# FOX7/GAP ROCKET PROPELLANTS FOR A SHOULDER LAUNCHED PROJECTILE

**Hendrik Lips[1] and Klaus Menke[2]**
[1]*Dynamit Nobel Defence, 57299 Burbach-Würgendorf, Germany*
[2]*Fraunhofer Institute für Chemische Technologie, 76327 Pfinztal, Germany*

Several Fox7 based propellant formulations were studied in order to obtain a minimum or reduced smoke composite propellant with inherent IM-properties. Two polymer binder systems are examined: the high energy GAP and a low energy poly-urethane binder containing a large fraction of high energetic plasticizers. Variation of the AP level in the Fox7/GAP propellants gives burn rates of between 10 and 20 mm/s with low pressure exponents. Crawford as well motor-firings of Fox7/AP/GAP formulations indicated a surprising plateau burning behaviour between 7 and 12 MPa, very similar to Double-Base propellants. Chemical stability and sensitivity data demonstrated acceptable values. Fox7/PU compositions with nitro plasticizers exhibit the best thermal stability within ARC measurements. Shock sensitivity test results correspond to values with a 1.3 hazard classification. The conclusion is that Fox7/GAP propellants are suitable for the rocket propulsion of projectiles in shoulder launched weapons, although the mechanical properties may need further improvement.

## INTRODUCTION

Future rocket propellants should be smokeless, high energetic, insensitive to external stimuli as well as being mechanically and chemically stable. Fox7 (DADNE) is an insensitive high energetic solid explosive, principally developed as a replacement for RDX and HMX. Compared to i-RDX it has a reduced thermal and shock to detonation sensitivity [1]. With these properties Fox7 becomes also an attractive ingredient as a high energetic and less-sensitive compound which maintains the energetic level in smoke-less composite rocket propellants with reducing the vulnerability, offering improved IM properties [2] as cook-off, bullet impact and sympathetic detonation.

The basic propellant formulation in this investigation included 70% Fox7 as solid energetic material dispersed in 30% elastomeric binder. Two binder systems have been studied, the energy-rich GAP and a low energy PU polymers, both with energetic plasticizers. Variation of nitramine/oxidizer (Fox7/AP) ratio together with the addition of burning catalysts and moderators opens up a wide range of burn rates. To survive extreme launch conditions, further variation of the polymeric cross-linking type, type and amount of energetic plasticizer and the addition of modifiers, have been tailored to suit the mechanical properties of the rocket propellant for propulsion of highly accelerated projectiles launched from shoulder launched weapons.

## THERMODYNAMIC PERFORMANCE

Composite propellants with active GAP binder and nitramine HMX as solid energetic filler are characterised by high performance that showed a favorable characteristic towards smokeless or minimum smoke signature. Unfortunately compared to AP composites the burning rates of these propellants are unacceptably low (≤ 5 mm/s at 70 bar) [3, 4, 5,]. Fox7/GAP propellants will behave in a similar manner [6]. In order to compensate for this disadvantage, a certain amount of AP in the formulation is necessary to further augment the burning rate. The smokeless autonomous burning monopropellant Fox7 is partly replaced by AP, a secondary HCl smoke producing perchlorate as oxidizer. So there is a compromise to be found for the maximum burn rate combined with a low plume signature. Processing and glass-transition temperature of the GAP elastomer are improved by incorporating energetic liquid plasticizers.

## PROPELLANT FORMULATIONS

The object of this study was to formulate and characterise Fox7 propellants and gain further knowledge and understanding about the behavior of the sensitivity, chemical and thermal stability and combustion characteristics.

The basic propellant formulation is composed of 70% Fox7 as energetic filler combined with the exothermic decomposing high energy GAP polymer. The seven most promising from 16 compositions, were selected to continue further investigations. In order to become the composition less sensitive and to be quite widely tailored to higher burn rates, the energetic solids are fractionized into different Fox7/AP ratios. The seven DNX compositions here studied are listed in table I.

