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Formulation and Characterization of a New Nitroglycerin-Free Double Base Propellant

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Abstract: Double base propellants composed of nitrocellulose (NC) and nitroglycerine (NG) are widely used. However, the inclusion of liquid NG presents both stability and performance problems: the NG may migrate from the propellant in storage, and it softens the propellant at high inclusion levels. In this work, the novel nitrate ester 1,4-dinitrato-2,3-dinitro-2,3bis(nitratomethylene) butane (SMX) is considered as a replacement for NG in a double base propellant. Thermochemical calculations indicate improved performance when compared with the common double base propellant JA2 at SMX loadings above 40 wt-%. Also, since SMX is a room temperature solid, migration may be mitigated. Both unplasticized and plasticized propellants were formulated to enable the study of the interaction of SMX with nitrocellulose. Thermal analysis of unplasticized propellant showed a distinct melt-recrystallization curve, which indicates that a solid phase solution is being formed between SMX and NC, and that SMX would not act as plasticizer. Analysis of propellant prepared with diethyleneglycol dinitrate (DEGDN) plasticizer indicates that the SMX is likely dissolved in the DEGDN. The plasticized material also showed similar hardness and modulus to JA2. Safety characterization showed that sensitivity is similar to JA2. In short, replacing NG with SMX results in a new family of propellants with acceptable safety characteristics and which may also offer improved theoretical performance.

Keywords: Double base propellant · SMX · Nitrate ester · Nitrocellulose · Nitroglycerin

1 Introduction

Double base propellants composed of nitrocellulose (NC) and nitroglycerin (NG) have been used in rocket and gun applications since the late 1800s [1]. Such propellants offer several benefits over their more modern composite counterparts, including simple formulation, high modulus and strength, and chlorine-free minimum smoke exhaust products [2,3]. Nevertheless, double base propellants are plagued with several drawbacks. The majority of these issues stem from the inclusion of NG as a major energetic ingredient. Like all nitrate esters, NG is capable of autocatalytic decomposition under certain storage conditions, and its tendency to migrate during propellant processing and storage has been widely observed and studied [4–6]. Additionally, due to the low melting point of NG (287 K), its quantity in propellants must be limited to prevent excessive degradation of grain strength, thus placing an upper bound on the performance of NG-based propellants. In an effort to overcome these issues, one might consider a room temperature-solid nitrate ester as a replacement. Pentaerythritol tetranitrate (PETN) is the standard bearer of this family, in wide manufacture and use since the 1930s [7], however its low oxygen balance (−10%), high sensitivity to friction and impact, and poor deflagration at atmospheric pressure make it an inferior prospective propellant ingredient.

In 2008, Chavez et al. [8] reported the synthesis of a new solid nitrate ester, 1,4-dinitrato-2,3-dinitro-2,3bis(nitratomethylene)butane (colloquially, SMX). SMX has a better oxygen balance (0%, CO_2 balanced) than PETN while surpassing it in density (1.917 g cm^{-3}). Its sensitivity to various initiating stimuli is similar to that of PETN [8]. Additionally, as a room temperature solid, SMX offers the potential for reduced migration and improved propellant physical properties at high concentrations. As such, SMX may have the combination of performance and stability to serve as a viable replacement for NG.

Though fielded double base propellants have changed little in the past few decades, recent work by Wolszakiewicz et al. [9] with 2,4-dinitrotoluene and related compounds reported the formation of an energetic solid-phase solution by combining a solid nitrate ester compound with nitrocellulose. Such a process would be ideal for the incorporation of SMX into an NC-based system, thus forming a new class of double base propellants.

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The objective of this work is to formulate a new double base propellant with SMX as a replacement for NG. The theoretical performance of the SMX-NC family of propellants is compared to that of a common propellant, JA2. Finally, the safety, thermal, and mechanical properties of the new material are characterized.

2 Experimental

2.1 Performance Prediction

The gun impetus performance of SMX-NC propellants was calculated using the Cheetah v6 thermochemical code [10] with the Blake product library, assuming a loading density of 0.25 g cm^{-3}. Rocket specific impulse calculations were performed at 6.89 MPa chamber pressure and shifting equilibrium sea level expansion with the JCZS product library. An existing propellant formulation, JA2, was used as a baseline for comparison in each case. The formulation for JA2 is listed in Table 1. Additional calculations were run using 25% diethyleneglycol dinitrate (DEGDN) plasticizer in an SMX-NC formulation to allow further comparison between NG-based and SMX-based formulas.

