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Smokeless GAP-RDX Composite Rocket Propellants Containing Diaminodinitroethylene (FOX-7)

Tomas L. Jensen,[a] Erik Unneberg,[a] and Tor E. Kristensen*[a]

Abstract: Composite rocket propellants prepared from nitramine fillers (RDX or HMX), glycidyl azide polymer (GAP) binder and energetic plasticizers are potential substitutes for smokeless double-base propellants in some rocket motors. In this work, we report GAP-RDX propellants wherein the nitramine filler has been partly or wholly replaced by 1,1-diamino-2,2-dinitroethylene (FOX-7). These smokeless propellants, containing 60% energetic solids and 15% *N*-butyl-2-nitratoethylnitramine (BuNENA) energetic plasticizer, exhibited markedly reduced shock sensitivity with increasing content of FOX-7. Conversely, addition of FOX-7 reduced the thermochemical performance of the propellants, and samples without nitramine underwent unsteady combustion at lower pressures (no burn rate catalyst was added). The mechanical characteristics were quite modest for all propellant samples, and binder-filler interactions improved slightly with increasing content of FOX-7. Overall, FOX-7 remains an attractive, but less than ideal, substitute for nitramines in smokeless GAP propellants.

Introduction

For some years, we have actively pursued new smokeless composite rocket propellants based on nitramine fillers (RDX or HMX), glycidyl azide polymer (GAP) binder and low sensitivity nitratoethylnitramine (NENA) energetic plasticizers – the intent being the possible replacement of double-base propellants with such propellants for certain applications in tactical missiles [1,2]. This development has been partially motivated by the hazards connected to handling of sensitive nitrate ester plasticizers during transport and propellant manufacture, as well as the tightening regulations associated with the use of certain heavy metal burn rate modifiers in traditional smokeless propellants.

In general, GAP-nitramine-NENA rocket propellants are detonable compositions [2], but their shock sensitivity compares favorably with that of similar propellant compositions containing more sensitive nitrate ester plasticizers [2,3]. Partial or complete replacement of the nitramine in such propellants with 1,1-diamino-2,2-dinitroethylene (FOI Explosive-7, FOX-7 or DADNE), a low sensitivity explosive first reported by Swedish researchers in 1998 [4,5], could perhaps further attenuate their shock sensitivity. FOX-7 is commercially available through the company Eurenco Bofors in Sweden.

Composite rocket propellants containing ammonium perchlorate (AP) and FOX-7 have been developed by Lips, Menke and co-workers [6,7]. These propellants contained 68–70% AP/FOX-7, 14–15% GAP or polyester-polyurethane binder and 14–15% energetic plasticizers. The AP content helped to endow these propellants with several favorable attributes, such as advantageous burn rate behavior, low shock sensitivity and good mechanical characteristics. However, only the AP-free propellant composition conformed to the smokeless AGARD coefficient label AA classification, and the properties of this particular composition are less satisfactory [7].

We were curious as to whether addition of FOX-7 could attenuate the shock sensitivity of GAP-nitramine propellants – without accompanying detrimental effects on other attributes of the propellant. Herein, we report our work with AP-free, smokeless GAP-RDX-BuNENA composite propellants in which the nitramine has been partly or completely substituted by FOX-7.

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Results and Discussion

We prepared three simplified GAP propellants containing FOX-7 on 1.5 kg scale (Table 1). All formulations contained 60% FOX-7/RDX energetic solids, 15% BuNENA energetic plasticizer and 0.75% standard nitrate ester stabilizers. The particle size distributions for the respective classes of FOX-7 are detailed in the experimental section. The RDX employed (I-RDX®) was a reduced sensitivity type supplied by Eurenco.

The first formulation (Prop. 1) contained 60% FOX-7 in trimodal particle size distribution. The second formulation (Prop. 2) contained 40% trimodal FOX-7 and 20% unimodal RDX. The third formulation (Prop. 3) contained 20% unimodal FOX-7 and 40% bimodal RDX. All formulations were cured for 120 h at 60 °C, using a standard curing system consisting of isocyanate N100 curing agent (NCO/OH curing ratio = 1.0 for all samples) in combination with the curing catalyst triphenylbismuth (TPB). No burn rate modifier was added to any of the formulations, but a neutral polymeric bonding agent (NPBA) was added to the two formulations containing RDX, in the belief that it could enhance the mechanical characteristics of the propellant samples [8].

