Insensitive Minimum Smoke Propellants for Tactical Missiles

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Abstract

Modern weapon systems have a high demand for insensitive minimum smoke propellants that are not inflicted by REACH regulations. In that respect, the development of new minimum smoke propellants has to be pushed towards less hazardous and less sensitive energetic fillers and plasticizers. Additionally, its successful implementation is also dependent on replacing existing hazardous ballistic modifiers based on lead and copper compositions while maintaining the good ballistic and mechanical properties at the same time.

In this work, FFI and NAMMO are presenting the extension of their family of GAP-nitramine-NENA propellants with different insensitive energetic fillers like FOX-7 or AN. In these formulations, the nitramine was partly or completely substituted by FOX-7 or AN.

The results are compared to previously tested minimum smoke propellants with special emphasis on the developed specific GAP-RDX-Bu-NENA propellant for the LMM boost motor.

Even though seen as a promising candidate as well due to preliminary results with good prospects, the tested FOX-7 formulations unfortunately only show similar shock sensitivity performance as pure nitramine based GAP-Bu-NENA propellants. Strain and strength of the propellant is reduced compared to pure GAP/nitramine propellant while the modulus is increased. However, tensile testing at -40℃ indica te a better low temperature behavior of the GAP/FOX-7 propellant compared to pure GAP/nitramine propellant. Burn rates are reduced and pressure exponents increased by incorporation of FOX-7.

Propellants containing AN show the best mechanical properties, also the best low temperature behavior, of all tested formulations. However, on the downside, the burn rate dropped dramatically for the pure GAP/AN propellant compared to a GAP/nitramine propellant. Shock sensitivity is reduced by incorporation of AN in the propellant.

Introduction

In Norway, the systematical investigation of minimum smoke rocket propellants based on glyzidyl azide polymer (GAP) and energetic fillers such as cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), hydrazinium nitroformate (HNF) and hexanitrohexaazaisowurtzitane (CL-20) was initiated in the early 1990s, as a close collaboration between Norwegian Defence Research Establishment (FFI) and Nammo Raufoss AS (NAMMO). Although promising in many respects, issues associated with sensitivity, stability, mechanical characteristics and production costs hindered industrial scale-up of such formulations based on these compounds.

Since 2011, FFI and NAMMO have made renewed and intensified efforts to develop a family of minimum smoke composite propellants based on reduced sensitivity nitramines (RS-RDX and RS-HMX), GAP binder and low sensitivity nitratoethylnitramine (NENA) energetic plasticizers. The development effort has been reported by Kristensen *et. al.* [1].

In 2013, NAMMO was awarded a contract for the development and qualification of the propulsion section of the Lightweight Multirole Missile (LMM). LMM is developed by Thales Land & Air Systems as a precision lightweight weapon for light platforms to counter the modern and emerging threats of land, sea and air targets. Results from the LMM propellant qualification effort were shared on the 2016 IM & EM Technology Symposium [2,3].

1,1-diamino-2,2-dinitrotoluene (FOX-7 or DADNE) is a promising candidate due to an explosive performance similar to RDX. Additionally, it is inherently less sensitive than RDX and HMX which allows for a safer handling of the material. On the downside, the current price of FOX-7 is high and the availability of ground material has been limited. This is mainly caused by the absence of demand as HTPB/AP-based rocket propellants are still the workhorse for the rocket industry.

Ammonium nitrate (AN) on the other hand is cheap and like FOX-7 less sensitive than nitramines, but possesses on the downside lower energy content and a lower explosive performance than RDX or HMX.

Composition and thermochemical performance

The propellant compositions and calculated thermochemical performance are shown in Table 1. All formulations contained 65% energetic solids. As its performance is comparable to double-base (DB) propellants, the GAP propellants presented here are free from certain undesirable DB compounds, such as sensitive nitrate ester plasticizers and burn rate modifiers based on lead and copper. The propellants exhaust signature has been classified as AA according to STANAG 6016, which is a minimum smoke signature classification. The main combustion products are CO, CO_2, N_2 and H_2O.

Table 1: Composition and thermochemical performance of the investigated GAP propellants. The thermochemical performance has been calculated using standard software (described in NASA RP-1311 part I and II), applying standard conditions (chamber pressure = 6.9 MPa, equilibrium expansion to 1 atm = 0.101 MPa).