Table 1. JA2 reference propellant formulation.

Constituent	wt-% of total
Nitrocellulose (13.4% N)	59.5
Nitroglycerin	14.9
Diethylene glycol dinitrate	24.8
Ethyl centralite	0.7
Magnesium oxide	0.05
Graphite	0.05

2.2 Propellant Processing

Nitrocellulose fibers (Type B, 13.4% N, RFAAP, Radford, VA) were swelled in a 3:1 blend of anhydrous ethanol (100% USP, Koptec) and diethyl ether (anhydrous ≥99% ACS Reagent, Sigma-Aldrich) for 30 min. SMX was dissolved at its lower solubility limit (0.897 g cm^{-3}) in acetone, and this solution was added to the swollen nitrocellulose fibers. The resulting ternary solvent blend was allowed to stir uncovered until dry. The material was heated at 10 °C min^{-1} to 120 °C and held at temperature for 40 min, allowing the SMX to melt onto the surface of the NC fibers. Following this period, the material was cooled prior to handling.

Material was used as prepared for the bulk of the characterization work, including safety testing and microstructural characterization. Additionally, small samples of the SMX-NC formulation were pressed using a 6.35 mm die at 172 MPa die pressure to enable evaluation of the physical properties of the compacted material.

Additional propellant was processed with diethyleneglycol dinitrate (DEGDN) plasticizer (Picatinny Arsenal, NJ). In this formulation, SMX was added to a 1:1 blend of ethanol and acetone. The appropriate amount of DEGDN was added via micropipette and the resulting solution stirred to dissolve the SMX and homogenize the DEGDN. This solution was then kneaded with the nitrocellulose fibers on a polytetrafluoroethylene (PTFE) sheet to form a gelatinous mixture. A small amount of additional solvent blend was added during kneading to keep the mixture wetted. Once mixed, the material was spread into a thin layer and allowed to dry. Material was tested either in powder form or pressed using a stainless steel die in a Carver press at 172 MPa die pressure.

2.3 Material Characterization

Safety characteristics of the material were evaluated using standard procedures from MIL STD 1751A [11]. Drop weight impact height was determined using method 1012 (ERL). The go/nogo criterion was complete destruction of the sample and the 180 grit underlayment. Electrostatic discharge (ESD) was tested using method 1032 (ARDEC). Friction was tested using method 1024 (BAM) on a Chilworth machine. All test statistics were calculated using a D-optimal analysis technique [12].

The microstructure of the prepared material was examined with scanning electron microscopy (SEM) with a FEI Nova NanoSEM. Specific surface area measurements were conducted using the Brunauer, Emmett and Teller method (BET) on a Micromeritics Tristar 3000. Prior to surface area measurement, the materials were degassed under nitrogen for 2 h at 60 °C. Thermal analysis was conducted with a TA Instruments Q600 simultaneous differential scanning calorimeter/thermogravimetric analyzer (DSC/TGA) at a heating rate of 10 K min^{-1}, under ultra high purity argon at a flow rate of 100 mL min^{-1}. Open alumina pans (90 μL) were employed. The density of the powdered material was measured with a Micromeritics AccuPyc II 1340 gas pycnometer in a 10 cm^3 chamber using helium gas adsorption. Shore D hardness testing was conducted on the compacted samples using a REX RX-1600-D hardness tester.