TABLE I. LIST OF FOX7 PROPELLANT COMPOSITIONS TESTED IN THIS STUDY.

| **Sample** | DNX-08 | DNX-06 | DNX-14 | DNX-16 | DNX-13 | DNX-09 | DNX-10 |
|---|---|---|---|---|---|---|---|
| **Energetic solids** | wt. % | wt. % | wt. % | wt. % | wt. % | wt. % | wt. % |
| Fox7 | 68 | 48 | 33 | 28 | 38 | 28 | 28 |
| AP | 0 | 20 | 36 | 42 | 30 | 42 | 42 |
| **Binders** | | | | | | | |
| GAP | 15 | 15 | 15 | 14 | 14 | | |
| PU | | | | | | 14 | 14 |
| **Plasticizers** | | | | | | | |
| BTTN /TMETN | 15 | 15 | 14 | 14 | | | 14 |
| BDNPF/A | | | | | 15 | 14 | |
| **Stabil. & modifiers** | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| Ox-balance | - 43 | - 31,9 | - 22,6 | - 17,8 | - 30,8 | - 23,6 | - 28,1 |

The AP ratio in the Fox7 propellant composition varied with DNX-08 (without AP) up to a maximum level of 42% AP in DNX-16. Other than the AP ratio, the binder composition in the Fox7 propellant was varied in order to get an overall impression of their influence on burning characteristics, mechanical properties and sensitivity.

DNX-06, DNX-14 and DNX-16 propellants were formulated with energetic GAP polymer and high energetic nitrate-ester plasticizers, DNX-13 with active GAP polymer and a nitro-plasticizer, DNX-10 with a low energy polyester-urethane elastomer, an inert PU binder containing a large fraction of high energetic nitrate-plasticizers and DNX-09 composed of the lower energetic but more stable nitro-plasticizers. To improve processing and low temperature properties all the propellant formulations used a relatively large plasticizer to polymer ratio pl/po of 50:50.

The Fox7/GAP propellant DNX-08, without AP, is the only formulation that fulfills the smoke-less AA labeling in table II.

TABLE II. SIGNATURE CLASSIFICATION OF FOX7/AP/GAP PROPELLANTS.

| Labelling | | smokeless | min. smoke | reduced-smoke | | |
|---|---|---|---|---|---|---|
| Sample identification | | DNX-08 | DNX-06 | DNX-13 | DNX-14 | DNX-16 |
| Fox7 | wt. % | 68 | 42 | 38 | 33 | 28 |
| AP | wt. % | 0 | 20 | 30 | 36 | 42 |
| AGARD coefficients | | **AA** | **AB** | **AC** | **AC** | **AC** |

The DNX-06 with the lowest level of 20% AP, is classified with theoretical AGARD coefficient label AB, for minimum smoke. The other Fox7 propellants with over 30 % AP levels fall into the AC label category but are still within the reduced smoke category.

## STABILITY AND SENSITIVITY RESULTS AND DISCUSSION

Four types of NATO standard tests were performed to collect data to determine chemical stability, mechanical sensitivity, thermal and shock sensitivity. The results of the mechanical sensitivity and chemical stability are summarized in table III.

TABLE III. STABILITY AND SENSITIVITY RESULTS.

| Sample number | | | **DNX-06** | **DNX-14** | **DNX-16** | **DNX-13** | **DNX10** | **DNX-09** |
|---|---|---|---|---|---|---|---|---|
| **Mechanical sensitivity** | friction | N | 252 | 80 | 144 | 288 | 192 | 240 |
| | Impact | Nm | 7.5 | 20 | 20 | 20 | 4 | 20 |
| **Chemical stability** | Dutch Test | % | 0.49 | 0.31 | 0.48 | 0.63 | 0.17 | 0.23 |
| | Vacuum Stab. | ml/g | 0.9 | 0.9 | 0.8 | 0.2 | 0.6 | 0.1 |
| | Flash point | °C | 190 | 191 | 190 | 221 | 193 | 236 |

Solid AP is mechanically sensitive to friction and impact and is, depending on its particle size, classified as a 5.1 oxidizer or being in hazard class 1.1D as explosive, but is less thermally sensitive. The energetic Fox7 insensitive solid explosive is compared to i-RDX and rs-HMX thermally more stable and has a reduced shock to detonation sensitivity. Liquid BTTN/TMETN nitrate-esters are highly energetic, but relatively sensitive to thermal, impact, shock and detonation stimuli. Liquid BDNPF/A nitro-plasticizers are thermally stable, less sensitive to impact and shock to detonation stimuli, but less energetic. Liquid GAP prepolymer is very sensitive to fire and impact but less sensitive to detonation. The cured solid GAP polymer is less thermally sensitive, but more sensitive to mechanical and detonation stimuli [7]. The high energetic azido-group is responsible for reduced chemical stability (N3 -group inducing N2 -loss).

