

Composite Propellant Based on a New Nitrate Ester

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Abstract: Composite propellants based on the solid nitrate ester 2,3-hydroxymethyl-2,3-dinitro-1,4-butanediol tetrani-trate (SMX) were theoretically and experimentally examined and compared to formulations based on ammonium per-chlorate (AP). Thermochemical equilibrium calculations show that aluminized SMX-based formulations can achieve theoretical sea level specific impulse values upwards of 260 s. Both ignition sensitivity (tested via drop weight impact, electrostatic discharge, and BAM friction) and physical properties (hardness and thermal properties) are com-parable to those of the AP-based formulations. However, the SMX-based formulation could be detonated using

a high explosive donor charge in contact with the propel-lant. Differential scanning calorimetry of the SMX-based propellant indicated an exotherm onset of 140 °C, which corresponds to the known decomposition temperature of SMX. The propellant has a high burning rate of 1.57 cm s⁻¹ at 6.89 MPa, with a pressure exponent of 0.85. This high pressure sensitivity might be addressed using various ener-getic and/or stabilizing additives. With good performance and high density, SMX-based composite propellants may offer a promising perchlorate-free alternative to existing AP-based formulations.

Keywords: Nitrate esters • SMX • Composite propellants

1 Introduction

Many solid composite propellants are based on the oxidizer ammonium perchlorate (AP). With its high oxygen content, good density, and gas-phase combustion products, AP sets a high standard for performance, stability, and low cost. However, AP remains far from the ideal oxidizer; the per-chlorate ion, essential for its stable arrangement of oxygen atoms, proves problematic from both a health and environ-mental standpoint, issues which are reflected in the modern regulatory climate. As such, much research is cur-rently ongoing to evaluate suitable replacements for AP [1–4].

One oxygen-rich functional group that has been consid-ered for the supplementation or replacement of AP is the nitrate ester group, R-ONO₂. As the backbone of the double-base propellant family, nitrate esters have been widely used in propulsion applications for decades. Howev-er, most high energy nitrate esters are liquid at room tem-perature, making them impossible to use as a direct re-placement for AP. A notable exception, pentaerythritol tet-ranitrate (PETN), is a stable solid at room temperature, but proves of little utility for propellant applications due to its low oxygen balance (–10.12%) and inability to sustain stable combustion at atmospheric conditions, even when intimately mixed with fuels [5,6].

Recently, Chavez et al. [7] synthesized a new nitrate ester: 2,3-hydroxymethyl-2,3-dinitro-1,4-butanediol tetranitrate. This molecule, colloquially referred to as SMX [8], ap-pears promising for propellant formulation: it is a room-temperature solid (M.P. = 85 °C) with an oxygen balance of

0% (CO₂-balanced) and impact, friction, and electrostatic discharge sensitivity similar to that of PETN.

The objective of this work is to examine the use of SMX as an ingredient for composite rocket propellants, both theoretically and experimentally. Theoretical performance calculations were performed using the NASA Chemical Equilibrium with Applications (CEA) thermochemical code [9]. The results were used to formulate a basic propellant for physical evaluation. Safety and handling characteristics were evaluated using standardized methods, and physical properties were measured and compared to existing AP-based propellants. The thermal behavior of the propellant was also characterized using DSC/TGA. Finally, the burning rate of the propellant was evaluated over a range of pres-sures to determine whether safe operation in a solid rocket motor is feasible.

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Table 1.

Propellant formulation characterized in this work.

Constituent	wt.-%
SMX	83.00
Aluminum, $-44\ \mu\text{m}$	2.00
R45HTLO HTPB	11.15
Isodecyl Pelargonate	2.23
Desmodur E744 MDI	1.62

2 Experimental Methods

Prior to laboratory work, theoretical performance calculations were performed using NASA CEA. Propellants based on hydroxyl-terminated polybutadiene (HTPB) were considered over a range of solids loadings typical for HTPB-based propellants (78–88 wt.-%). Aluminum inclusion over the range of 0–20 wt.-% was also considered. Specific impulse (I_{sp}) was used as the performance parameter of merit, calculated assuming a chamber pressure of 6.89 MPa and ideal sea level equilibrium expansion.

