JOURNAL OF PROPULSION AND POWER
Vol. 15, No. 5, September–October 1999

Industrial Constraints for Developing Solid Propellants with Energetic Materials

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The safety, processability, and performance of new advanced composite propellants have to be fully characterized during the phases of development and preindustrialization. In fact, the use of alternative materials can involve risks of incompatibility with the current aereospace technology. The major industrial constraints for a short-term application of innovative clean energetic propellants are exposed in this paper. Starting from the improvement of the actual performance, several formulations have been taken into account, mainly under the processability and safety points of view. This last aspect was deeply investigated by detonability tests aimed to correlate the sensitivities of new energetic components with the hazard characteristics of the relevant propellants.

Introduction

SOLID-PROPULSION technology has been under development for many years and has reached a suitable level of reliability to enable its routine use. For example, present commercial space launch systems generally utilize solid rocket propulsion during the launch and/or boost phases either as the main engines (small launchers) or as strap-on boosters (large launchers). However, improvements in propulsive performance and environmental compatibility are still sought after within operational parameters. BPD Difesa e Spazio (since January 1997 Fiat Avio) has been working in this area for more than 20 years as major industrial shareholder in the manufacturing of solid motor strap-on boosters (for European Launchers Ariane 4 and Ariane 5) and the ongoing development of the VEGA family lightsat launchers. In this paper we will address the issues of performance improvement and environmental issues real or supposed from the standpoint of eventual process industrialization with emphasis on real-world constraints from the start of the development cycle.

Commercial launch system are conceived based on multiple layers of requirements that cascade from the system-level final launcher requirements down through component and subassembly level requirements including the solid motor materials and propellants. Solid-rocket motor performance has a major impact in defining the flight path and launcher attitude. Significant mission compromises and economic impacts can result whenever anomalies with respect to the nominal performance requirements occur.

To minimize these types of risks, the solid propulsion technology has been deeply investigated and is still the object of further upgrading focusing the attention on the following criteria: 1) safe handling and operations, 2) performance reliability and reproducibility, and 3) cost minimization. At the solid propellant level that is, the heart of the propulsion, these topics are translated in several requirements involving not only the final characteristics but also the overall manufacturing cycle starting from the raw materials up to the equipments and the relevant process parameters controls.

In the aim to improve the solid-rocket propulsion, the worldwide research activities are working on new energetic ingredients as hexanitrohexaazaisowurtzitane (Cl20), ammonium dinitramide (ADN), hydrazinium nitroformate (HNF), and energetic binders, either for environmental impacts or for energetic upgrading. Fiat Avio is strongly engaged in this field, focusing its contribution not only on scientific aspects but also on the industrial consideration in the perspective of real full-size application. Any future generation of propellants, in fact, have to meet the preceding criteria before any fruitful utilization by the space or military communities.

This paper summarizes the results of the industrial approach connected to the use of some new energetic materials and the relevant obtained propellants.

Improved Propellants Formulations

Better Theoretical Performance

Although generally accepted, data suggest that HCl emissions from the use of solid propellants are not a contributor to any environmental impact; a search continues into nonchlorine propellants.

The redox performance of the ammonium perchlorate/aluminum (AP/Al) combination represents the best optimization of this technology, achieved through more than 20 years of applications and developments. For this other conventional oxidizers [as Ammonium Nitrate (AN)] give lower performance in terms of specific impulse and density.

In the aim to increase performance and minimize the HCl evolution of a new generation of propellants, several classes of energetic oxidizers have been the object of studies for the AP substitution. Some of the new oxidizers come from the explosives industry, whereas the remaining have been conceived and synthesized specifically for their use in composite propellant formulations.

In Table 1 a comparison between new and conventional oxidizers is given, focusing the attention on the information necessary for theoretical calculations and safety processing assessment.[1–3]

The genesis of a new propellant have to pass through two phases: theoretical calculations and experimental testing.

The first step is the preliminary screening of the materials, aimed to define the best combination of the ingredients for the energetic output. Computer codes such as ODE or GORDON (NASA codes) are commonly used for this purpose. The second phase is really the first critical gate, representing the feasibility verification of the families arising from the theoretical evaluation, which includes not only experimental performance, but also processability in terms of safety and reliability.

Processability

Taking into account the sensitivity data of the materials in Table 1, several constraints have to be considered for their safe handling and processing.