3 Results and Discussion

3.1 Predicted Performance

As hypothesized, the predicted performance of the SMX-NC propellant compositions compares quite favorably with that of the baseline JA2 (NG-NC) propellant composition. Direct comparisons of the predicted SMX-NC performance and the predicted JA2 performance in both rocket (specific impulse) and gun (impetus) applications are shown in Figure 1. The SMX-NC propellant theoretically outperforms JA2 in guns at SMX concentrations greater than about 35 wt-%, and in rockets at SMX concentrations greater than about 15 wt-%. In addition to NG, JA2 also contains the energetic plasticizer diethyleneglycol dinitrate (DEGDN). The addition of DEGDN reduces the predicted performance of
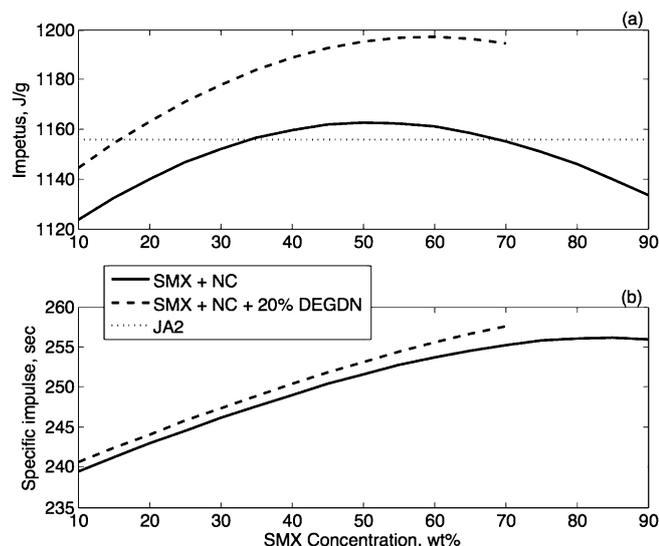
Figure 1. Predicted performance of SMX-NC propellants as a function of SMX content in (a) guns and (b) rockets. The predicted performance of JA2 is is included as a reference.

JA2 when compared to that of a pure NG-NC propellant. However, DEGDN addition further improves the predicted performance of SMX-NC compositions in guns, allowing them to surpass the predicted performance of JA2 at SMX loadings of only about 30 wt-%. Significant performance increases are predicted at higher SMX concentrations with 25 wt-% DEGDN. As a result of the higher melting point of SMX, these higher concentrations may be feasible without significant degradation of propellant strength. With the favorable oxygen balance of SMX, further increases in performance may be achieved with the inclusion of high-enthalpy fuels (e.g., nanoaluminum; see Figure 2). These performance increases must be balanced with the requirement
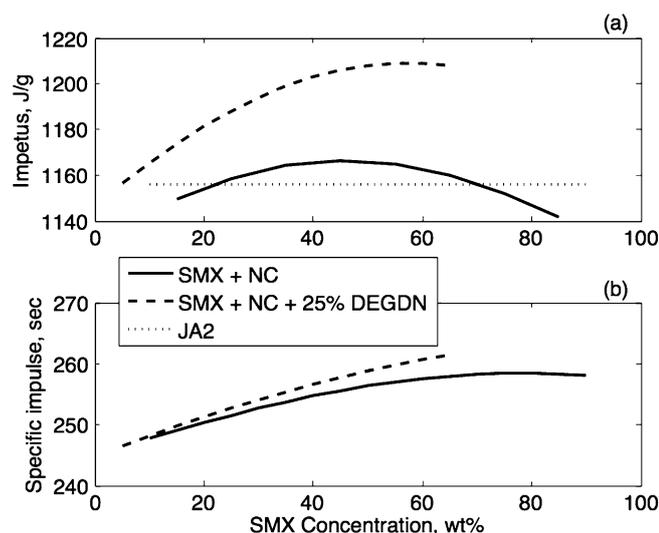
Figure 2. Performance of plasticized and non-plasticized SMX-containing double base propellants with 5 wt-% aluminum in (a) guns and (b) rockets.

for a strong finished product that is easily processed; since solid SMX is replacing liquid NG in the blend, propellant modulus and processing viscosity may become a concern at high loading levels.

As a result of these performance calculations, we elected to focus processing and characterization efforts at an SMX loading of 40 wt-%. This level of SMX surpasses the impetus performance of JA2 while maintaining a similar energetic material content, thus providing a reasonable compromise between sensitivity and performance.

3.2 Propellant Processing

The processing of NC-based propellants is somewhat of an art form, which balances the dispersion of liquid and solid ingredients with careful destruction of the outer layers of the NC fibers, resulting in a final product with constituents bound at the physical and molecular levels. To achieve such equilibrium, large quantities of solvents at select ratios are often employed – popular choices include 3:1 blends of ether and ethanol, acetone, and 2-propanol, and ethyl acetate and ethanol. The fibers and energetic additives must be kneaded in the solvent to form a gelatinous dough and facilitate mixing. This is accomplished using twin-screw extrusion in large scale production of current propellants.