Propellant	GAP/HMX	GAP/RDX	GAP/RDX/ AN	GAP/AN	GAP/FOX-7
Composition					
RS HMX, 50-60 micron and RS HMX, ground	65	-	25	-	-
RS RDX kl. 8 and RS RDX, ground	-	65	-	-	-
AN and AN, ground	-	-	20	65	-
FOX-7, class 2, FOX-7, class 3 and FOX-7, ground	-		-	-	65
GAP, di- and polyfunctional isocyanates, Bu-NENA, stabilizers, burn rate modifiers and additives	35	35	35	35	35
Calculated thermochemical performance					
Characteristic velocity, c* [m/s]	2234	2243	2213	2148	1290
Theoretical specific impulse, Isp [Ns/kg]	1430	1437	1414	1365	2061

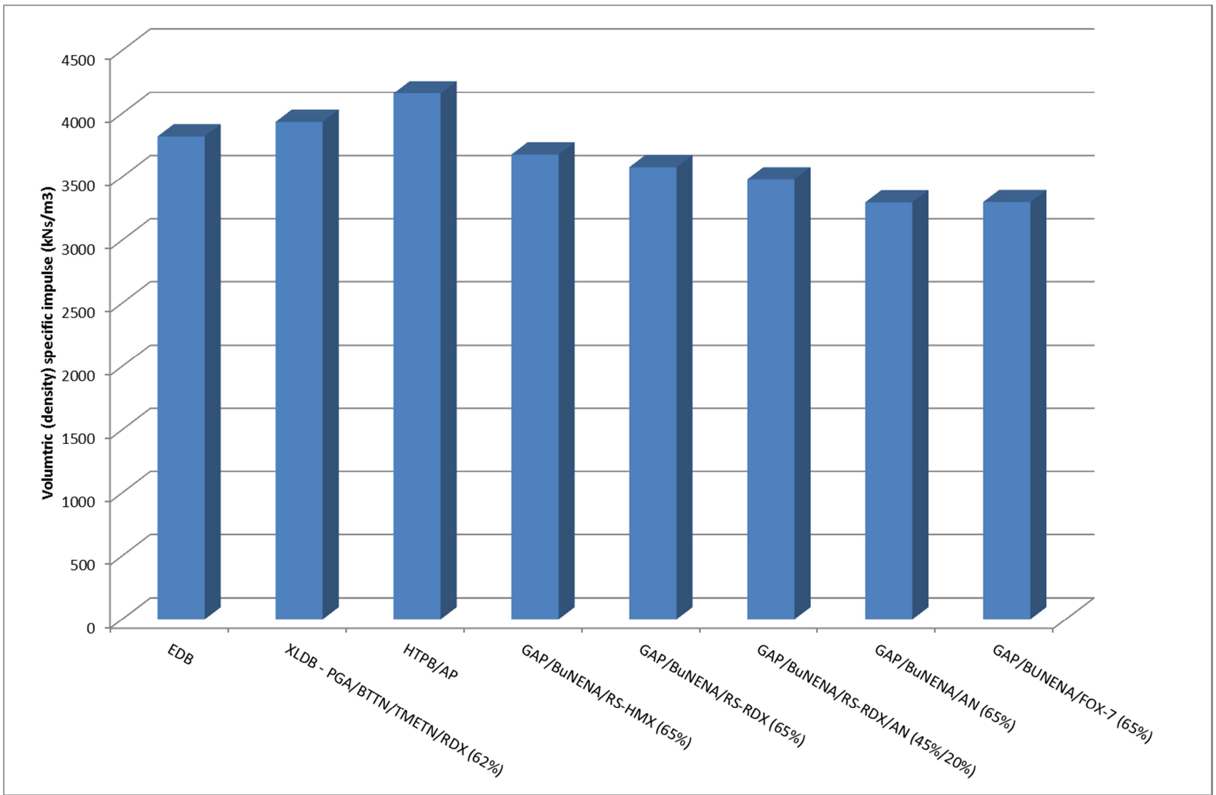

Figure 1: Volumetric specific impulse of investigated GAP propellants. The thermochemical performance has been calculated using standard software (described in NASA RP-1311 part I and II), applying standard conditions (chamber pressure = 6.9 MPa, equilibrium expansion to 1 atm = 0.101 MPa).