Preliminary experiments had shown that the viscosity of the propellant mixtures was heavily dependent on their content of fine-particulate FOX-7 (classes 1 and 2) – to a greater extent than observed for comparable propellants containing only nitramine solids. Accordingly, the final three propellants (Prop. 1–3 in Table 1) had a relatively modest content of fine-particulate FOX-7 (typically 10%).

While FOX-7 has a detonative performance similar to RDX, and an identical oxygen balance (–21.6%), its thermochemical performance with respect to specific impulse in a rocket motor is considerably less satisfactory. Calculated using standard computer software (EXPLO5 V6.03), FOX-7 at its crystal density

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of 1.88 g·cm^{-3} has a detonation pressure of ~33 GPa, compared to ~34 GPa for RDX. In a rocket motor, upon equilibrium expansion from a chamber pressure of 6.9 MPa to ambient conditions (1 atm), pure FOX-7 has a specific impulse of ~239 s, compared to ~266 s for pure RDX. Calculated thermochemical performances of the three propellant compositions are given in Table 2.

Table 1. Smokeless GAP-FOX7/RDX-BuNENA propellant formulations.[a]

Constituent	Prop. 1 (wt-%)	Prop. 2 (wt-%)	Prop. 3 (wt-%)
FOX-7 (class 1)	5.00	5.00	
FOX-7 (class 2)	5.00	5.00	20.00
FOX-7 (class 3)	50.00	30.00	
I-RDX® (~200 µm)		20.00	30.00
I-RDX® (class 5)			10.00
GAP Diol	21.11	21.08	21.08
Isocyanate N100	3.12	3.12	3.12
BuNENA	15.00	15.00	15.00
MNA[b]	0.50	0.50	0.50
2-NDPA[c]	0.25	0.25	0.25
TPB	0.025	0.025	0.025
NPBA		0.025	0.025

[a] All three propellants were prepared on 1.5 kg scale. [b] *N*-Methyl-*p*-nitroaniline. [c] 2-Nitrodiphenylamine.

Table 2. Calculated thermochemical properties of smokeless GAP-FOX7/RDX-BuNENA propellants.[a]

Property	Prop. 1	Prop. 2	Prop. 3
Maximum density [g·cm^{-3}]	1.56	1.54	1.53
Oxygen balance [%]	–62.8	–62.9	–62.9
Specific impulse [s]	208	214	219
Characteristic exhaust velocity [m·s^{-1}]	1187	1237	1289

[a] Calculated with EXPLO5 V6.03, using a chamber pressure of 6.9 MPa (1000 psi) and equilibrium expansion to 0.101 MPa (1 atm).

Replacement of RDX with FOX-7 had a notable effect on the thermochemical performance of the propellants (Table 2), with the specific impulse dropping about 11 s from the most nitramine-rich propellant (Prop. 3) to the most FOX-7-rich one (Prop. 1). It should be kept in mind that all propellants had relatively modest solids loading (60%). This reduced their thermochemical performance, but allowed us to better probe the mechanical attributes of the propellants.

Of more concern to us were the burn rate characteristics of the propellant formulations. Burn rates and pressure exponents from Crawford measurements are outlined in Table 3. No burn rate catalyst had been added to any of the three propellants. Non-catalyzed GAP-nitramine propellants generally have low burn rates and high pressure exponents [8,9]. The addition of FOX-7 to GAP-RDX propellants seemed to reduce the burn rate only slightly (Table 3), but the propellant containing only FOX-7 (Prop. 1) exhibited erratic burn rate behavior at low pressures. Accordingly, data of sufficient quality could not be obtained from this propellant. Both from thermochemical and kinetic perspectives, the use of FOX-7 in composite propellants apparently necessitate the application of additives. For the time being, it is unknown to what extent the use of burn rate catalysts may remedy the burn rate characteristics of GAP propellants containing FOX-7. Moreover, burn rates are affected by particle size distributions, and the content of fine-particulate FOX-7 was modest in all propellants.