In fact, the new ingredients show sensitivity characteristics comparable to the cylotetramethylene tetranitramine (HMX) (explosive, class 1.1 when flegmatized with 15% water minimum). As

Presented as Paper 97-2925 at the AIAA/ASME/SAE/ASEE 33rd Joint Propulsion Conference, Seattle, WA, 6–9 July 1997; received 12 September 1997; revision received 27 March 1999; accepted for publication 8 April 1999.

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Table 1 Raw materials sensitivity and technical characteristics

Material	Density, g/cm^3	Enthalpy of formation, kj/mole	Melting point, °C	Decomposition point, °C	O_2 balance, %	Impact sensitivity, Nxm	Friction sensitivity, N
AP	1.950	−16.7	235	235	34	15	>100
AN	1.720	−20.9	169	210	20	>49	353
HMX	1.960	74.4	282	287	−21.6	7.4	120
ADN[a]	1.800	−8.3	93	134	25.8	3.7	>350
HNF[b]	1.860	−72	≥115	≥115	13	3	20
CL20[c]	2.040	23.3	>195	N/A	10.9	2.5	124

[a]Data from Ref. 1. [b]Data from Refs. 2 and 3. [c]Data from Ref. 1.

Table 2 Propellant performance and hydrochloric emissions

Propellants	Acronym	Computed Isp, s	d, g/cm^3	Computed volumetric impulse, sxg/cm ^{3}	HCl emission, g_{HCl} per kg of propellant
$HTPB_{14}/AP_{68}/Al_{18}$	STD	264.5	1.759	465.2	192
Scavenged 0.5[c]	SCAV	256.3	1.810	463.9	100
$HTPB_{14}/AP_{58}/HMX_{10}/Al_{18}$	HMX-1	265.9	1.765	469.3	164
$PNIMMO_{30}/HNF_{70}$	HNF-1	261.3	1.633	426.7	0
$PNIMMO_{30}/HNF_{60}/Al_{10}$	HNF-2	271.6	1.679	456.0	0
$PNIMMO_{30}/HNF_{50}/AP_{15}/Al_5$	HNF-3	264.8	1.665	440.9	45
$GAP_{20}/HNF_{60}/Al_{20}$[a]	HNF-0	284.6	1.940	552.1	0
$HTPB_{15}$ ADN_{65}/Al_{20}[b]	ADN-0	274.0	1.670	456.0	0

[a]See Ref. 3. [b]See Ref. 1. [c]$HTPB_{14}/AP_{53}/NaNo_{315}/Al_{18}$.

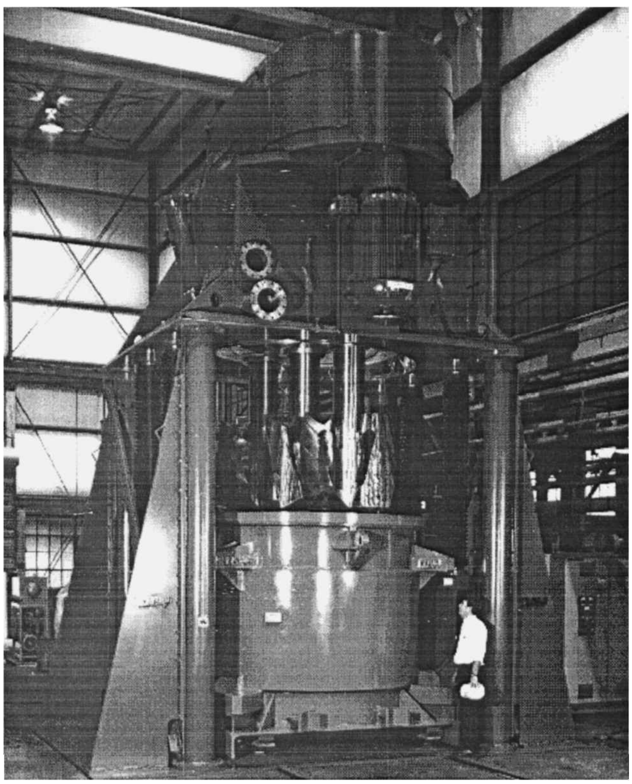


Fig. 1 12-ton-size mixer for processing composite propellant for ARIANE 5 boosters in Regulus (Kourou, French Guyane).

consequence, the main process steps involving some friction and impact stimuli, such as the oxidizer adding to the mixer and the mixing phase, have to be carefully considered for the possible reaction effects. This aspect is taken under control by explosive factories working in the military ammunition field as a normal part of the work, but it may cause some problems in the aerospace propulsion area for the larger masses to be processed.