Typical thermal stability results of cured propellant probes analyzed by the ARC method are illustrated in Figure 1.

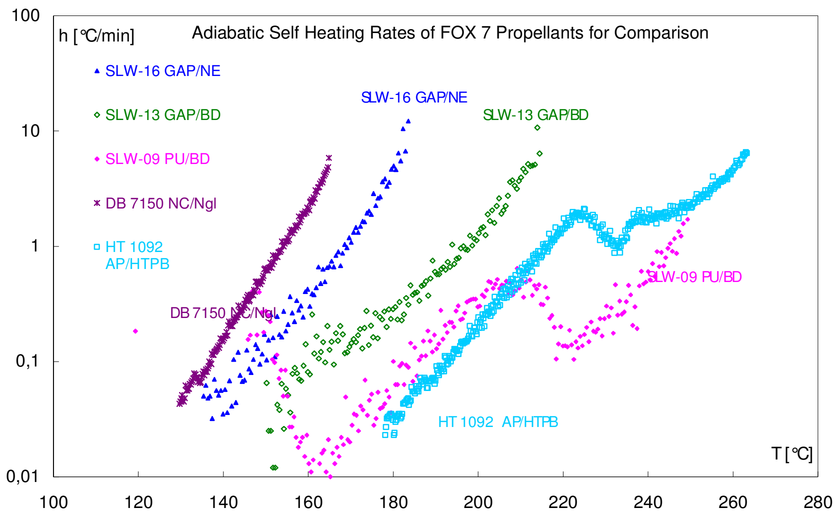



Figure 1. ARC spectra of self-heating rates of Fox7 propellants DNX-16, DNX-13 and DNX-09 compared with EDB and AP/HTPB composite propellant.

The graph in Figure 1 shows the results of the ARC self heating tests of Fox7/GAP propellants compared quantitative to that of a NC/NG double base propellant (EDB-7150) and a smoke-reduced conventional composite propellant (85%AP/HTPB). The high energetic Fox7/GAP/NE propellant starts with a higher onset temperature, presents a slower gradient and deflagrates at a higher temperature than the double base propellant.

Significant reduction in thermal sensitivity occurs with DNX-13 by replacing the nitrato-plasticizers by nitro-plasticizers in the Fox7/GAP formulation. With the energetic GAP/BDNPF/A binder system the deflagration temperature shifts to higher temperatures at values over 210°C and with the inert PU/BDNPF/A binder system no deflagration until 250°C is observed and provides the DNX-09 composition with the same temperature range as the conventional insensitive AP/HTPB composite propellant.

The shock to detonation transition (SDT) test results is presented in figure 2.

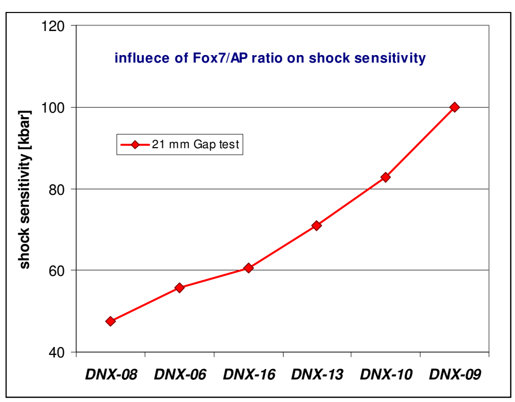



Figure 2. Shock-sensitivity plot of GAP/AP propellant with different Fox7 fractions.

The Fox7/GAP/NE propellants show an evident reduction in sensitivity to detonation with decreasing the amount of Fox7 and are further reduced with replacement of BTTN/TMETN by BDNPF/A. The energetic GAP/BDNPF/A propellants detonate at an initiation pressure of 71 kbar. Fox7 propellants containing the "medium-energetic"

PU/NE binder system shifts to higher pressures of 83 kbar. The PU/BDNPF/A formulations were so insensitive that no reaction occurred; its critical diameter is too large for the small scale gap test. The classification of the nitro-plasticized PU propellants needs to be proved by further experiments with the large scale gap test. According to comparative STANAG 4488 standards, shock sensitivities above 60 kbar will correspond to a 1.3 explosive hazard classification [8].