Based on the results of these calculations, an 85% solids propellant was formulated for laboratory testing. The formulation for this propellant is listed in Table 1. Aluminum was included at a 2 wt.-% loading to opacify the propellant and to promote combustion stability while minimizing the presence of condensed-phase products in the exhaust plume. The mixing process began by hand-blending the binder components: R45HTLO HTPB, isodecyl pelargonate (IDP) plasticizer, and Desmodur E744 isocyanate (all from RCS Inc., Cedar City, UT, USA). Once all components were well-mixed, $-44\ \mu\text{m}$ aluminum (Alfa-Aesar, Ward Hill, MA, USA) was added and hand-stirred until completely wetted. Finally, SMX (Nalas Engineering, Centerbrook, CT, USA) was added in multiple small increments, hand-stirring between each to fully incorporate the material.

Once completely wetted, the propellant was placed on a LabRAM mixer (Resodyn, Butte, MT, USA) and mixed at a 50% intensity level until homogeneous (10 min). The propellant was then packed into 7 mm diameter polyethylene sleeves and allowed to cure at ambient temperature. Once cured, these strands were cut into segments 1 cm long for characterization.

Hardness measurements were taken using a REX RX-1600D Shore D durometer and compared to measurements on an identically-prepared composite propellant based on 90 μm ammonium perchlorate at the same metallization and solids loading. Thermal properties were measured using the transient plane source (TPS) method [10] with a Hot Disk AB TPS 2500S thermal property analyzer. Neat SMX samples were prepared by die pressing to $95.00\% \pm 0.05\%$ theoretical maximum density, and propellant samples were cut directly from cured blocks. All samples were 12 mm in diameter and 5 mm in height, with both dimensions chosen so as to be greater than the penetration depth of the thermal wave during the test time. Thermal

analysis was conducted with a TA Instruments Q600 simultaneous thermogravimetric analyzer/differential scanning calorimeter (TGA/DSC) at a heating rate of $10\ \text{K min}^{-1}$, under ultra-high purity argon at $100\ \text{mL min}^{-1}$, using 90 μL open alumina pans.

Safety characteristics of the propellant samples were evaluated using three standardized techniques: drop weight impact (ERL Method 1012), electrostatic discharge (ARDEC Method 1032), and friction (BAM Method 1024), fully described in MIL-STD-1751A [11]. Propellant samples for these tests were cut to the powder sizes specified in the standards. All test statistics were computed using the Bruceton method. Shock sensitivity (detonability) of the propellant was evaluated using a small-scale zero-gap technique, as described by Sippel et al. [12]. Each test used 3 g of propellant with a 1.5 g donor charge of Primasheet 1000 explosive, fired by a Teledyne-Risi RP-501 detonator. The deformation of each aluminum witness plate was measured using a Hirox KH-8700 microscope with an OL-140-II lens.

The combustion of the propellant was evaluated in an optically accessible combustion vessel under quiescent nitrogen gas. Samples were ignited using 30 gauge Nichrome wire. Vessel pressure was measured using a Setra Model 207 0–70 MPa pressure transducer. Combustion progress was tracked using a Phantom Miro EX2 high-speed camera with a Nikkor 200 mm lens. GraphClick software (Arizona Software, Neuchâtel, Switzerland) was used to determine the position of the burning surface over the course of the video. The position vs. time data was then plotted and a linear regression performed to determine the burning rate of the propellant. Three burns were conducted at each pressure, and the mean burning rate from these experiments was used to determine the relationship between pressure and burning rate.

3 Results and Discussion

3.1 Theoretical Performance

The performance potential of SMX-HTPB propellant was evaluated using NASA CEA [9]. As typical propellants formulated with an HTPB binder system use a solids loading in the range of 80–88%, this range was considered for the SMX-based propellants. The inclusion of aluminum was also considered, as such addition is widely known to increase performance and improve combustion stability. The resulting performance contours are shown in Figure 1.

Since SMX is a CO_2 -balanced molecule, increasing SMX concentration in the propellant formulation increases theoretical performance. At solids loadings above 87%, non-aluminized propellants surpass an I_{sp} of 240 s, near that of existing cross-linked double base (XLDB) propellant systems. Aluminized propellants, theoretically delivering upwards of 260 s, compare quite favorably with AP-HTPB-Al systems, which peak at a sea-level I_{sp} near 264 s [13].