As a major example, for loading large-size booster motors (240 tons, ARIANE 5 boosters), a multibatch process is required by the use of 3.5 and 12 ton size mixers (Fig. 1). The importance of the hazard aspects of the materials under manufacturing, considering any accidental failure of the system with the consequent reaction of the substances in the pot and/or in the feeding lines and tanks, is immediately obvious.

Additional problems can arise if a milling or recrystallization of the raw materials are required to achieve the suitable particle size or shape. These are directly linked to the propellant castability and is a non-negligible characteristic for obtaining propellant grains free from voids, bubbles, or cracks that could compromise the structural integrity of the final motor.

This criticality has been confirmed during the preparation of the new propellant samples, recording shorter pot-lives and increased viscosity values (after 4 h from cross-linking agent adding, the viscosity reaches 1500 Pa · s or more). Despite these challenges, specimens free of defects under X-ray inspection have been obtained following the small-scale process that allowed more flexible parameters for reduced manufacturing time and propellant quantities.

Energetic and Clean Propellants

Several samples have been manufactured and investigated using some oxidizers listed in Table 1 in combination with an energetic poly-3-nitratomethyl-3-methyoxane (PNIMMO) or inert hydroxy-terminated polybutadiene (HTPB) binder.

Table 2 summarizes the energetic and HCl emissions performance of the experimented formulations together with standard chlorinated or acid-reduced propellants (scavenged).[1,4] In addition, further formulations proposed in the international scenario are taken into account, drawing data from Ref. 1.

AN-based propellants have not been taken into account because they do not present any significant impact on the technology for the insensitivity of the raw materials. The problems connected to their processing are mainly linked to the phase transition and hygroscopicity of the AN crystals, as well as to drastically reduced performance such that AN formulations are not viable replacements in current booster configurations. The considered formulations, in fact, have been selected to evaluate at which level the hazard characteristics of the propellants are affected by the sensitivites of the oxidizers.

For this purpose, three hydrazinium nitroformate (HNF)-based formulations have been manufactured and tested, not to optimize performance but only to draw information about processability and safety. For a concept of maximum energy with HNF, the formulation HNF-0 can be considered.[5] The adding of ammonium perchlorate

(AP) to HNF-3 is suggested by the low degree of burning-rate control of explosives when used in combustion conditions.

On the contrary, cylotetramethylenetetranitramine (HMX)-1 represents one of the best energetic optimization[4] using this additive. Anyway, to evaluate the boundaries of the use of an explosive as one of the main ingredients in propellant mixes, additional formulations with an increased amount of HMX (replacing 20 and 40% of AP in STD propellant) have been manufactured only for testing in hazard experimental topics. These formulations can be reasonably assumed as equivalent under the safety point of view to formulations containing high explosives as energetic oxidizers [i.e., hexanitrohexaazaisowurtzitane (CL20) (Ref. 6)]. In fact, if the raw materials' sensitivities are the major constraints for the propellant manufacturers, the propellant hazard classification and, still more, its mode of reaction under strong stimuli must be in interest of the overall community.

Propellants Hazard Testing

To establish the potential way of the reaction of the new propellants' families, the following formulations have been subjected to the solicitation of the shock wave generated by an explosive donor charge [glycidyl azide polymer (Gap) test]: STD, SCAV, HMX-1, HMX-2 (composite propellant with 20% HMX), HMX-3 (composite propellant with 40% HMX), HNF-1, HNF-2, and HNF-3.

Because of the raw materials availabilities and costs, two different topics of Gap test have been used for HMX and HNF series (Card Gap test and modified BICT Gap test, respectively). In addition, to characterize fully the nature of the reaction and the order of magnitude of the reaction velocity, X-ray tests have been carried out in line with the detonic experiments.

Card Gap Test Experimental Layout

This test measures the sensitivity of the material to detonation shock generated by a donor charge establishing its attitude to propagate the detonation wave. The test apparatus (Fig. 2) consists of one piece of steel tube, an electric detonator, a 95/5 cycletrimethylene trinitramine (RDX)/wax donor charge ($\Phi = 40$ mm, $h = 160$, 4 mm thick), a $15 \times 15 \times 1$-cm steel witness plate, and the cylindrically shaped ($\Phi = 40$ mm, $h = 200$ mm) propellant specimen to be tested.