## PROPELLANT MECHANICAL PROPERTIES

The mechanical characteristics of shoulder launched projectiles have to fulfill special requirements to provide proper function in the weapon and to support high launch loads with accelerations of more than 20,000g without failure ("g-hardened" propellant).

The main selection criteria yielding applicable mechanical properties for free standing propellant grains at extreme launch load conditions, are maximal stress and effective strain. Although the polymer fraction in composite propellants exceeds not more than 15%, the quality of the matrix determines the mechanical properties significantly. These were measured with standard JANNAF dog bones in a standard tensile test at room temperature. Test results of E-modulus, tensile strength, grain hardness and glass transition temperatures of the cured solid propellants are illustrated in Figure 3.

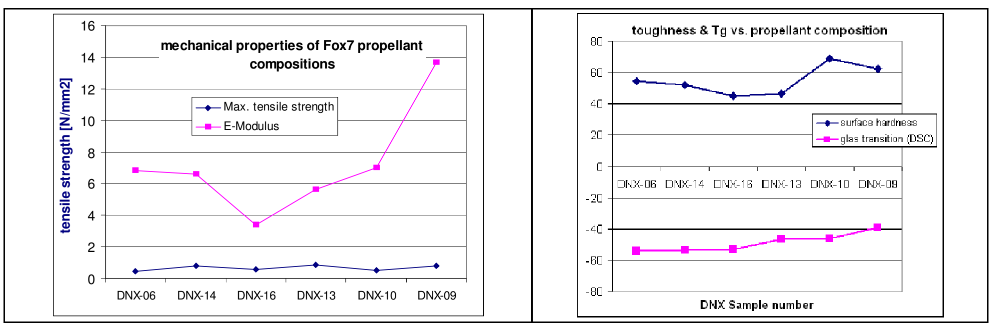



Figure 3. Mechanical properties of FOX 7 propellant compositions.

The propellant hardness gives a quick-look indication of the grains structural stiffness directly after curing. In comparison with the applied triol-cross-linked GAP/diisocyanate binder system, the DNX-07 and DNX-13 samples yielded much better stress and effective strain capability, however they have much poorer E-modulus than the commonly used GAP-diol poly-isocyanate cross-linked (N100/IPDI) DNX-02 and DNX-03 compositions. Variation between GAP and PU elastomer as well as the type of plasticizer has only a small effect on tensile strength and E-modulus. Stress and effective strain of the grain is significantly enhanced by the use of a bonding agent for Fox7, demonstrating a stronger filler-to-matrix bond (less formation of vacuoles around the solid particles). The glass transition temperatures for GAP/NE elastomers were in the range of -52°C and are very promising for military applications. In contrast to GAP/NE is the crystallization temperature of the elastic-plastic PU/NCO matrix with –46°C far more inferior.

## INTERIOR BALLISTICS

To determine the burn rate characteristics of the Fox7 propellants preliminary analysis were conducted using a chimney type strand-burner in the Crawford bomb. In order to keep the pressure level constant during the combustion of the strands, the pressurization of the vessel was varied with nitrogen from 20 to 250 bar. The size of the propellant samples was 5x5 mm in cross section and 150 mm in length, divided by three fuse wires.

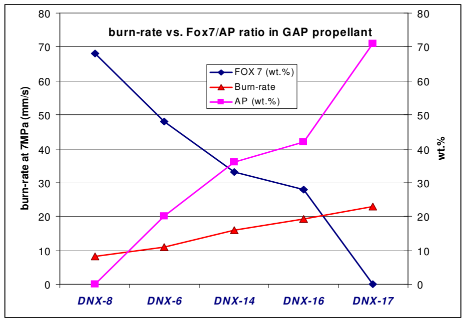



Figure 4. Ballistic properties of Fox7/GAP propellants measured in Crawford bomb.

Figure 4 shows the burning rate test results plotted as function of the Fox7/AP ratio in the Fox7/GAP propellants. The graphs 1, 2, 3 and 4 in figure 5 respectively give the appropriate results of the plotted burn rate versus pressure.