The use of conveniently handled Bu-NENA energetic plasticizer is a trade-off between sensitivity and performance. The reduction in sensitivity of the propellants is also favored by incorporation of reduced sensitivity (RS) nitramines. Both materials are delivered by Chemring Nobel AS, Norway, and are manufactured at their plant in Saetre, just south of Oslo. GAP and FOX-7 are delivered by the European Energetics Corporation (Eurenco), and the first is manufactured at their Sorgues plant in Southern France and the second is manufactured at their Karlskoga plant in Sweden. AN used in the formulations were two types, the coarse quality was spray crystallised AN manufactured by ICT Karlsruhe in Germany and the fine quality was from grinding of crystalline grade AN from Yara Rostock in Germany.

It is vital to balance the processing properties during mixing and casting operations with the optimization of mechanical and ballistic properties. This is achieved by adjusting the formulation with respect to the binder/curatives, bonding agent system, burn rate modifier system, and the type and particle size distribution of the energetic fillers.

FFI has developed a number of neutral polymeric bonding agents (NPBAs), each tailor-made for its certain application in GAP-nitramine propellants [2,4]. Mixed isocyanate curatives have been used to adjust crosslinking and to tailor chain extension.

FFI and NAMMO have developed a lead-free burn rate modifier system that is compliant with existing and upcoming environmental regulations (REACH). The system provides adequate ballistic properties, while it at the same time opens up for industrial scale propellant processing through the attainment of a sufficient pot life.

FOX-7 characteristics

FOX-7 is a high explosive with similar performance as RDX. At the same time, FOX-7 exhibits a significantly lower sensitivity towards shock friction and heat than RDX. As well, FOX-7 is stable towards hydrolysis and can therefore tolerate humidity. According to data published by Eurenco Bofors and FOI, FOX-7 has excellent compatibility with most materials used in energetic compositions. Prior to application, compatibility towards all propellant ingredients was tested and no incompatibility was found. FOX-7 is desensitized in water and has to be dried prior to use. Table 2 summarizes some of the available data on FOX-7.

Table 2: FOX-7 characteristics based on published data from Eurenco Bofors and FOI.

Property	Unit	Value
Density	[g/cm^3]	1,885
Detonation velocity	[m/s]	8870
Heat of formation	[kcal/mole]	-32
Activation energy	[kcal/mole]	58
Vacuum stability at 120°C	[ml/g]	0.1-0.4
Koenen Test, according to UN	[mm]	6, type F reaction
Measured detonation pressure	[GPa]	34
Calculated detonation pressure (Cheetah)	[GPa]	36.6
Friction sensitivity, typical	[N]	< 350
Impact sensitivity, typical	[J]	20-40
ESD	[J]	> 8

The particle sizes that are commercially available for FOX-7 are given in Table 3 and are compared to the particle sizes of the other energetic fillers used in this study.

Table 3 Commercially available particle sizes of FOX-7 and comparison to the particle sizes for the other energetic fillers used in this study. Particle size analysis was conducted by a MALVERN 2000 particle size analyzer.

Material	Typical particle size, d_{50} [microns]	Particle size, d_{50} used [microns]
FOX-7, class 1	20-40	38
FOX-7, class 2	50-100	87
FOX-7, class 3	100-200	120
FOX-7, class 4	200-350	-
FOX-7, ground	~10	10-13
RS-HMX, 50-60 micron, Grade B	50-60	44
RS-HMX, ground, Grade B	9-15	9
RS-RDX, class 8	40-60	49-55
RS-RDX, ground	5-8	6-9
AN	160	158
AN, ground	10-20	16

The friction and impact sensitivity of the energetic fillers used in this study is shown in Table 4. As can be seen, FOX-7 class 1, class 2 or class 3 are more insensitive than the BAM apparatus is able to measure. However, FOX-7 ground to 10 microns has a similar sensitivity as RS-RDX class 8.