Between the donor charge and the test specimen, cellulose acetate or equivalent material cards 0.02 cm thick can be inserted to attenuate the shock wave of the donor charge establishing the number necessary to prevent a reaction. The tests decribed in this paper have been carried out placing the donor charge directly in contact with the propellant specimen to operate under conservative conditions.

As reported in STANAG 4488 (Ref. 7), the nature of the reaction is indicated by the damages recovered on the witness plate.

BICT Modified Gap Test Experimental Layout

Similar to the Card Gap test, the BICT test[7] measures in a smaller scale the sensitivity of a sample to a shock wave generated by a donor charge and attenuated by water. For this experiment set the tests were carried out without water for incompatibility with HNF and for keeping conservative conditions.

The test apparatus (Fig. 3) consists of a piece of 2014 aluminum alloy tube ($\Phi = 21$ mm, $h = 40$, 3 mm thick) filled with the propellant sample, a 95/5 RDX/wax donor charge ($\Phi = 21$ mm, $h = 21$ mm) drilled on the top for the electric detonator positioning, and a $10 \times 10 \times 4$-mm aluminum alloy witness plate. Also in this test the nature of the reaction is identified by damages recorded on the witness plate.

Flash X-Ray Experimental Layout

The specimens equipped for detonation tests (either Card Gap and BICT) were placed between the film and the X-ray source (600 kV, exposure time 12×10^{-9} s). The specimens and the detonic equipment were scanned once at the beginning of each test before detonator initiation, to have a reference of the starting positions (T_0). The second impressions of the film were recorded for Card Gap and for BICT tests respectively 45.2 and 12.3 μs from the event. These times were selected on the basis on the results of the first detonic test series, formulating a hypothesis on the possible shock-wave velocity. The target, in fact, was to capture the moment of the burst of the metallic cases containing the propellant samples.

Table 3 Detonic tests results

Propellant	Type of reaction
STD	None
SCAV	None
HMX-1	Deflagration/detonation
HMX-2	Detonation
HMX-3	Detonation
HNF-1	Detonation
HNF-2	Detonation
HNF-3	Detonation

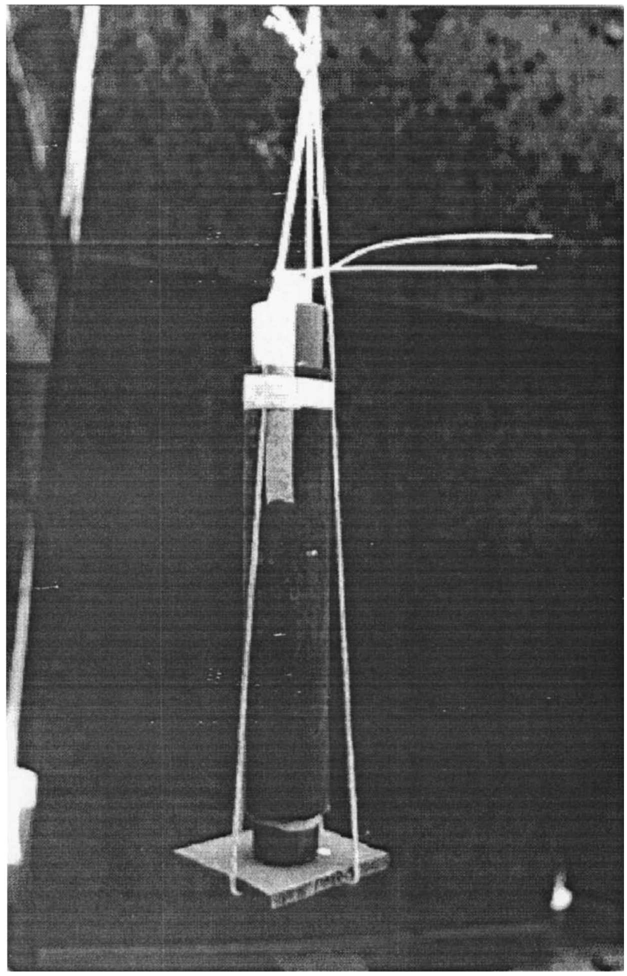


Fig. 2 Card Gap test specimen before firing.

Results and Discussion

The results of the detonic tests are summarized in Table 3. These conclusions arise from the appearance of damages on the witness plates and fragments size of the metallic cases, as shown in Figs. 4 and 5 for Card Gap tests and BICT Gap tests, respectively. The aptitude to propagate the detonation is evident for samples containing 20 and 40% of HMX, showing a detonation velocity proportional to HMX content, as expected. This is demonstrated both by the neat hole punched in the witness plates and the fragment sizes.