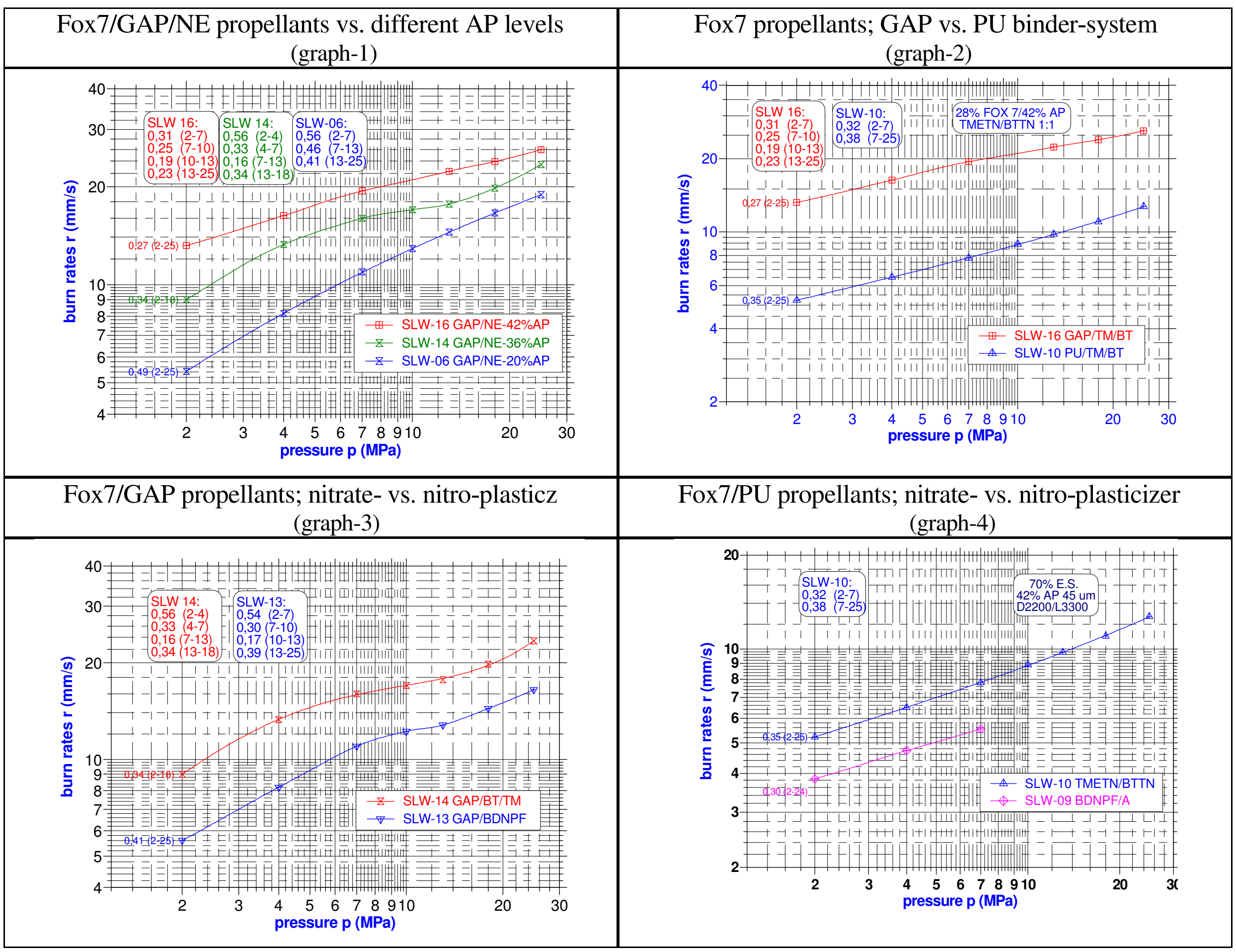



Figure 5. Relationship of burning rate vs. combustion pressure of tested Fox7 propellant compositions.

Graph 1 shows the range of burning rates attained by varying the AP weight fraction in the Fox7/GAP propellant. Increasing the amount of AP from 0 to 42 %, increase of the burn rate from 8.3 to 19 mm/s at 70 bar, is almost more as doubling.

Graph 2 shows the effect of the binder type on burn rate; comparison of the semi-energetic PU-BTTN/TMETN with the high energetic GAP-BTTN/TMETN formulation indicates a significant augmentation of about 12 mm/s at 70 bar.