Table 4: Friction and impact sensitivity of the energetic fillers used in this study. All values are determined in BAM equipment according to UN Test 3 (a)(ii) for friction sensitivity and UN Test 3 (b)(i) for impact sensitivity.

Material	Impact sensitivity, BAM Fallhammer [J]	Friction sensitivity, BAM [N]
FOX-7, class 1	> 49	> 353
FOX-7, class 2	> 49	353
FOX-7, class 3	> 49	> 353
FOX-7, ground	15	141
RS-HMX, 50-60 micron	N/D	N/D
RS-HMX, ground	N/D	N/D
RS-RDX, class 8	11	126
RS-RDX, ground	4,5	94
AN	N/D	N/D
AN, ground	47	283

Processing characteristics

The GAP propellants have been prepared in a 5-gallon (10 kg) Baker-Perkins twin-bladed planetary vertical mixer. All propellants have good flow through all mixing cycles, and exhibits a creamy behaviour at the end-of mix and during casting. The viscosity is around 150 – 200 Pa·s at end-of-mix (at 35°C), with lowest value for the propellants containing RS-HMX or FOX-7 and the highest value for the propellant containing RS-RDX. The propellants have an acceptable pot life of 10 hours at 35°C and the cure time is 168 hours at 60°C.

Mechanical properties

The mechanical properties of the investigated GAP propellants are shown in Table 5. Except for the GAP/AN propellant, the strength is rather low but still acceptable for small rocket motors. The GAP/FOX-7 propellant displays a high elastic modulus and low elongation properties at room temperature. GAP propellants containing AN as a minor or main oxidizer exhibit a lower degree of de-wetting and better low temperature properties than nitramine or FOX-7 based GAP propellants. As well, they show the highest strength at room temperature. This is due to the fact that a traditional bonding agent known from HTPB/AP propellants can be used for the GAP/(RDX/)AN propellant, while neutral polymeric based bonding agents (NPBA) are used in case of the GAP/nitramine and GAP/FOX-7 propellants.

Table 5: Mechanical and physical properties of the GAP propellants. Uniaxial testing of the propellant was performed according to STANAG 4506, using a crosshead speed of 50 mm/min. All values are reported as the mean value calculated from testing of five propellant specimens from the same batch. Engineering values are presented. DMA and TMA have been performed according to STANAG 4540 and 4525 respectively.

Propellant	**GAP/HMX**	**GAP/RDX**	**GAP/RDX/AN**	**GAP/AN**	**GAP/FOX-7**
Composition	65% RS-HMX	65% RS-RDX	45% RS-RDX 20% AN	65% AN	65% FOX-7
Mechanical properties at +21°C					
Max / break stress [MPa]	0.6 / 0.5	0.4 / 0.4	0.4 / 0.4	0.8 / 0.8	0.6 / 0.6
Strain at max / break	25 / 28	26 / 43	33 / 44	24 / 25	11 / 13
Elastic modulus [MPa]	3.1	2.9	3.2	5.6	9.0
Mechanical properties at -40°C					
Max / break stress [MPa]	2.6 / 1.8	2.3 / 1.6	2.0 / 1.9	2.9 / 2.8	2.2 / 1.8
Strain at max / break	40 / 91	27 / 80	20 / 27	57 / 62	25 / 65
Elastic modulus [MPa]	14.7	29.5	24.2	15.8	37.2
Physical properties					
Density [kg/m^3]	1646	1597	1573	1535	1601
Glass transition temperature by DMA, Tg [℃]	-52	-50	-51	N/D	N/D
Coefficient of thermal expansion, CTE [$1\cdot10^{-4}$ m/mK]	1.4	1.3	1.4	N/D	N/D

Burn rate characteristics

Table 6 summarizes the burn rate characteristics of the different GAP propellants at 21°C as evaluated through static firing of 2x4-inch test motors. Propellants with RS-RDX and RS-HMX show similar properties and burn rates of around 11 mm/s at 10 MPa are achieved together with pressure exponents of around 0.5. However, if the nitramine is partly or fully replaced by an insensitive energetic filler like AN or FOX-7, burn rates are greatly reduced and pressure exponents are significantly increased to values above 0.6. A propellant containing 65% AN only shows a burn rate of around 6 mm/s at 10 MPa while a propellant with 65% FOX-7 exhibits a burn rate of around 9 mm/s at 10 MPa. However, replacing only 20% of the nitramine with AN results in only 17% drop in burn rate and only in a slightly higher pressure exponent.