In the case of the sample HMX-1, (10%HMX) the size of the hole and fragments puts the reaction in the deflagration region even if its velocity of propagation seems very close to the supersonic limit.

The STD and SCAV propellant samples did not exhibit any reaction; in fact, the witness plates were recovered undamaged, and the

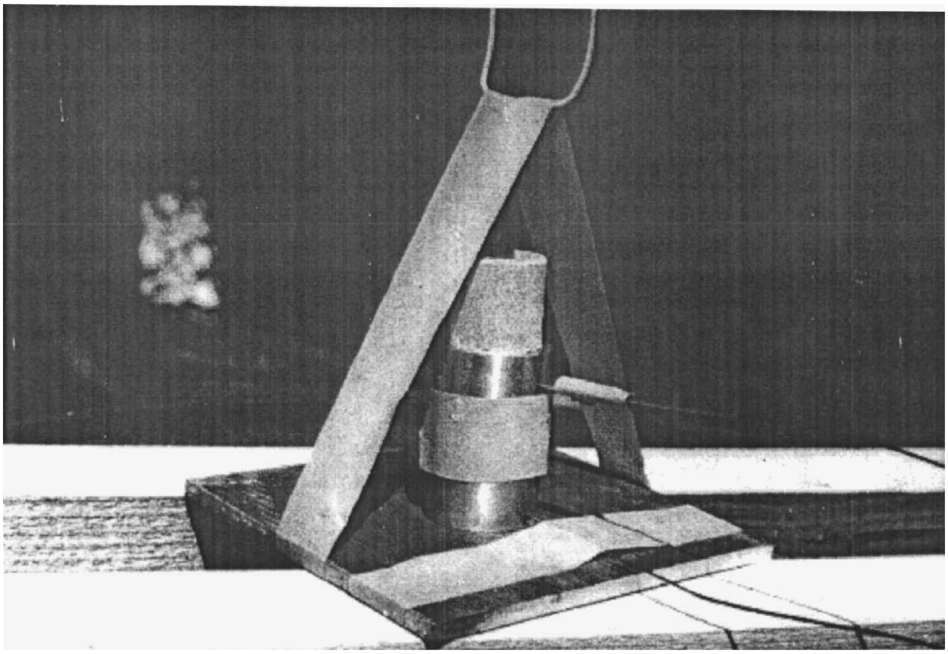
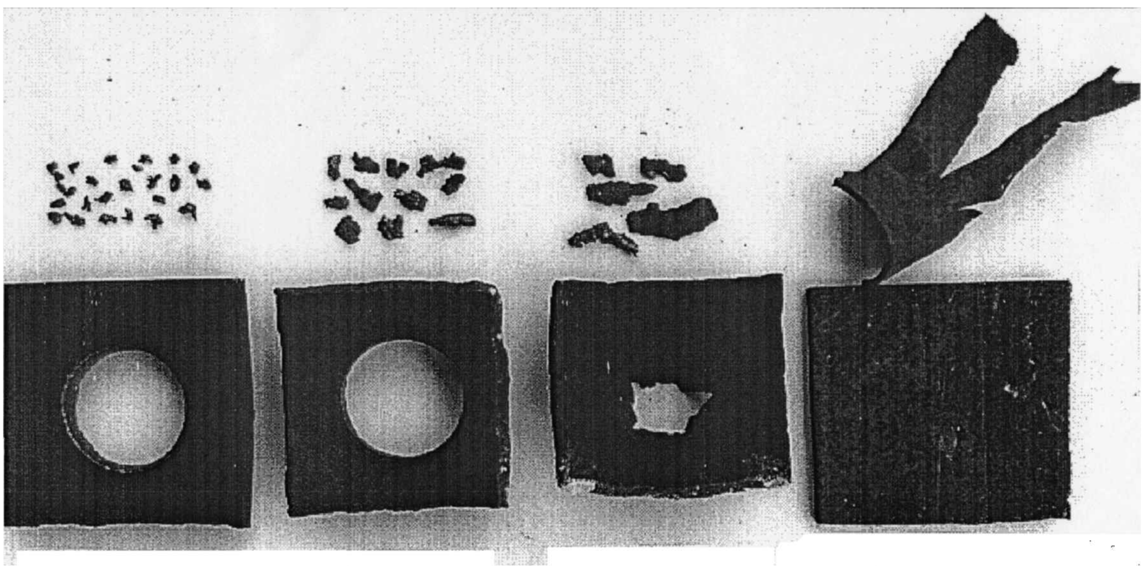


Fig. 3 Modified BICT Gap test specimen before firing.