Since SMX and NC are soluble in the same reagents, care must be taken to ensure the SMX is added to the softened fibers in a manner that does not fully destroy them (i.e., co-dissolution in acetone), as some amount of fiber must remain intact to give the finished product strength and flexibility.

The process developed results in deposition of micron-scale SMX crystals on and around the softened NC matrix, leaving the bulk of the fiber intact, as shown in the SEM image in Figure 3a. Subsequent heating to beyond the melting point of SMX causes these crystals to melt, allowing the SMX to wick onto the surface and into the NC fibers. Following cycling, no crystals are apparent in the SEM image (Figure 3b).

To confirm that the SMX had in fact wetted and coated the NC fibers, BET analysis was conducted to evaluate the specific surface area of the fibers before and after SMX addition, and again after thermal cycling. Swelled NC fibers (without SMX) have a relatively high surface area of $3.5 \pm 0.08 \text{ m}^2\text{g}^{-1}$. Following SMX addition, this surface area drops to $1.9 \pm 0.03 \text{ m}^2\text{g}^{-1}$ as the large, smooth SMX crystals decrease the area for adsorption. Finally, following thermal cycling, the surface area drops further to $1.1 \pm 0.02 \text{ m}^2\text{g}^{-1}$ as the SMX wets the NC fibers, and more intimate mixing is achieved. This reduction in surface area indicates that additional processing of the NC is possible; further destruction of the NC fibers prior to SMX addition should improve finished propellant properties and provide an opportunity for more intimate SMX/NC contact.
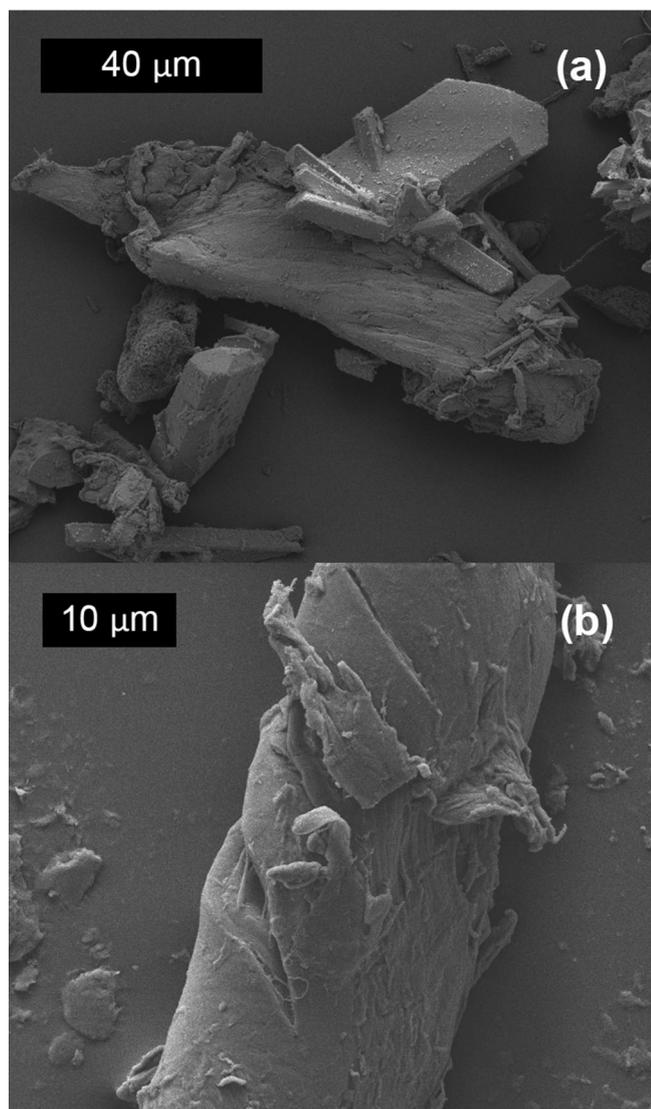
Figure 3. SEM images showing 40 wt-% SMX-NC prior to thermal cycling (top) and after thermal cycling (bottom). Note disappearance of large crystalline structures around fibers.

To investigate the potential of improved fiber destruction, additional material samples were processed with the addition of 25 wt-% DEGDN plasticizer. This processing method is more concomitant with traditional double base mixing techniques, and resulted in a pliable, homogeneous propellant that appears similar to JA2 in consistency. This propellant was also characterized, as it not only shows superior theoretical performance, but was also far easier to process.

