-Al suffers production costs larger than micrometric Al (micro-Al) and may cause a decrease of mechanical properties. Moreover, using nano-Al may involve a less effective damping of pressure fluctuations in the combustion chamber.

The presence of polymorphic transformations in the AN crystal is another important problem to be solved, if AP compositions have to be replaced by AN compositions. In this respect, Phase Stabilized Ammonium Nitrate (PSAN) or AN/AP co-crystals offer a possible solution. Phase stabilization of AN is carried out by resorting to various additives. The presence of these additives should not affect the energy characteristics of AN, while intensifying its thermal decomposition and promoting combustion.

The reduced specific impulse and density, with respect to the widely used AP, make AN an oxidizer less than ideal for space propulsion. However, the suggested dual oxidizer system allows to reach a convenient trade-off between the two ingredients. Thus, the long-range objectives of this research program is to identify the (PSAN+AP)-based formulations suitable for space exploration. The specific objective of this work is a trade-off analysis to identify the combination of micro- and nano-Al and the PSAN-AP mixtures optimizing ballistic performance, cost, and environmental impact.

2. Phase Stabilized Ammonium Nitrate

As modifier of the crystalline lattice low-cost potassium nitrate was mainly used[5], while magnesium nitrate was investigated as inhibitor of kinetic processes at transitions. These ingredients were introduced into AN by co-crystallization from melts. The transition energy IV–III of AN, containing 4% of the binary addition potassium nitrate – magnesium nitrate, reveals a minimum if plotted vs. the magnesium nitrate mass fraction. Thus, AN with the addition of the investigated ingredients is stable within the limits from -50°C up to +90°C. A similar picture of phase stability is obtained by introducing into AN a binary addition, where one of the ingredients can virtually be any inorganic salt of potassium.

In a second phase of this research program, an increase of AN thermal decomposition was aimed at while preserving its phase stability. Salts of chromium are the best among the known catalysts of AN thermal decomposition and combustion. Therefore, potassium nitrate in the binary addition was partially or completely replaced by potassium dichromate. PSAN containing 5-6% of combined addition, with different structure, was used in all model solid propellants tested in this work.

The substitution of raw AN by PSAN allows to solve the phase transitions problems.

3. Metallized Dual-Oxidizer Formulations

Table 1 lists the metallized AN+AP dual-oxidizer formulations investigated at Politecnico di Milano – SPLab. All of them contain 68% AN+AP in the ratio 0.6 AN - 0.4 AP, 18% Aluminum, and 14% inert binder composed by HTPB R-45, DOA, and IPDI. The tested formulations only differ for the nano-Al fraction of the metal addition, up to at most 40% of the total metal fraction present in the propellant.

Two types of micro-Al were used in this experimental campaign: the first, called Al_06, is a commercial aluminum powder characterized by irregular shapes similar to flakes with a characteristic size of 50 μm; the second type, called Al_05F, is a propulsive grade aluminum characterized by spherical particles with a characteristic grain size of 30 μm. The nano-Al, called Al_01/a, was produced in Russia by the Electrical Explosion of Wires (EEW) technique; the characteristic grain size of the spherical particles is about 117 nm and its specific surface 15.3 m^2/g.

Table 1: Metallized AN+AP dual-oxidizer propellants investigated at SPLab

Name	Oxidizer 68%	Aluminum 18%		Binder 14%
		Micro Al_06	Nano Al_01/a	
Nano_0%	60% AN ($d_p < 200$ *μm*) + 40% AP (80*μm* < d_p < 140*μm*)	100%	0%	79,21% HTPB + 13,11% DOA + 7,68% IPDI
Nano_10%		90%	10%	
Nano_20%		80%	20%	
Nano_30%		70%	30%	
Nano_40%		60%	40%	
		Micro Al_05F	**Nano Al_01/a**	
F-Nano_0%	60% AN ($d_p < 200$ *μm*) + 40% AP (80*μm* < d_p < 140*μm*)	100%	0%	79,21% HTPB + 13,11% DOA + 7,68% IPDI
F-Nano_10%		90%	10%	
F-Nano_20%		80%	20%	
F-Nano_30%		70%	30%	
F-Nano_40%		60%	40%	

Table 2 reports the measured and calculated density values of all manufactured propellants, assuming for metallic Al its bulk density. The Nano_20% and the F-Nano _40% formulations show the closest density to the calculated value. For the explored test conditions, this suggests a better propellant matrix with respect to the remaining formulations.