HMX-3 (40%)	HMX-2 (20%)	HMX-1 (10%)	SCAV and STD
Test n°5	Test n°4	Test n°3	Tests n°1 and 2

Fig. 4 Card Gap test witness plates and fragments after firing.

cases showed only the effects of the donor charges. All HNF-based propellants (Fig. 5) propagated detonation, as is clearly shown from the neat holes on each witness plate and fragment, which are typical of a detonation reaction. Significant differences across the range of HNF compositions do not seem to be detectable. Naturally, they were not expected considering the high HNF amounts present in the formulations (70, 60, and 50%). To use lower percentages of HNF is not reasonable because it has the function of oxidizer, and the amount has to be linked to the binder and aluminum content.

To have a rough magnitude indication about the HNF-based propellants' reaction velocities, a BICT Gap test with a specimen of HNF-2 sample series has been carried out recording the flash X-ray test simultaneosly. This analysis was performed setting the time of the second impression at 12.3 μs, calculating the overall contributions of the firing, detonator, and donor charge propagation times and estimating the detonation sample velocity of about 8000 m/s. The result of this investigation is shown in Fig. 6, where the print of the X-ray film is given. As it can be seen, the predicted reaction velocity results are close to the experimentally determined values; in fact, the shock wave 12.3 μs after the firing just reached the bottom of the aluminum case but has not yet fragmented the case all the way to the bottom. Some analogies of this behavior can be found in the HMX-3 effect achieved by Card Gap test samples, as revealed by Fig. 7.

In the HMX-3 case the time of the second impression (45.2 μs) was established considering the detonation velocity of about 8000 m/s and including the contributions of the detonator, donor charge, and specimen height. In this event the detonation appears to have been faster than estimated because the shock wave seems to be broader than in the case of the HNF propellant.

New Propellants Hazard Classification

The experiments were not performed as discriminating for hazard classification of the new propellants by U.N. transportation rules.

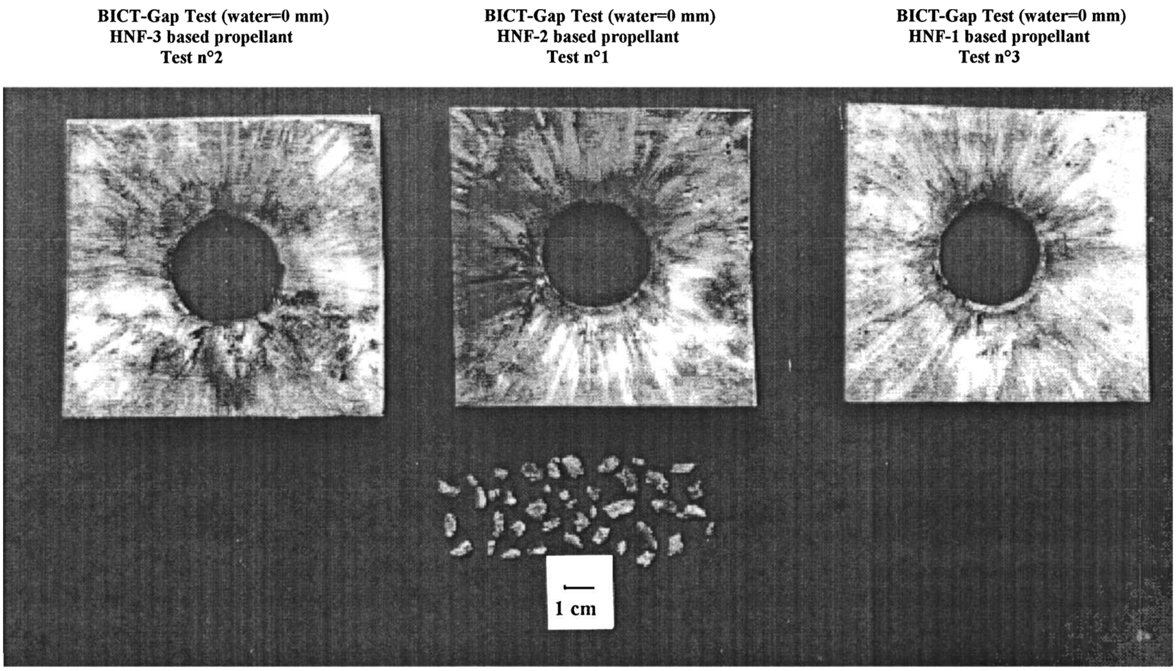


Fig. 5 BICT Gap test witness plates and fragments after firing.