3.3 Physical Characterization

The density of the thermally cycled powder was measured using gas pycnometry to be 1.814 g cm^{-3}. When pressed at 172 MPa die pressure into a variety of geometries (perforat-

ed and non-perforated cylinders), compact densities of 90–95 % were realized. These densities are in line with that for the baseline propellant JA2, indicating that SMX-NC propellant is competitive on a volumetric basis with existing fielded options.

Compacted pellets were also subjected to hardness testing. The 40 % SMX-NC pellet was significantly harder than the JA2 baseline – 67 Shore D, vs. 41 Shore D. This high hardness indicates a very high modulus for the propellant [13]. High modulus propellants tend to experience undesirable deconsolidated burning at elevated pressures [14]. The 25 wt-% DEGDN plasticized formulation has a Shore D hardness level of 37. With hardness and modulus values much closer to the values of JA2 that are acceptable, this propellant should avoid the tendency for deconsolidated burning.

3.4 Thermal Property Testing

Thermal behavior of the material was analyzed using DSC/TGA. The thermally cycled 40 wt-% SMX-NC exhibited a lowered melting point onset than non-cycled material (see Figure 4). Additionally, when freshly cycled material was cooled and reheated within a shorter period (24–48 h), no re-melt was visible. As such, it appears that a solid-phase solution may be formed between SMX-NC, in a similar fashion as shown in previous work with other nitrate esters [9]. To further evaluate this behavior, small samples of propellant were prepared at SMX loadings ranging from 20 wt-% to 80 wt-% and assessed with DSC. Increasing the concentration of SMX raised the melt onset temperature, gradually approaching the melt onset temperature for neat SMX as the concentration approached 100 %. The melt endotherm maximum temperature also increased with increasing SMX concentration. However, the melt endotherm maximum
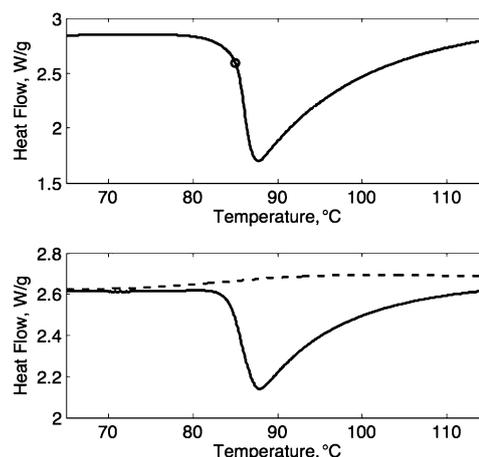
Figure 4. DSC-TGA results for 40 % SMX-NC, after long-term storage (top) and during/immediately following thermal cycling.The measured melt onset point of neat SMX (as indicated) is identical to the range reported in the literature [8].
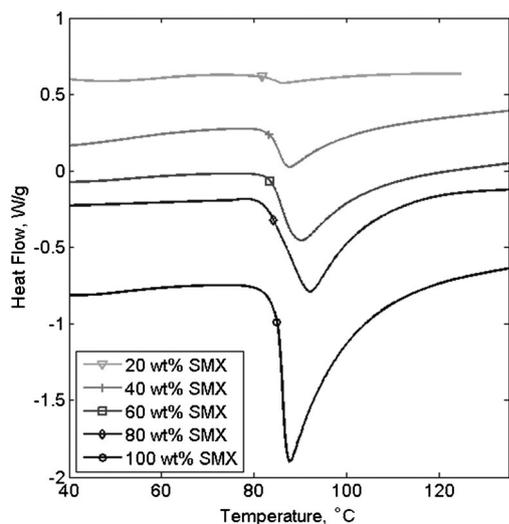
Figure 5. Top to bottom: DSC-TGA results for NC with 20 wt-%, 40 wt-%, 60 wt-%, 80 wt-%, and 100-% SMX, showing the increasing melt onset temperatures with increasing SMX concentration.

temperature was higher than that of neat SMX in most cases, illustrating the interaction between NC and SMX. Figure 5 and Table 2 show this trend.