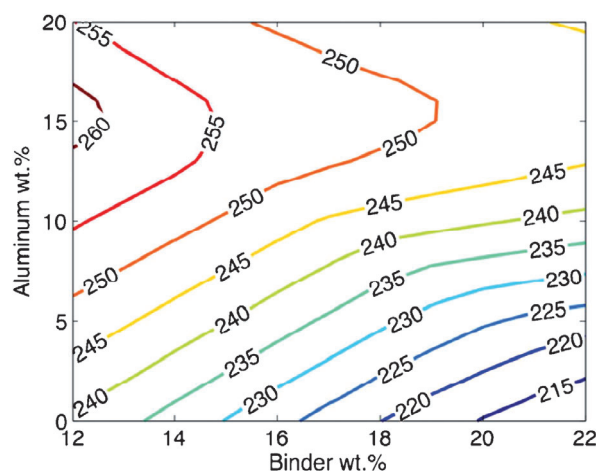


Figure 1. Calculated specific impulse (*s*) of SMX-HTPB propellants over various binder and aluminum loadings.

In addition to its high theoretical specific impulse, SMX also theoretically performs well from a density standpoint: the crystalline density of SMX ($\rho = 1.92 \text{ g cm}^{-3}$) is very similar to that of AP ($\rho = 1.95 \text{ g cm}^{-3}$), and is much higher than other solid nitrate esters (e.g., PETN, $\rho = 1.77 \text{ g cm}^{-3}$) [6]. Additionally, SMX may also prove useful as an additive in high energy composite propellants which currently contain HMX ($\rho = 1.91 \text{ g cm}^{-3}$) or RDX ($\rho = 1.82 \text{ g cm}^{-3}$) [14].

3.2 Safety & Physical Characterization

As delivered from the manufacturer, the SMX powder has a mean particle size of approx. $90 \mu\text{m}$, measured via optical microscopy. The particles (Figure 2) range from needle-like to jagged in morphology, which is typical for SMX crystals grown directly from 2-propanol solution. It may be possible to prill or rotary round the particles to improve the rheology

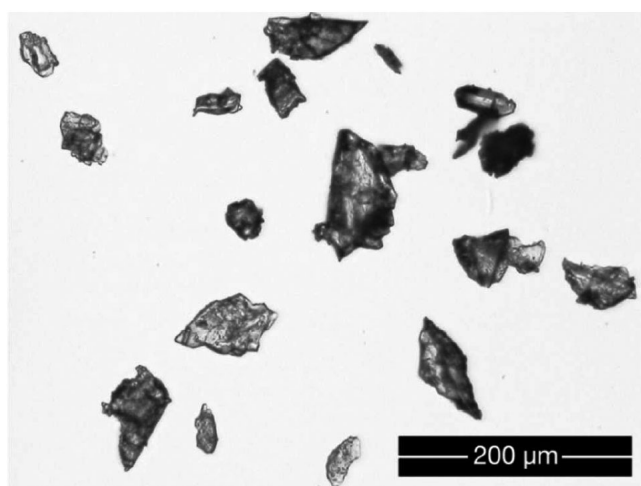


Figure 2. Optical microscopy showing SMX crystals used in this work.

Table 2. Thermal properties of SMX-HTPB-Al propellant and reference AP-HTPB-Al propellant.

Material	k [W (m-K)^{-1}]	α [$\text{mm}^2 \text{s}^{-1}$]
Neat SMX	0.266 ± 0.005	0.118 ± 0.006
Neat HTPB	0.263 ± 0.005	0.19 ± 0.01
AP-HTPB-Al	0.426 ± 0.007	0.20 ± 0.01
SMX-HTPB-Al	0.244 ± 0.005	0.14 ± 0.01

Table 3. Safety characteristics of SMX-HTPB-Al propellant.

Material	Impact [J]	ESD [mJ]	Friction [N]	Deformation Depth [mm]
PETN	4.9	160	60	3.7 [12]
Neat SMX	4.9	172	75	–
AP-HTPB-Al	2160	> 250	265 ± 50	0.2
SMX-HTPB-Al	2160	> 250	206 ± 20	6.0
Primasheet 1000	–	–	–	1.2

of the propellant during casting. However, even at 85% solids loading, the test propellant mixed quite easily, and the finished product was dough-like, allowing the use of casting methods previously employed for AP-HTPB propellants. The finished product had a hardness value of 21 Shore D, as compared with 22 Shore D for a baseline AP-HTPB-Al propellant at the same solids loading, and was flexible and easily cut.