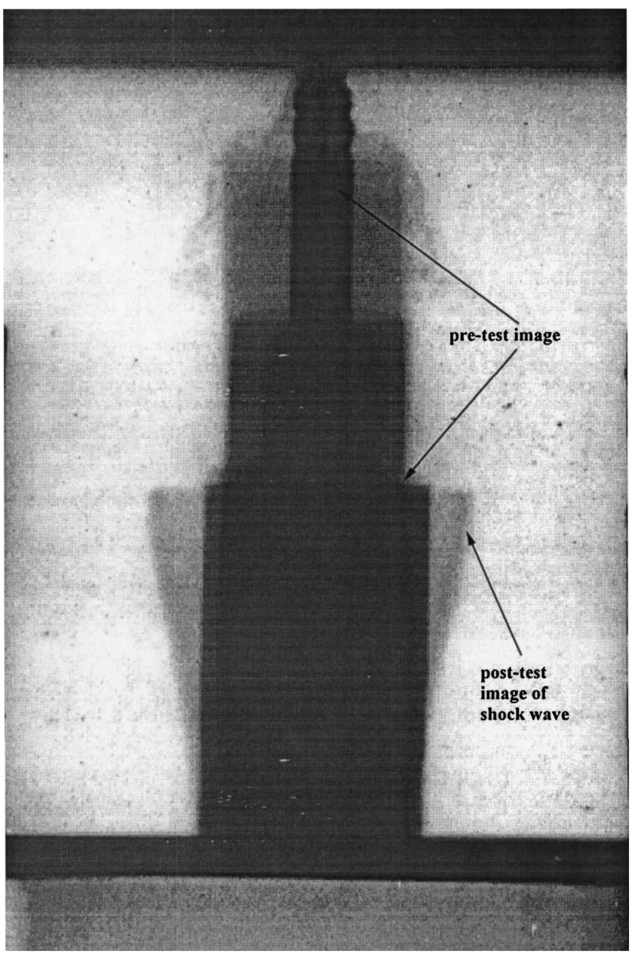


Fig. 6 Print from X-ray film of BICT Gap test, HNF-2 sample.

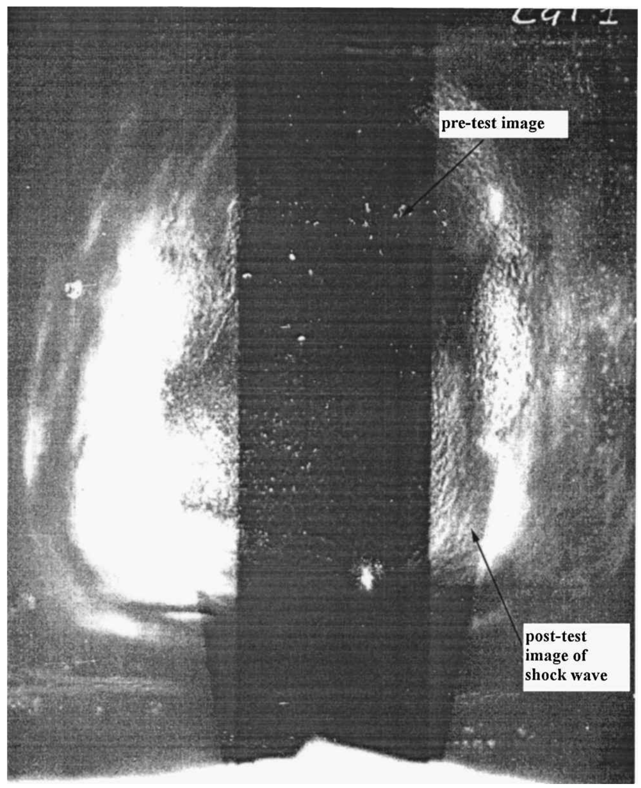


Fig. 7 Print from X-ray film of Card Gap test, HMX-3 sample.