Table 6: Reference burn rates and pressure indices of the GAP propellants calculated from firing data of 2x4-inch test motors, using Vielle's burn rate law and least square method. Data recorded at +21°C.

Propellant	GAP/HMX	GAP/RDX	GAP/RDX/AN	GAP/AN	GAP/FOX-7
Composition	65% RS-HMX	65% RS-RDX	45% RS-RDX 20% AN	65% AN	65% FOX-7
Ballistic properties at +21°C					
Burn rate at 6.9 MPa [mm/s]	8.8	9.1	7.5	4.8	6.7
Burn rate at 10 MPa [mm/s]	10.7	10.8	9.2	6.1	8.8
Burn rate at 15 MPa [mm/s]	13.1	13.2	11.5	7.9	11.9
Pressure exponent (~ 5-15 MPa)	0.52	0.48	0.55	0.66	0.74

Safety characteristics

The safety characteristics of the investigated GAP propellants are shown in Table 7. Compared to traditional DB propellants and composite propellants based on inert binders, the GAP propellants demonstrate lower impact and friction sensitivities. It is expected that the sensitivity is lowest for the GAP propellant containing AN as the solid filler, but the impact sensitivity is quite similar for all propellants regardless of type of solid filler. The GAP propellant with FOX-7 has somewhat lower friction sensitivity than the propellants containing nitramines, which is expected based on the lower sensitivity of the coarse FOX-7 compared to both RS-HMX and RS-RDX. The temperatures for the peak maximum exotherms denote the decomposition of the respective solid fillers.

Table 7: Safety characteristics for GAP propellants.

Propellant	GAP/HMX	GAP/RDX	GAP/RDX/AN	GAP/AN	GAP/FOX-7
Composition	65% RS-HMX	65% RS-RDX	45% RS-RDX 20% AN	65% AN	65% FOX-7
Impact energy[(a)] [J]	20 J	19 J	22 J	23 J	18 J
Friction load[(b)] [N]	192 N	184 N	192 N	342 N	240 N
Initial onset exoterm[(c)] [°C]	200	191	163 / 187	N/D	224
Peak maximum exotherm[(c)] [°C]	221	218	180 / 208	N/D	248

(a) UN test 3(a)(ii), BAM lowest impact energy;
(b) UN test 3(b)(i), BAM lowest friction load
(c) STANAG 4515(B2), differential scanning calorimetry (DSC), heating rate 2 °C/min

The shock sensitivity of the GAP propellants have been evaluated by the intermediate-scale gap test according to STANAG 4488, annex B. Figure 2 depicts the detonation threshold pressure. Although initial small-scale gap test (21mm diameter water gap test) showed good prospects with reduced shock sensitivity with increasing content of FOX-7 as reported by Kristensen et.al. [5], the tested GAP propellant with FOX-7 unfortunately show similar shock sensitivity as pure nitramine based GAP propellants. The shock sensitivity is reduced by incorporation of AN in the propellant. The results indicate that the GAP propellants can propagate a detonation, but compared to data reported by others [6,7] the GAP propellants are at least as insensitive to SDT as Azamite® and Azalane® propellants and good insensitive explosives such as I-PBXN-109. The results also demonstrate that the GAP propellants can withstand a somewhat higher shock initiation pressure compared to traditional NEPE propellants plasticized with nitroglycerin.