Propellant prepared with DEGDN plasticizer showed much different thermal behavior, analogous to that of JA2. At a 15 wt-% DEGDN concentration, the endotherm maximum temperature was decreased to 70 °C. Further reduction was seen at a 25 wt-% DEGDN (to 62.6 °C), but little total heat flow was observed. It is likely that the SMX is nearly completely dissolved in the DEGDN. This curve is very similar to that exhibited by JA2, as shown in Figure 6.
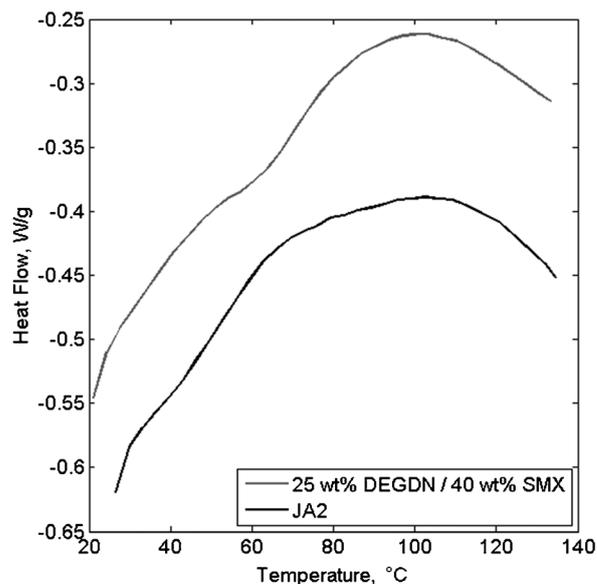
3.5 Safety Characterization

As specified in the MIL STD [11], powdered material was used for safety characterization to represent worst-case scenario handling conditions. Characterization results are summarized in Table 3. The response to stimulus from friction, electrostatic discharge (ESD), and drop weight impact was similar to that of the baseline JA2 propellant: mildly friction and impact sensitive, and insensitive to ESD. Addition of plasticizer lowered the mean friction sensitivity, but also lowered the drop weight impact go height. However, both differences are within the error tolerance for the measure-

Figure 6. DSC-TGA results comparing NC + 40 wt-% SMX + 25 wt-% DEGDN, and JA2 propellant, shifted for clarity. The plasticized propellant behaves in a manner very similar to that of the reference JA2.

Table 3. Sensitivity test results for the 40 wt-% SMX-NC materials, compared to results for neat SMX and results for JA2 propellant.

SMX concentration [wt-%]	Melting onset point [°C]
20	81.78
40	83.18
60	83.43
80	84.15
100	84.90

ment, indicating little actual change in handling properties – both propellants are similar to JA2 in sensitivity.

4 Conclusions

SMX appears to be an interesting and viable replacement for nitroglycerin in propellant applications. As a room temperature solid, it can be loaded to higher levels in propellant formulations than nitroglycerin, allowing potential gains in performance beyond the range available today

Table 2. Melting onset points as a function of SMX concentration for SMX/NC compounds. The melting point onset increases monotonically with increasing SMX concentration.

	Drop weight [cm]	ESD [J]	Friction [kgf]
Neat SMX	20	0.172	7.6 [a)]
NC + 40 wt-% SMX	115 ± 30	> 0.25	17.4 ± 1.1
NC + 40 wt-% SMX + 25 wt-% DEGDN	103 ± 25	> 0.25	25.8 ± 2.3
JA2	115 ± 15	> 0.25	21.6 ± 2.6

a) From Chavez et al. [8].

with conventional double base propellants. We present two methods of processing SMX with nitrocellulose: one which forms a solid-phase SMX-NC solution at the surface of the NC fibers, and one which incorporates SMX and the energetic plasticizer DEGDN into partially destroyed NC fibers, in a manner similar to that of existing double base processing methods. Both formulations show promise for high performance.

At the 40 wt-% level, and in concert with the energetic plasticizer DEGDN at a 25 wt-% level, the resulting material is a pliable propellant compound with similar physical and sensitivity characteristics to the reference propellant JA2. However, such a formulation delivers higher theoretical performance than JA2, and has potential for reduced migration due to the solid phase of the energetic ingredient. With additional work to quantify its burning rate, delivered impetus, and aging characteristics, such a propellant may be useful to replace JA2 in the next generation of guns and rockets.

Acknowledgments

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