According to International Agreements, several tests have to be carried out on new energetic materials for establishing their class of risk: 1.1, potential detonation attitude; 1.2, deflagrating; or 1.3, burning. Among these tests, in addition to detonic analysis, the sensitivity to impact, friction, spark, and thermal solicitations must be checked. In particular, for detonic test the results are evaluated by the number of cards able to give the reaction/no reaction answer. From Allied Ordnance Publication #7 (Ref. 8) the dividing line between 1.1 and 1.3 classes is ≥70 cards. Experiments on this topic are under investigation by Fiat Avio on HMX-1 samples.

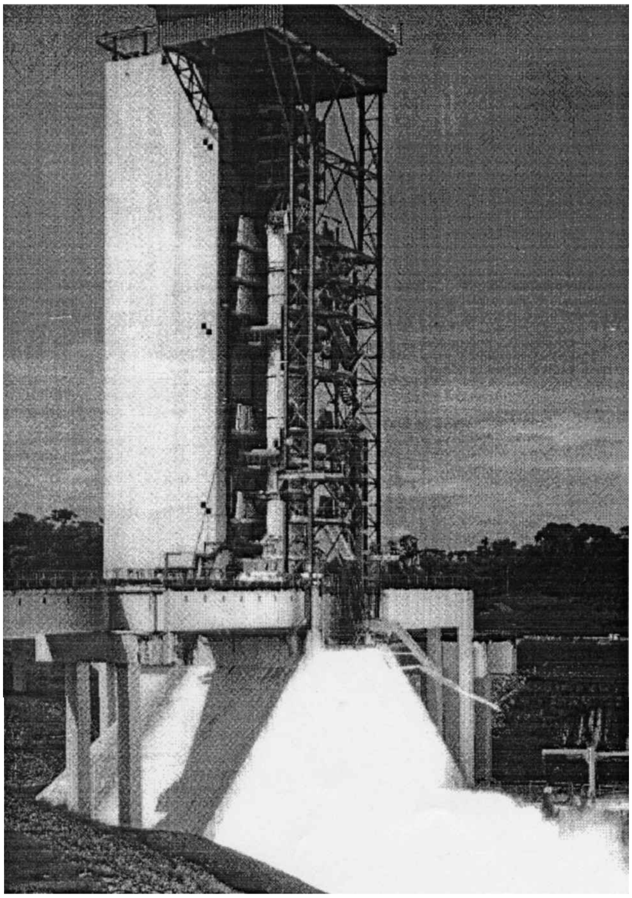


Fig. 8 ARIANE 5 strap-on booster static firing motor test (237 tons of propellant).

For thermal stability all HMX-based propellants analyzed according to STANAG 4480 rules gave results inside specification requirements. HNF propellant samples showed thermal stability, yet they had to be tested under milder temperature conditions (60°C), according with the supplier data sheet.[2]

Conclusions

The work described in this paper demonstrated the need to carry out a simultaneous scientific and industrial approach in developing new materials for advanced composite propellants. The results show that new oxidizers give appreciable reduction in the HCl content and improvements in energetic performance in composite propellant formulations, but, on the other side, they seem to affect the sensitivity of the final composition in a dramatic way.

The observed trend of samples containing increasing amounts of HMX reveals that the propellants behavior becomes more like nitramine as a function of percent nitramine content. This tendency can be extended[6] to other energetic oxidizers even if not investigated by such kinds of tests. Probably this problem can be minimized where it is acceptable to reduce the amount of explosive in the propellant formulations, i.e., if used as an energetic additive in combination with another oxidizer, particularly with AP.

On the contrary, where the energetic materials having high sensitivity characteristics must be used as main oxidizer (i.e., HNF), the propellant must be expected to exhibit hazard properties closer to the explosive class. These aspects, say the scientific community, must work hard to reduce the raw material hazards in the synthesis phase. Simultaneously, the propellant manufacturers have to contribute by developing technological steps to enable the safe workability. The joint effects of these synergistic activities could result not only in reducing the economic impact on the plants and equipments needed to process class 1.1 explosives but also to better the overall characteristics of the final product (Fig. 8).

Without any improvement of the raw materials or relevant technologies, new generations of advanced composite propellants, based on ingredients like HNF, will be 1.1 class, which is considered too hazardous for launch vehicle use. This should be taken into account at the beginning of a motor development phase among the requirements of its propellant. If necessary, lower hazard classification of the whole system can be achieved by suitable design of the motor layout. Otherwise, the new class of risk can reduce the potential application of the propellants in light of some specific hazard requirements.

Acknowledgments

The authors wish to acknowledge the technical team of Fiat Avio Colleferro Detonic Laboratory and in particular A. Dell'Orco for his contribution in setting up the tests.

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