Graph 3 shows the effect of plasticizers in the Fox7/GAP formulation, compared at identical pl/po values (50/50); BTTN/TMETN plasticized GAP has a burning rate of 16 mm/s, whether the GAP-BDNPF/A propellant is about 5 mm/s slower.

Graph 4 shows the effect of the plasticizer in the PU formulations; burn rates of PU-BTTN/TMETN and PU-BDNPF/A with 8 and 5 mm/s are far below the required values.

It was a surprise that the burn rate was not controlled by the AP particle size!? The tri-modal DNX-11 composition, containing 7% fine AP in the 20% AP fraction, develops the same combustion velocity as DNX-06 with the medium and coarse AP particle size distribution. With the 20% AP composition, no prominent plateau is affected. GAP/Fox7 compositions approaching an AP/Fox7 ratio of 1,5:1 (with an AP amount between 36 and 42%) exhibit a pronounced plateau burning behavior between 7 and 13 MPa is evident with favorable pressure exponents.

High Fox7 levels create a low burn rate and significantly higher pressure exponents compared to high percentage AP propellants. Fox7/GAP propellants without AP maintain the highest pressure exponent of all tested formulations ($n \sim 0.46$ at 10 MPa). Fox7/PU propellants with the nitrate or nitro plasticizer are characterised with favorable low pressure exponents demonstrating values ranging between $0.35 \leq n \leq 0.30$.

The PU/BDNPF/A DNX-09 strands did not burn at all above a pressure level of 7 MPa in the Crawford lab tests, caused by the enhanced heat extraction generated by the relatively high nitrogen flow, which extinguished the combustion.

## BALLISTIC MOTOR FIRINGS

Real burn rates were obtained by testing the Fox7/GAP propellant grains in a rocket motor. In order to test the quality of the propellants at different K-values a standard ∅70 mm test motor with a series of nozzles with different throat diameters and expansion ratios was used. Combustion pressure and thrust were measured to determine the pressure dependence and combustion efficiency of the propellants. These data points were then compared with those measured by the Crawford strand burning tests.

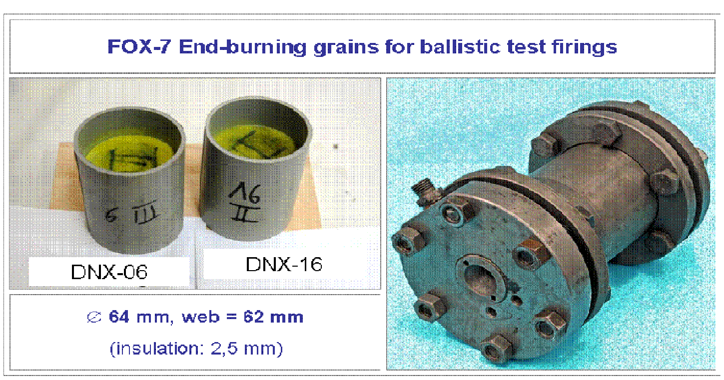



Figure 6. DNX-06 and DNX-16 inhibited Fox7/GAP propellant grains tested in Ø 70mm rocket motor.

Figure 6 shows a photograph of the end-burning Fox7/GAP grains inside the thermal and inhibiting insulation.

For the ballistic motor test firings two Fox7/AP/GAP propellant versions were selected, the minimum-smoke DNX-06 and the reduced-smoke DNX-16 propellant. They were cast cured into cylindrical end-burning grains with a net weight of 430g, 64 mm diameter and a neutral burning web length of 60 mm. The inhibiter insulation was slurry cast around the propellant grain with a wall thickness of 2.5 mm.