Thermal conductivity k and thermal diffusivity α of propellant samples were measured three times and averaged, resulting in the data listed in Table 2. Additionally, thermal properties of the major constituents (SMX and HTPB) were measured, as well as those of the baseline AP-HTPB-Al formulation. In the propellant mixture, the thermal properties of the SMX dominate; this is to be expected, as the loading of SMX is 83% by weight (71.4% by volume). The measurements for the AP-HTPB-Al formulation also correspond well with thermal property measurements from the literature [15,16].

The results of the safety characterization tests are detailed in Table 3. The HTPB binder significantly decreases the sensitivity of the SMX in the propellant mixture, with resulting impact and friction sensitivities near those of the baseline AP-HTPB-Al propellant. During drop weight impact testing, the SMX propellant often would ignite only in very small locations, resulting in a wide spread in the data. Both propellant formulations were insensitive to electrostatic discharge at the level specified in the MIL STD [11].

In small-scale zero gap testing, the SMX-HTPB-Al propellant easily propagated a detonation, significantly deforming the aluminum witness plate in multiple tests. The AP-HTPB-Al propellant produced results which were much less dramatic; the witness plate deformation was an order of magnitude smaller. As a control, a sample of Primasheet 1000 was also tested in the same configuration as the SMX-

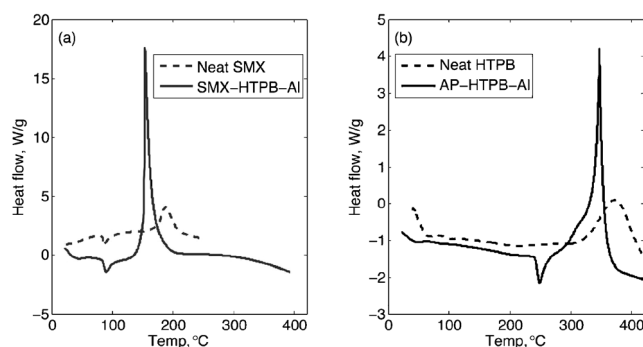


Figure 3. Normalized DSC trace comparison of (a) SMX-HTPB-Al with neat SMX, and (b) AP-HTPB-Al with neat HTPB.

HTPB-Al sample, with an air gap in place of the SMX-HTPB-Al propellant; this test resulted in a deformation level between those of AP-HTPB-Al and SMX-HTPB-Al. As a result of this testing, it appears that SMX-HTPB-Al propellant is safe to handle under normal conditions, but may present a detonation hazard if initiated via a strong shock wave.

3.3 Thermal Characterization

DSC curves for neat SMX and HTPB are shown in Figure 3. The thermal behavior of SMX was characterized by Chavez, et al. [7] during their initial investigation of the molecule. SMX was shown to have a melting point of 85 °C and an exotherm onset at approximately 140 °C. The material used in these experiments shows identical behavior. The thermal behavior of HTPB has been widely investigated [15–18]. For the binder system used in this study, melt onset occurs almost immediately, with decomposition and pyrolysis occurring in distinct exothermic and endothermic reactions at 360 and 470 °C. DSC curves for AP have been exhaustively documented in previous work [19–21].

DSC traces of the SMX-HTPB-Al system and the AP-HTPB-Al system are also shown in Figure 3. Logically, the thermal trace of the SMX-HTPB-Al propellant is dominated by the behavior of the SMX. The SMX melt occurs at 85 °C, and the decomposition exotherm of SMX occurs before HTPB decomposition begins. As such, the exothermic reaction proceeds quickly, with onset at 140 °C. This is a significantly lower onset temperature than is seen with AP-HTPB-Al, which shows the expected phase transition at 240 °C and onset of ignition above 300 °C.

Interestingly, the relative normalized heat output of the SMX-HTPB-Al system is significantly higher than that of the AP-HTPB-Al system. This is likely due to the fact that the ignition and combustion of the SMX-based propellant is occurring during the melting of the HTPB binder, rather than during the endothermic pyrolysis of the polymer, as is the case for the AP-based propellant.