Table 2. Density of metallized AN+AP dual-oxidizer propellants investigated at SPLab

Name	Density, g/cm^3 (measured)	Density, g/cm^3 (theoretical)
Nano_0%	1.566	1.680
Nano_10%	1.587	
Nano_20%	1.652	
Nano_30%	1.640	
Nano_40%	1.603	
F-Nano_0%	1.586	1.680
F-Nano_10%	1.550	
F-Nano_20%	1.622	
F-Nano_30%	1.655	
F-Nano_40%	1.676	

Table 3 lists and provides details about the metallized PSAN-AP co-crystallized dual oxidizer propellants investigated at SPLab.

Table 3. Details of metallized PSANco-cry dual oxidizer propellants.

Propellant	ϕ	Aluminum	Binder	Oxidizer	Grain size (μm)
Co-cry_(200-400)	1.502	Al_06 18%	14%	68%Co-cry	200-400
Co-cry_(200)	1.502	Al_06 18%	14%	68% Co-cry	<200
Co-cry_(70)	1.502	Al_06 18%	14%	68% Co-cry	<70
Co-cry_bimodal	1.502	Al_06 18%	14%	68% Co-cry	40% 200-400 28% 80-140
Co-cry-AP	0.525	Al_06 18%	14%	40% Co-cry, 28%AP	Co-cry <70 AP 80-140
Co-cry SPLab	1	Al_06 18%	14%	68% Co-cry	40%200-400 28% 80-140

4. Experimental results

The experimental ballistic testing systematically carried out at SPLab includes in particular measurement of steady burning rate and ignition delay. Propellants containing AN as oxidizer are characterized by high PDL values. Notice that below some critical pressure, only the oxidizer takes part in the combustion process and the sample leaves a carbon skeleton with a size comparable to that of the burning surface. For the investigated propellants, this critical pressure was about 10 bar and therefore burning rates were measured at pressures of 20, 30 and 50 bar.

The Nano_0% propellant (i.e., the formulation containing only micrometric Al) is characterized by steady burning rates sensibly depending on pressure and lower compared to those of current space launchers. For increasing nano-Al amount, pressure sensitivity decreases while steady burning rates increase thanks to larger specific surfaces. However, for nano-Al above 20%, these positive effects tend to vanish, probably due to an increasing influence of chemical kinetics with respect to diffusive mechanism. Thus, the optimum formulation seems to be the one denoted as Nano_20%, combining suitable burning rates and low pressure sensitivity.

The measured ballistic laws of the tested SPLab propellants are shown in Figs. 1 and 2 and summarized in Tab. 4. The F-propellants containing spherical micro-Al exhibit a similar ballistic law as the flaked micro-Al propellants.