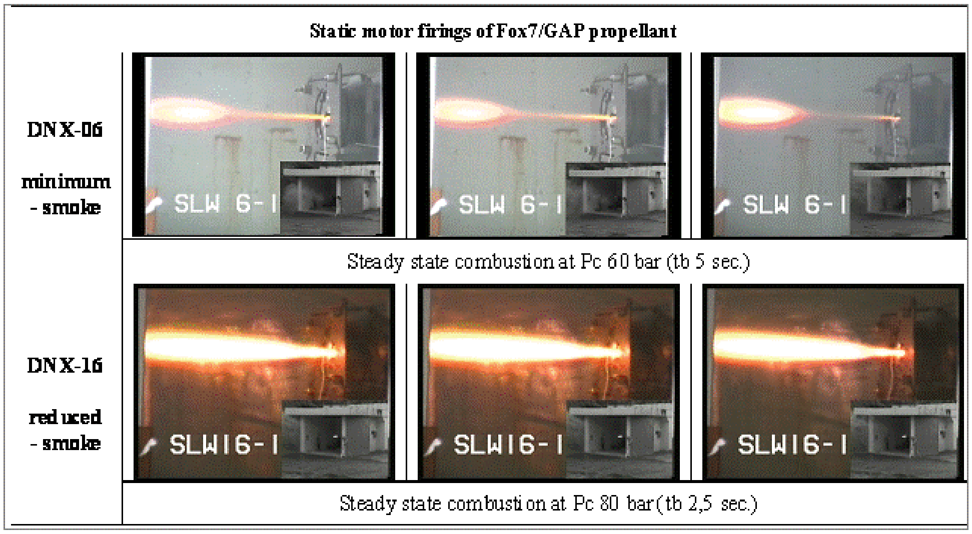
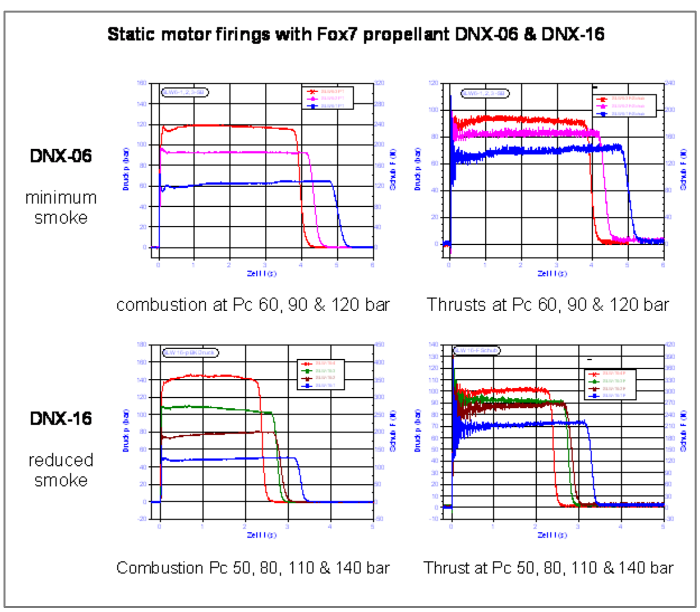


Figure 7. Static motor firings of two Fox7/AP/GAP propellant versions.

After ignition all motor firings burned smoothly with steady state combustion as is shown in video pictures of figure 7 and by the pressure vs. time and thrust vs. time curves in Figure 8.




Figures 8. Measured curves of pressure and thrust from the ballistic tests of Fox7/AP/GAP/NE propellant DNX-06 and DNX-16.

The Fox7 propellant DNX-16 with a grain weight of 430g burn-out in 2,8 seconds with a mass flow of 114,7 g/s, nearly twice as fast as the DNX-06 grain with burn time of 5 s and a mass flow of 66,0 g/s. (see table IV)

TABLE IV. GRAIN CONSUMPTION OF Fox7/GAP/AP PROPELLANTS.

| Sample Nr. | **grain wt.** | **web** | **Pc** | **tb** | **mass-flow** | **burn rate** |
|---|---|---|---|---|---|---|
| | g | mm | bar | s | g/s | mm/s |
| DNX-16/2 | 334,8 | 59,7 | 77 | 2,81 | 114,7 | 21,3 |
| DNX-06/1 | 330,5 | 60,3 | 62 | 4,98 | 66,1 | 12,1 |

For the small size of propellant grains the delivered thrust level of 213 N for DNX-06 and 296 N for DNX-16 provide combustion efficiencies with excellent experimental values of 93% and 92% respectively. With suitable grain geometry, the relatively slow burning Fox7 DNX-06 propellant can deliver sufficient thrust at 70 bar to exceed the required values for adaptable propulsion of projectiles for shoulder launched weapons.