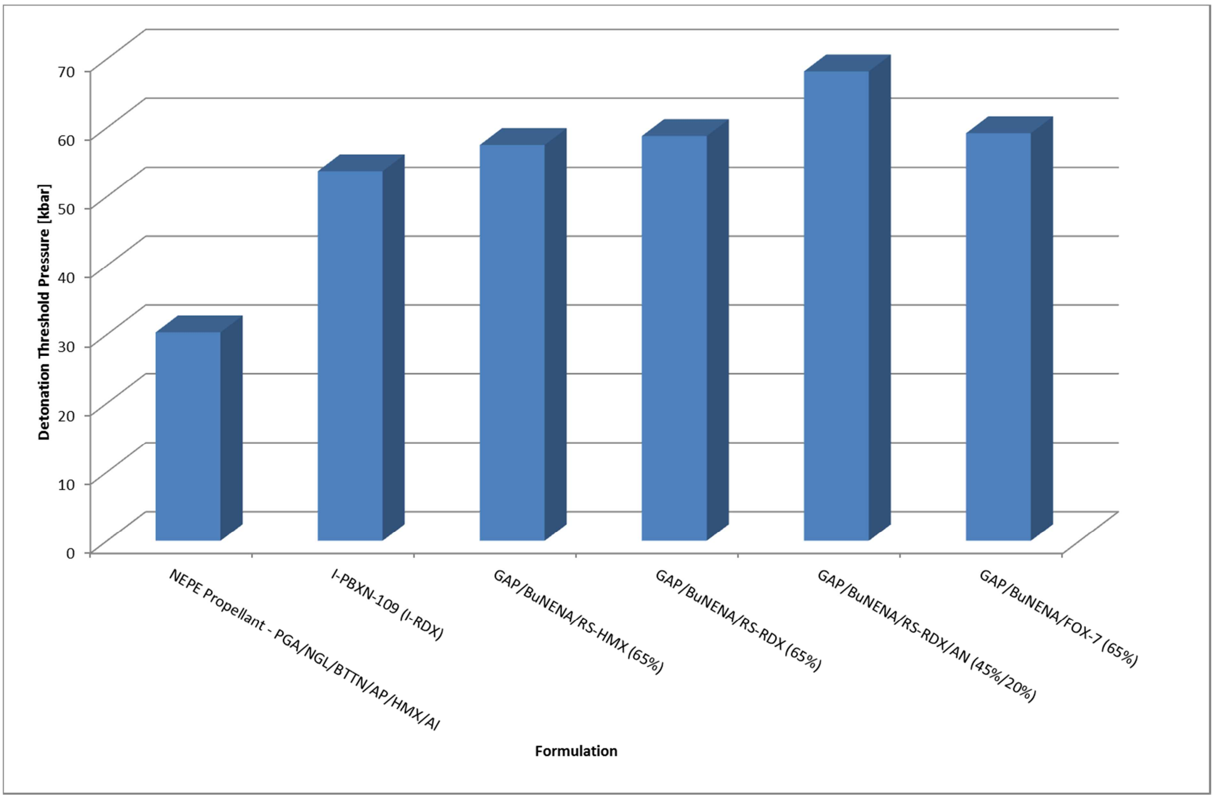

Figure 2: Intermediate scale gap test according to STANAG 4488, annex B. The detonation threshold pressure value is calculated from the acetate card barrier thickness giving the 50% point for GO/NO GO reactions. Twelve trial shots in accordance with the standard Bruceton statistical approach are performed. The diameter of the acceptor charge (test sample) is 40mm and the length is 200mm. The explosive charge used as donor and witness charges, is 95% RDX / 4.5% Wax / 0.5% Graphite and the detonator contains 0.6 g of PETN as the base charge. The reference values for a standard NEPE propellant and I-PBXN-109 are from Nguyen et. al. [7].

Conclusions

FFI and NAMMO have studied sensitivity, and ballistic and mechanical properties of GAP propellants containing 65% energetic fillers. The difference in properties between propellants containing either RS-RDX or RS-HMX is only marginal. Shock sensitivities according to the intermediate scale gap test can only be reduced by incorporation of Ammonium nitrate. GAP/FOX-7 propellants exhibit similar shock sensitivities as GAP propellants containing reduced sensitivity nitramines. Impact and friction sensitivity of either AN or FOX-7 based GAP propellants are in the lower region compared to nitramine based GAP propellants. Both insensitive fillers FOX-7 and AN dilute the energy content of the propellant and reduce burn rates significantly. The use of only AN or FOX-7 as energetic filler indicates a too low energy content for propellant purposes. Due to the usage of traditional bonding agents, GAP propellants containing AN as a minor or main oxidizer exhibit a lower degree of de-wetting and show better low temperature properties than nitramine or FOX-7 based GAP propellants.

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