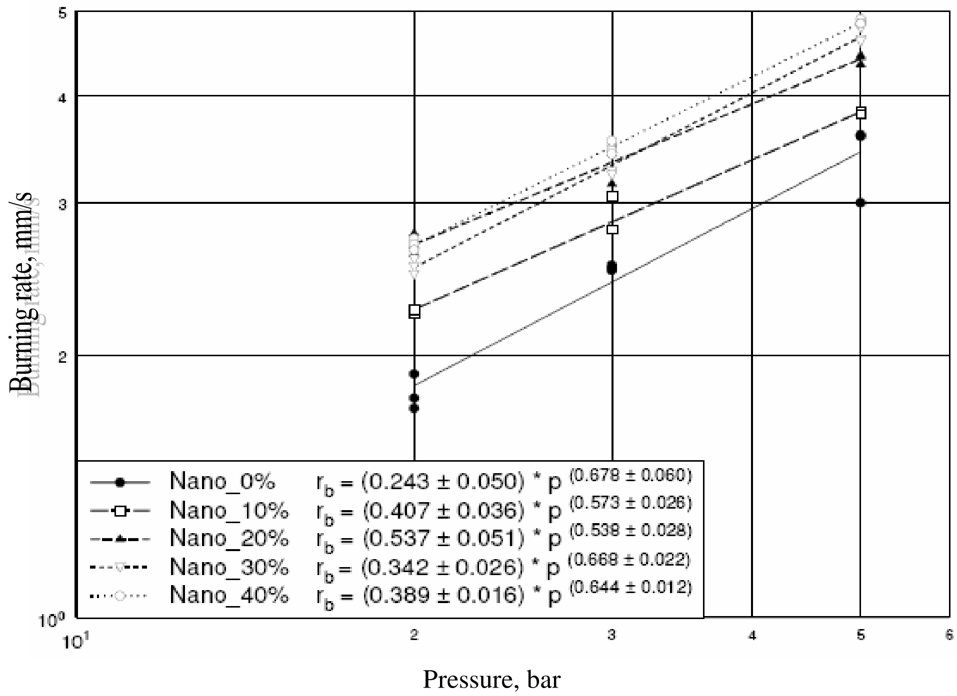

Figure 1. Burn rate vs. pressure for SPLab propellants with flaked micro-Al

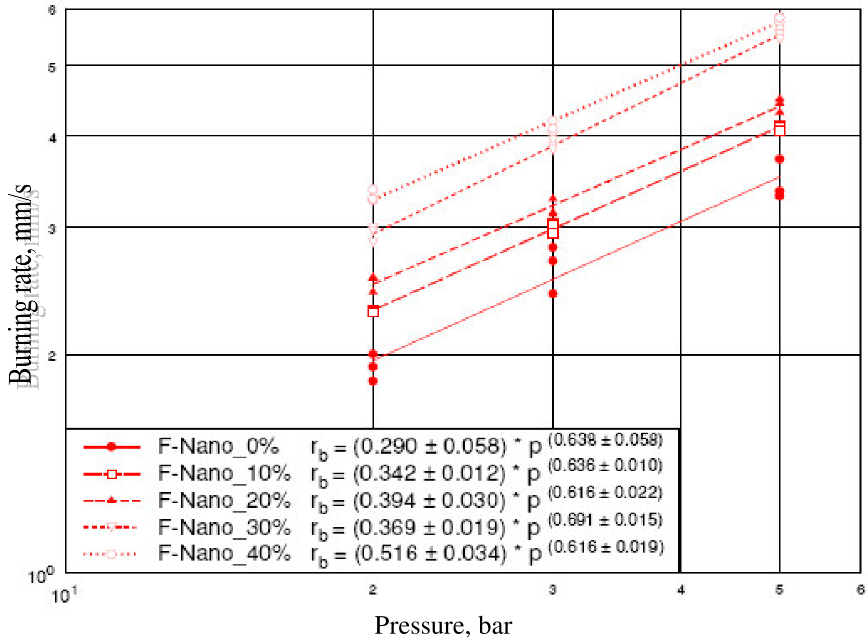

Figure 2: Burn rate vs. pressure for SPLab propellants with spherical micro-Al

Table 4. Vieille's Law and GDF model for SPLab propellants

Propellant	*Vieille's Law* $r_b = a \cdot p^n$	R^2	*GDF model* $p / r_b = a + b \cdot p^{(2/3)}$ *a* [bar·s/m]	*b* [bar$^{(1/3)}$·s/m]	*a / b* [bar$^{(2/3)}$]	R^2
Nano_0%	$r_b = (0.243 \pm 0.050) \cdot p^{(0.678 \pm 0.060)}$	0.931	6.219	0.625	9.950	0.791
Nano_10%	$r_b = (0.407 \pm 0.036) \cdot p^{(0.573 \pm 0.026)}$	0.987	3.812	0.686	5.557	0.980
Nano_20%	$\mathbf{r_b = (0.537 \pm 0.051) \cdot p^{(0.538 \pm 0.028)}}$	0.984	2.842	0.629	**4.518**	0.977
Nano_30%	$r_b = (0.342 \pm 0.026) \cdot p^{(0.668 \pm 0.022)}$	0.993	4.639	0.450	10.309	0.968
Nano_40%	$r_b = (0.389 \pm 0.016) \cdot p^{(0.644 \pm 0.012)}$	0.998	4.117	0.458	8.989	0.989
F-Nano_0%	$r_b = (0.290 \pm 0.058) \cdot p^{(0.638 \pm 0.010)}$	0.937	5.294	0.668	7.925	0.865
F-Nano_10%	$r_b = (0.342 \pm 0.012) \cdot p^{(0.636 \pm 0.010)}$	0.998	4.645	0.554	8.384	0.995
F-Nano_20%	$\mathbf{r_b = (0.394 \pm 0.030) \cdot p^{(0.616 \pm 0.022)}}$	0.992	4.094	0.537	**7.624**	0.974
F-Nano_30%	$r_b = (0.369 \pm 0.019) \cdot p^{(0.691 \pm 0.015)}$	0.997	4.234	0.357	11.860	0.983
F-Nano_40%	$r_b = (0.516 \pm 0.034) \cdot p^{(0.616 \pm 0.019)}$	0.994	3.179	0.406	7.830	0.976

The above results point out that the metallized dual-oxidizer AN+AP propellants, with bimodal micro-nanometric Al addition in the ratio 0.80 micro flakes - 0.20 nano, takes on ballistic properties similar to those of the current mono-oxidizer propellants. Using spherical micro-Al the situation is the same or sometimes worst: in fact F-Nano_20% has a lower multiplicative factor "a" than Nano_20%, a larger pressure sensitivity and also a bigger a/b ratio in the GDF model. The F-Nano_40% shows similar ballistic properties as Nano_20% but is more expensive because of the larger nano-Al fraction.

4.1 Burning rate of PSAN-AP propellants

Steady burning rates of propellants based on PSAN are important to understand the role of the additives and to search ecologically compositions featuring ballistic performance comparable to those of AP-based propellants. Previous experimental tests, carried out at SPLab about PSAN oxidizers created in Russia, indicated that PSAN+AP mixtures (60% PSAN and 28 % AP) produce energetic formulations with steady burning rates comparable to those of AP-based propellants. Co-crystals of PSAN and AP, an innovative oxidizer produced through co-crystallization of Ammonium Nitrate and Ammonium Perchlorate, allow obtaining burning rates even higher than those of AP-based formulations. Co-crystals are obtained from a watery solution, where AN and AP are in the form of eutectic mixture.

This oxidizer burns at atmospheric pressure and may help to solve the problems connected with the high PDL and high pressure exponent observed in the steady burning rate analyses. These positive effects might take place thanks to the close contact between AN and AP particles in the eutectic mixture. Under the operating pressures typical of rocket motors, PSAN-AP or Co-cry formulations show burning rates comparable to those of AP-based propellants (see Fig. 3). The difficulty of the ballistic performance in PSAN-AP or Co-cry formulations is the pressure exponent that, compared to AP-based propellants, turns out higher also in bimodal-co-cry formulations.