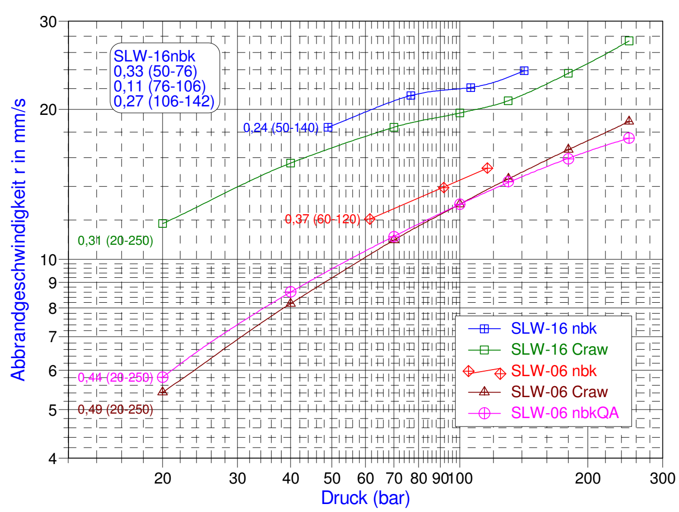



Figure 9. Burn rates vs. Pressure from ballistic firing tests of DNX-06 and DNX-16 propellants.

For the DNX-16 propellant formulation the burn rates vary from 18.5 to 23.7 mm/s between 49 and 141 bar and exhibited a plateau at a chamber pressure between 77 bar and 105 bar, moreover is the plateau characteristic much more pronounced than in the Crawford bomb measurements.

Measured, at three pressure levels for DNX-06 propellant, the burn rate varies from 12 to 15 mm/s between 62 and 116 bar. The plateau characteristic is much less pronounced but determined with acceptable low pressure exponents. It is noteworthy that for the high energetic DNX-06 and DNX-16 propellants, the actual measured burn rates in the motor firings are in good agreement with the Crawford measurements. The real burn rates are slightly higher than the strand measurements, which indicated that the flow rate near the end-burning grain surface was more effective to the plateau burning characteristics [9].

## CONCLUSION

High energetic Fox7 formulations have been prepared successfully with 70% solids, including 0% to 42% AP, bonded in 30% of GAP- or PU- polymeric matrix with high energetic plasticizers. Typical results of the seven most promising compositions are presented in this investigation.

All propellants exhibited convenient chemical stability, an acceptable friction and impact sensitivity as well as being remarkably thermal stable, offering the potential for a mild reaction when exposed to aggressions due to fires. Small scale gap tests show relatively low shock to detonation sensitivity which correspond to a 1.3 hazard classification.

From all manufactured Fox7 propellants only the PU-BDNPF/A binder system provided reasonable mechanical properties and thermal stability, although its burn rate is rather too slow. The energetic GAP-BTTN/TMETN binder system has a suitable burn rate of more than 20mm/s, but the strength/strain values are insufficient for a free standing grain application. Further improvement will have to be undertaken to prevent failures at high launch loads.

With values of –52°C the glass transition temperatures of GAP/NE propellants yield excellent low temperature flexibility, while for BDNPF/A plasticizer formulations the values shifts to inferior temperatures of –46°C.

Burn rates increase with the increasing binder energy and higher amounts of AP oxidizer in the formulation. The smokeless Fox7/GAP (without AP) has with 8,3 mm/s the lowest combustion velocity measured at 7MPa, followed by the minimum smoke composition containing 20% AP with 10,9 mm/s at 7MPa. PU- and GAP- bonded Fox7-propellants with a BDNPF/A plasticizer exhibit lower burn rates, so that they need higher amounts of AP to reach adequate values.

The highest measured burn rate at 7 MPa is 19,3 mm/s obtained by the reduced-smoke Fox7/AP/GAP/NE formulation containing 42% AP. A highlight in this investigation and biggest surprise was the dominant plateau-burning behavior of this formulation. Within the pressure range from 7 to 13 MPa, the plateau characteristic becomes more pronounced as the AP content in the Fox7 propellant is between 36 and 42%, however this is accompanied by a higher smoke signature.

For the ballistic motor firings two versions of Fox7/AP/GAP/NE propellants, the minimum-smoke and reduced-smoke formulation, were selected and successfully tested. The end-burning propellant grains are characterised by easy ignition and a smooth neutral burning behavior. The plateau-burning characteristic was even more pronounced compared with the Crawford tests, combined with very low pressure exponents at chamber pressures ranging between 48 and 141 bar. The generated thrust level fits well with the required values for projectile rocket propulsion in shoulder launched weapons.

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