Table 3. Burn rate characteristics of smokeless GAP-FOX7/RDX-BuNENA propellants.[a]

Property	Prop. 1	Prop. 2	Prop. 3
Burn rate at 6.9 MPa [mm·s^{-1}]	–	5.44	5.40
Burn rate at 10 MPa [mm·s^{-1}]	–	7.41	7.44
Burn rate at 15 MPa [mm·s^{-1}]	9.91	10.67	11.19
Pressure exponent	–	0.86	0.93

[a] Measured by strand burning of inhibited propellant strands in the Crawford bomb, in a pressure interval of ~5–20 MPa.

In previous work, we have investigated the processing and mechanical properties of GAP-nitramine composite propellants in much detail [1,2,8], including propellants containing ammonium dinitramide (ADN) [10]. We were expectant as to how the inclusion of FOX-7 in such formulations might influence these characteristics. Processing parameters, mechanical characteristics and thermal properties of the three propellants in Table 1 are given in Table 4.

As previously mentioned, FOX-7, and then finely divided FOX-7 in particular, influenced the viscosity of the propellant mixtures appreciably. The propellant with only FOX-7 (Prop. 1) as energetic filler had a substantially higher viscosity than the two other RDX-containing mixtures (Table 4). All three mixtures had more than adequate pot lives, testifying to the chemical inertness of FOX-7 under such conditions. The curing was carefully monitored by FTIR spectroscopy – the continuous depletion of the curing agent was accompanied by formation of urethane bonds, and all isocyanate was consumed. FOX-7 did not adversely affect the isocyanate curing process.

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Samples of all three propellants had quite modest mechanical properties (Table 4). As this had been anticipated, a small quantity of a neutral polymeric bonding agent (NPBA) had been added to the two RDX-containing propellants (Prop. 2 and 3) in an attempt to improve binder-filler interactions. This apparently did not remedy the rather meek mechanical behavior of the propellant samples. Furthermore, the measured tensile strengths in fact indicated that samples with a higher content of FOX-7 might have a slightly improved performance relative to samples containing more RDX – with any evaluation on the basis of sample elongations being assessed as too random to be of a definitive value (Table 4). As the applied RDX was of a reduced sensitivity type (I-RDX®), with rounded, spherical crystals, the differences among the propellant samples could possibly be an effect of crystal character rather than any innate characteristic of FOX-7 vs. RDX.

Table 4. Processing parameters, mechanical characteristics and thermal properties of smokeless GAP-FOX7/RDX-BuNENA propellants.

Processing parameters	Prop. 1	Prop. 2	Prop. 3
Viscosity[a] [Pa·s]	310	43	24
Pot life (tan δ = 1) [h]	38	24	25
Mech. properties at 21 °C[b]	Prop. 1	Prop. 2	Prop. 3
Max tensile strength [MPa]	0.29	0.26	0.22
Strength at break [MPa]	0.26	0.22	0.21
Elongation at max strength [%]	10.5	7.5	18
Elongation at break [%]	18.9	14.7	24.4
Elastic modulus [MPa]	4.71	4.53	2.25
Thermal properties	Prop. 1	Prop. 2	Prop. 3
T_g by DMA 1 Hz [°C]	–55.2	–55.5	–55.5
Initial onset exotherm[c] [°C]	173	172	173
Peak maximum exotherm[c] [°C]	256	242	240

[a] Measured 1 h after addition of curing agent. [b] Uniaxial tensile testing of dog bone samples (crosshead speed = 50 mm·min^{-1}). [c] Measured by differential scanning calorimetry (DSC) at a heating rate of 10 K·min^{-1}.

All three propellants had encouraging glass transition temperatures around –55 °C (Table 4), as measured through dynamic mechanical analysis (DMA). These values are similar to those of regular GAP-nitramine-BuNENA propellants [1,2].