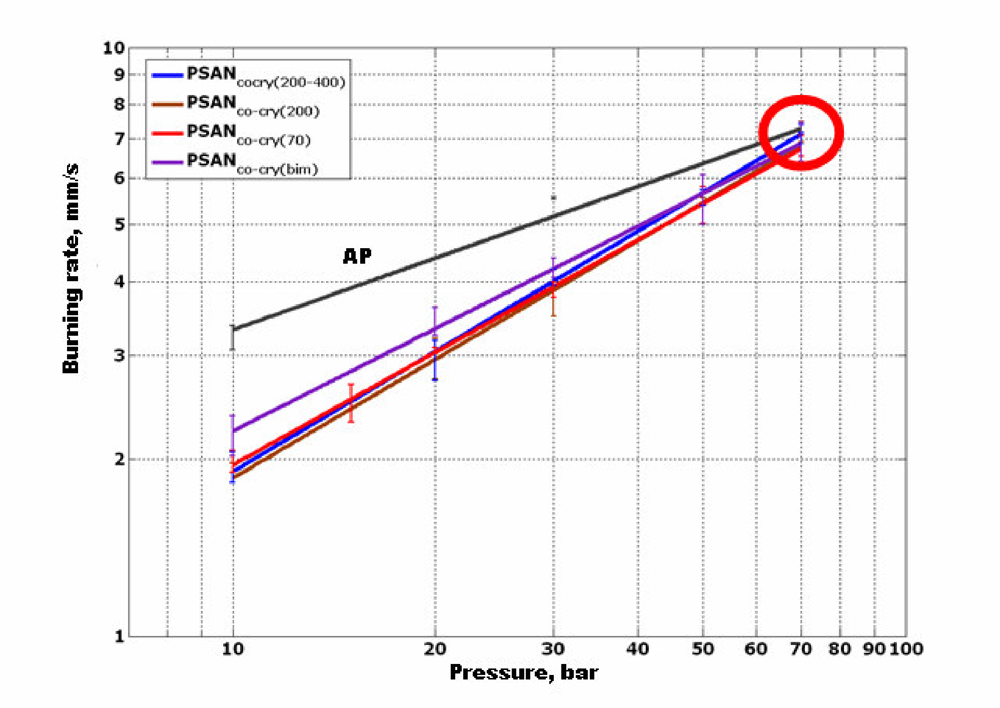

Figure 3. Comparison between performance of PSANco-cry based propellants and AP-based propellant.

To resolve the problem of the high pressure exponent of PSAN formulations, a new compositions based on Co-cry with mechanical addition of AP (AN / AP = 0.525) was tested, to understand how the ballistic properties depend on increasing AP percent. The obtained results point out that the addition of AP implies higher burning rates but no change in the pressure exponent (see Fig. 4).

On the contrary, if the AP addition in the formulations occurs through an eutectic mixture, pressure exponents lower with a lower AP percent are found. To verify this co-crystallization trend, a new Co-crystal oxidizer synthesized at SPLab with the ratio AN/AP = 1 was tested. This formulation is characterized by a pressure exponent exactly alike the characteristic value of AP formulations (see Fig. 5).

The important conclusion about ballistic performance of PSAN co-cry is that co-crystallization of the eutectic mixture (PSAN+AP) allows obtaining formulations with a ballistic behavior similar to those of AP-based propellants, but with a lower AP percent. Regarding the pressure exponent, the optimal ratio PSAN/AP is 1 (50% PSAN co-crystallized with 50% AP) yielding $n = 0.42$.