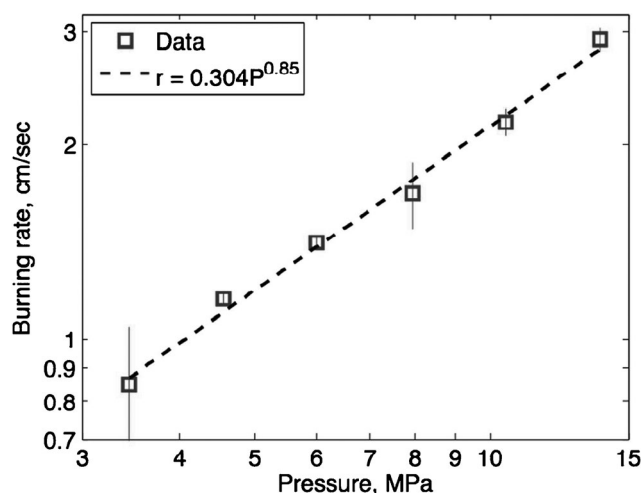


Figure 4. Burning rate data and curve fit for SMX-HTPB-Al propellant.

3.4 Combustion & Burning Rate

The burning rate of the SMX-HTPB-Al propellant was measured over a range of pressures appropriate for rocket applications (3.4–13.8 MPa). Typically, the burning rate r is fitted as a power law function of pressure P ,

$$r = aP^n \quad (1)$$

where a and n are the burning rate coefficient and exponent, respectively. The results of these measurements and the resulting curve fit are shown in Figure 4.

With burning rate parameters of $a = 0.304 \pm 0.030$ and $n = 0.85 \pm 0.04$ (for P in MPa and r in cm s^{-1}), the SMX-HTPB-Al propellant burns faster than a comparable AP-HTPB-Al propellant; for example, at 6.89 MPa, the baseline AP-HTPB-Al propellant burns at 0.6 cm s^{-1} , vs. 1.6 cm s^{-1} for the SMX-HTPB-Al propellant.

The high value of n (i.e., near 1) is advantageous for throttling and control purposes, but could be problematic from a motor design and sensitivity standpoint. This exponent could likely be lowered with the inclusion of an energetic binder (e.g., glycidylazide polymer) or other ingredient that reacts in the condensed phase and/or near the surface of the propellant. Addition of iron-based compounds (e.g., iron(III) oxide) may also lower the value of n . Since SMX is a nitrate ester, it may be possible to further stabilize the burning rate by including any number of ballistic additives typically applied in double base propellants, such as copper or bismuth salts [17].

4 Conclusion

As an oxygen-rich high density room temperature solid, SMX appears to hold potential as a solid propellant ingredient. In theoretical calculations, it nearly matches the perfor-

mance of existing state-of-the-art propellants using ammonium perchlorate (AP), and offers the added benefit of lower environmental toxicity. SMX-HTPB-AI has a lower thermal conductivity than AP-HTPB-AI, but a similar thermal diffusivity. It is also quite similar to AP in its handling characteristics: initiation via impact, friction, and electrostatic discharge occurs at nearly the same level of stimulus. However, SMX-based composite propellant will propagate a detonation wave – a characteristic that may limit its application.

Thermally, SMX-based propellants behave quite differently than those based on AP – the SMX melting endotherm occurs much earlier, at 85 °C, and the exotherm onset occurs at 140 °C, far below that of AP-based propellants, and below the endothermic HTPB pyrolysis. This exotherm is significantly larger than that of AP-based propellants. The burning rate was measured to be 1.6 cm s^{-1} at 6.89 MPa with a burning rate exponent of 0.85 ± 0.04 , which may potentially be lowered using existing ballistic stabilizers commonly used in double base formulations. Future work should investigate such stabilization.

These experiments show that it is indeed possible to harness the potential of SMX for propellant applications – from perspectives of performance, processing, safety, and combustion; it is another competitive option for supplementing or replacing AP in the next generation of solid rocket propellants.