In previous work, we have employed a specialized DMA technique, so that one may probe the binder-filler interactions in GAP composite propellants [8]. The analysis of the three propellants according to this procedure, in the most relevant temperature region, is presented in Figure 1, where the damping factor (tan δ) is plotted as a function of temperature. Decreased damping may be a sign of improved binder-filler interactions because tan δ is the ratio of the loss modulus to the storage modulus of the samples – decreased damping is thus an indication of increased elastic response and decreased dissipative losses due to viscous flow [8]. The method is only suggestive, because clear differences among the propellant samples are only pronounced in the temperature interval given in Figure 1. Nevertheless, our results indicate that the damping factor increases at higher levels of I-RDX®, signifying less efficient binder-filler interactions. This could perhaps substantiate some of the results from the tensile testing.

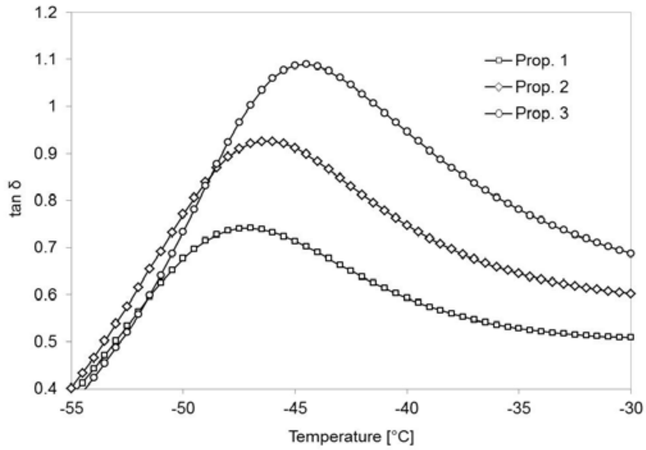

Figure 1. Dynamic mechanical analysis of GAP-FOX7/RDX-BuNENA propellant specimens (oscillating frequency: 1 Hz, heating rate: 1 K·min^{-1}, amplitude: 20 μm).

FOX-7 has a thermal stability that is comparable to RDX [4], but the presence of FOX-7 in GAP-RDX propellants lowered the temperature for onset exotherm about 20 °C when compared to regular GAP-RDX-BuNENA propellants (Table 4) [1,2].

FOX-7 has impact and friction sensitivities that are favorable compared to RDX [4,5]. These safety characteristics are quite satisfactory for GAP-RDX-BuNENA propellants [1,2]. However, and perhaps because of the angular and sharp character of the FOX-7 crystals, the impact and friction sensitivities of the FOX-7 propellants were actually higher than those for similar propellants containing only RDX as energetic filler. We obtained impact sensitivities on the order of 3–4 J and friction sensitivities in the range of 170–190 N for the three propellants in Table 1 (with no pronounced differences among the propellants). The results were not conclusive, and we believe them to be highly dependent on the exact crystals characteristics of the employed FOX-7.

Of more importance to us was the shock sensitivity of the propellants, as this is a serious weakness of GAP-nitramine propellants compared to regular AP composite propellants. Shock testing was conducted according to equipment specified in STANAG 4488, using the small scale (21 mm) water gap test originally developed by Bundesinstitut für chemisch-technische Untersuchungen (BICT) – often referred to as the BICT gap test

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[11]. The donor charge, consisting of a booster pellet of pressed HWC (RDX, wax and graphite pressed to 1.60 g·cm^{-3}) equipped with a standard detonator, and the acceptor charge of rocket propellant (21 mm diameter, 40 mm in length) were confined in a polymethyl methacrylate (PMMA) tube with an adjustable water gap in between.

Due to the limited quantities of material available, a slightly simplified test procedure – with respect to the standard Bruceton type statistical approach – was applied for the shock testing. The water gap height was gradually decreased until five consecutive detonative transmissions had been realized – this gave the water barrier thickness for detonation of the propellant test sample (positive result, “go” reaction). The water gap height was then gradually increased until no successful detonative transmissions were attained on five consecutive trials – this gave the water barrier thickness for no detonation of the propellant test sample (negative result, “no go” reaction).

The results from the shock testing according to this test procedure are summarized in Table 5. A distinctive decrease in shock sensitivity with increasing content of FOX-7 is evident from Table 5. Previous intermediate scale (40 mm) gap testing of comparable GAP-RDX-BuNENA propellants with 65% RDX solid loadings, undertaken by the company Nammo Raufoss [2], had resulted in a threshold pressure of ~59 kbar. No calibration data for water gap heights less than 7 mm, and their affiliated shock pressures (~49.5 kbar for 7 mm), are available for the small scale water gap test. Nevertheless, the shock testing brought out a clear trend in which the propellant shock sensitivity decreased with increasing content of FOX-7.