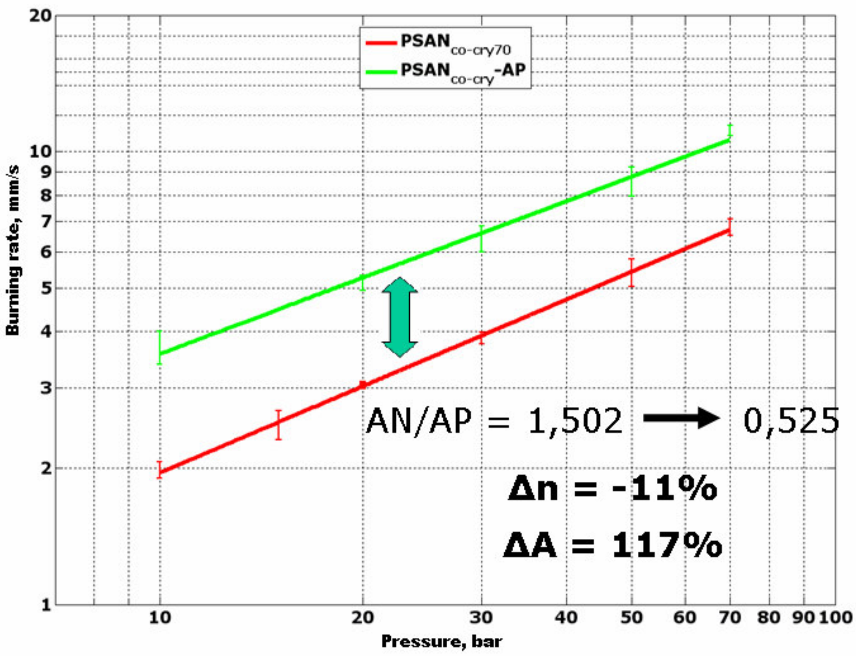

Fig. 4- Ballistic comparison between PSANco-cry propellant and PSANco-cry propellant with a mechanical addition of AP in the formulation.

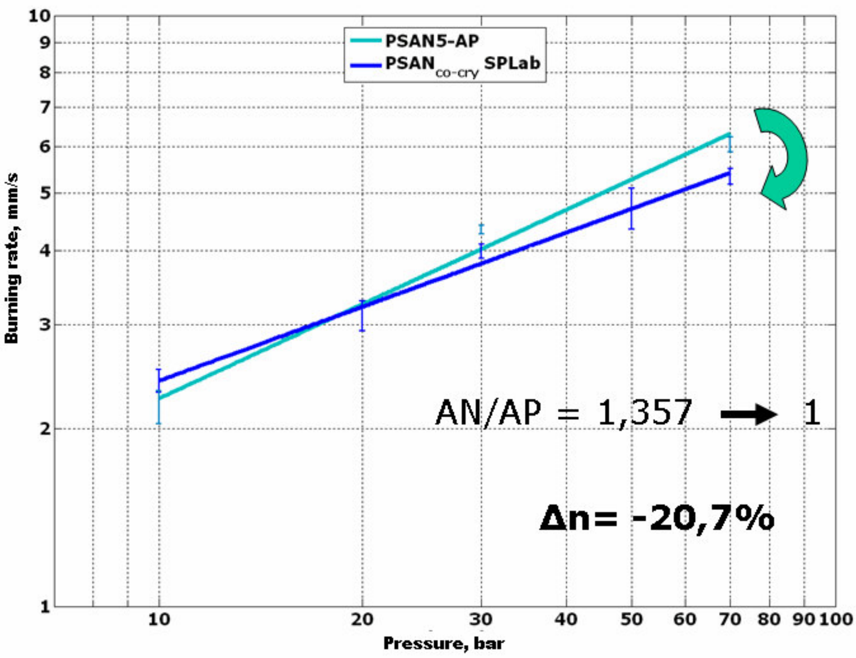

Fig. 5- Ballistic comparison between a generic PSAN-AP propellant and a PSANco-cry SPLab propellant.

4.2 Ignition Delay on PSANCo-cry compositions

Ignition delay tests were carried out on PSANco-cry compositions, to understand the influence of the eutectic mixture on the ignition time. Also in terms of ignition delay, PSANco-cry and AP formulations show a similar behavior (see Fig. 6).