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References

- [1] J. DeFlon, S. Andreasson, M. Liljedahl, C. Oscarson, M. Wanhatalo, and N. Wingborg, Solid Propellants based on ADN and HTPB, *47th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit*, San Diego, CA, USA, July 31–August 3, **2012**.
- [2] K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boat, N_5^+ : A Novel Homoleptic Polynitrogen Ion as a High Energy Density Material, *Angew. Chem. Int. Ed.* **1999**, *38*, 2004–2009.
- [3] M. B. Talawar, R. Sivabalan, T. Mukundan, H. Muthurajan, A. K. Sikder, B. R. Gandhe, A. Rao, Environmentally Compatible Next Generation Green Energetic Materials (GEMS), *J. Hazard. Mater.* **2009**, *161*, 589–607.
- [4] J. Louwers, *Combustion and Decomposition of Hydrazinium Nitroformate (HNF) and HNF Propellants*, Ph. D. Thesis, Technische Universiteit Delft, The Netherlands, **2000**.
- [5] T. L. Davis, *Chemistry of Powder and Explosives*, MIT Press, Cambridge, **1943**, pp. 191–286.
- [6] B. T. Fedoroff, O. E. Sheffield, *Encyclopedia of Explosives and Related Items*, Vol. 8, Picatinny Arsenal, NJ, USA, **1972**, pp. P86–P121.
- [7] D. E. Chavez, M. A. Hiskey, D. L. Naud, D. Parrish, Synthesis of an Energetic Nitrate Esters, *Angew. Chem. Int. Ed.* **2008**, *47*, 8307–8309.
- [8] D. L. Naud (Los Alamos National Laboratory), Personal Communication, **2013**.
- [9] S. Gordon, B. McBride, *Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations*, Report SP-273, NASA Lewis Research Center, Cleveland, OH, USA, **1976**.
- [10] S. E. Gustafsson, Transient Plane Source Techniques for Thermal Conductivity and Thermal Diffusivity Measurements of Solid Materials, *Rev. Sci. Instrum.* **1991**, *62*, 797–804.
- [11] Department of Defense, *Safety and Performance Tests for the Qualification of Explosives*, Report MIL STD, Washington, D.C., USA, 1751A, **2001**.
- [12] T. R. Sippel, T. L. Pourpoint, S. F. Son, Combustion of Nanoaluminum and Water Propellants: Effect of Equivalence Ratio and Safety/Aging Characterization, *Propellants Explos. Pyrotech.* **2013**, *38*, 56–66.
- [13] Davenas, Main Families and Use of Solid Propellants, in: *Solid Rocket Propulsion Technology* (Ed.: A. Davenas), Pergamon Press, Oxford, **1993**, p. 333.
- [14] T. Fedoroff, O. E. Sheffield, *Encyclopedia of Explosives and Related Items*, Vol. 9, Picatinny Arsenal, NJ, USA, **1972**, pp. R120–R146.
- [15] S. Benli, Ü. Yilmazer, F. Pekel, S. Özkaz, Effect of Fillers on Thermal and Mechanical Properties of Polyurethane Elastomer, *J. Appl. Polym. Sci.* **1998**, *68*, 1057–1065.
- [16] M. K. King, Analytical Modeling of Effects of Wires on Solid Motor Ballistics, *J. Propul. Power* **1991**, *7*, 312–321.
- [17] D. Hanson-Parr, T. Parr, Thermal Properties Measurements of Solid Rocket Propellant Oxidizers and Binder Materials as a Function of Temperature, *J. Energ. Mater.* **1999**, *17*, 1–48.
- [18] H. Austruy, Double-base Propellants, in: *Solid Rocket Propulsion Technology* (Ed.: A. Davenas), Pergamon Press, Oxford, **1993**, pp. 376–377.
- [19] R. C. Musso, A. F. Grigor, Decomposition Studies of Propellant Ingredients and Ingredient Combinations, *ICRPG/AIAA 3rd Solid Propulsion Conference*, Atlantic City, NJ, USA, June, **1968**.
- [20] M. Kohga, Burning Characteristics and Thermochemical Behavior of AP/HTPB Composite Propellant Using Coarse and Fine AP Particles, *Propellants Explos. Pyrotech.* **2011**, *36*, 57–64.
- [21] E. Santacesaria, A. Morini, S. Carra, Ammonium Perchlorate Decomposition in the Presence of Metallic Oxides, *Combust. Flame* **1978**, *31*, 17–23.

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