Table 5. Shock testing of GAP-FOX7/RDX-BuNENA propellants in the small scale (21 mm) BICT water gap test.

Propellant	No detonation[a] [mm water]	Detonation[b] [mm water]
Prop. 1 (60% FOX-7)	5	2
Prop. 2 (40% FOX-7, 20% RDX)	7	4
Prop. 3 (20% FOX-7, 40% RDX)	9	7

[a] No detonative transmission on five consecutive trials. [b] Five successive detonative transmissions.

Conclusions

We found that application of FOX-7 in smokeless GAP-RDX propellants was encouraging from a safety perspective – the shock sensitivity of the propellants decreased notably with increased content of FOX-7. Additionally, the mechanical characteristics of the propellants were not adversely affected by the addition of FOX-7, although there remains some ambiguity in the exact interpretation of the results obtained from the mechanical testing.

In terms of thermochemical performance, the addition of FOX-7 to GAP-RDX propellants was associated with a non-trivial loss of specific impulse. The burn rate of non-catalyzed GAP-FOX7/RDX-BuNENA composite propellants was low (~5.5 mm·s^{-1} at 6.9 MPa), and propellant samples without RDX tended to undergo unstable combustion at low pressures.

Taken together, FOX-7 is an attractive, but less than ideal, substitute for nitramines in smokeless GAP propellants. The inclusion of additives, in combination with proper balancing of the particle size of the energetic fillers, might open up for a more widespread application of FOX-7 in propellants.

Experimental Section

FOX-7 was supplied by Eurenco Bofors (Sweden). The crystalline material has a characteristic, bright yellow color. Three classes of FOX-7 were used in this work: Class 1 (d50 = 20–25 μm), Class 2 (d50 = 45–50 μm) and Class 3 (d50 = 110–130 μm). GAP diol (M_n = 1796, M_w = 1951, equivalent weight = 1230) and I-RDX® (class 5, with particle sizes ~1–10 μm, and a coarse fraction with particle sizes ~150–200 μm) were obtained from Eurenco (France), and BuNENA plasticizer was acquired from Chemring Nobel (Norway). BuNENA was used as received, while FOX-7 and I-RDX® were dried at 60 °C for 3 days before use. The NPBA type bonding agent was synthesized in accordance with our previous work [8].

Propellant mixtures were prepared on 1.5 kg scale in an IKA vertical mixing system (HKV-5), as reported earlier [8,10]. Uniaxial tensile testing was conducted with an 810 MTS (Material Testing System) according to the procedure of STANAG 4506. Dynamic mechanical analysis (DMA) was carried out with a TA Instruments DMA Q800, and differential scanning calorimetry (DSC) was carried out using a TA Instruments DSC Q1000. Rheology measurements were performed with an Anton Paar MCR 102 rheometer. FTIR spectra were recorded on a Nicolet iS10 spectrometer equipped with a heated diamond plate for ATR measurements.

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Keywords: Propellant • RDX • HMX • GAP • FOX-7

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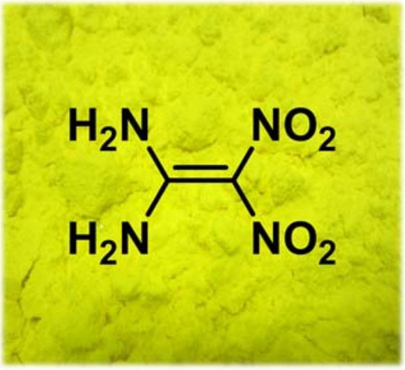
Diaminodinitroethylene (FOX-7) is a potential substitute for nitramines (RDX or HMX) as energetic filler in smokeless composite rocket propellants. Herein, we report our work with composite propellants based on RDX and/or FOX-7 fillers, glycidyl azide polymer (GAP) binder and butyl-2-nitratoethylnitramine (BuNENA) energetic plasticizer.



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