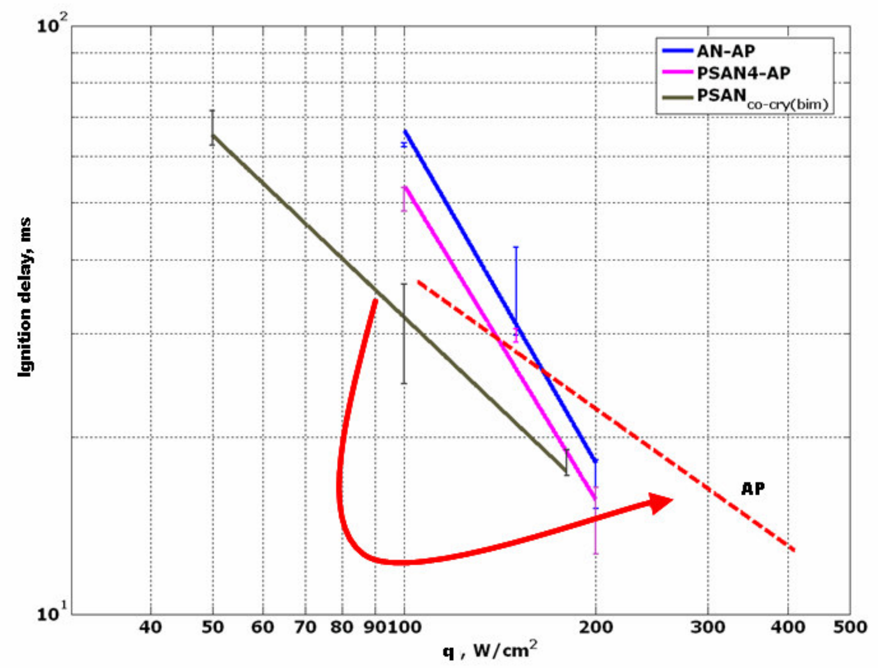

Fig.6 – Ignition delay of propellants based on PSAN and PSANco-cry

5. Conclusion

AP/AN based propellants with bimodal Al concentrations tend to show interesting performance even with a limited use of nanoAl (expensive) and using flaked microAl (low-cost) instead of spherical microAl. On the other hand, to reach a performance virtually equivalent to pure AP-based propellants, one can use a PSAN/AP formulation (with 50 % AP + 50% AN) to strongly reduce the pollutant emissions, even if costs are comparable to those of AP-based propellants. At this stage of the underlying research work, it is fair to say that Ammonium Nitrate (AN) is potentially capable to assure the manufacture of ecologically safe solid propellants, but certainly further work is needed to assure acceptable costs and performance.

References

[1] Politzer, P. and Lane, P. Energetics of Ammonium Perchlorate Decomposition Steps. *Journal of Molecular Structure (Theochem),* Vol. 454, pp. 229-235, 1998.

[2] Price, E.W. and Sigman, R.K. Combustion of Aluminized Solid Propellants. *Solid Propellant Chemistry, Combustion, and Motor Interior Ballistics, Progress in Astronautics and Aeronautics,* Vol. 185, edited by V. Yang, T.B. Brill, W.Z. Ren, AIAA, 2000, pp. 663–687.

[3] Dokhan, A., Seitzman, J.M., Price, E.W. and Sigman, R.K. The Effects of Al Particle Size on the Burning Rate and Residual Oxide in Aluminized Propellants. *37th AIAA / ASME / ASEE Joint Propulsion Conference and Exhibit,* July 2001, AIAA Paper No. 2001–3581.

[4] Il'in, A.P., Gromov, A.A. and Yablunovskii, G.V. Reactivity of Aluminum Powders. *Combustion, Explosion and Shock Waves,* Vol. 37, No. 4, pp. 418-422, 2001.

[5] Vorozhtsov, A.B., Arkhipov, V, Bondarchuk, S., Popok, N., Klyakin, G., Babuk, V., Kuznetsov, V., Sinogina, E., DeLuca, L.T. and Galfetti, L. Ballistic Characteristics of Solid Propellants Containing Dual Oxidizer. *European Conference for Aerospace Sciences (Eucass),* Moscow 2005.

[6] Babuk, V.A., Glebov, A. , Arkhipov, V.A., Vorozhtsov, A.B., Klyakin, G.F., Severini, F., Galfetti, L. and DeLuca, L.T. Dual Oxidizer solid rocket propellant for low-cost access to space. *10 IWCP*, Grafiche GSS, Bergamo, Italy, Nov 2005, paper 15.

[7] Sinditskii, V.P., Egorshev, V. Yu, Tomasi, D. and DeLuca, L.T. Combustion mechanism of AN based propellants. See Proceedings of this Conference.

A revised version of this article is availabe here.