

Effects of Nano-sized Energetic Ingredients in High Performance Solid Gun Propellants

T.G. Manning, N.M. Masoud and D.P Thompson

US Army, Army Research and Development
Engineering Center (ARDEC)
Picatinny Arsenal, NJ 07806

J.R. Luman, B. Wehrman, K.K. Kuo*, and R.A. Yetter

The Pennsylvania State University
University Park, Pennsylvania 16802

and

H. A. Bruck

University of Maryland
College Park, MD 20742

1. INTRODUCTION

Unique propellant configurations, such as fast-core designs, require a layered propellant with tailored burn rate. The use of these layered propellants is expected to improve the energy management during the ballistic cycle and hence increase the muzzle velocity. These new propellants under development have different thermochemistry from that of traditional nitrocellulose-based propellants (such as JA2 propellant). The layered propellant is typically stacked as laminated disks in the cartridge chamber. Because there is no need for perforations and interstitial space, the layered configuration allows for high loading densities that may exceed 1.3 g/cc. Since this high loading density configuration greatly exceeds the average loading density used in tank rounds (~ 1.0 g/cc), an improvement in ballistic performance can be expected. Layered

propellants (also called fast-core propellants) consist of an inner layer of fast burning high-impetus propellant imbedded in two layers of slower burning low-impetus propellant. The inner layer is typically four times thicker than the outer layer with a burning rate about three times larger than the outer layer. Figure 1 shows a schematic diagram of a typical layered propellant geometry. Propellant geometries are tightly controlled such that the fast burning inner-core layer does not start burning until the volume available has slightly increased due to the projectile motion. This allows the pressure to be maintained at a high level for a relatively long duration, and often results in a double hump in the pressure-time response. This double pressure peak or extended pressurized interval is advantageous because there can be a greater total impulse imparted to the projectile.

The challenge with respect to layered-propellant development is to enhance its performance significantly while trying to reduce the propellant flame temperature, keep a high burning rate ratio, and decrease the impact sensitivity. Higher performance propellants are always in demand and have been the major driving force behind the development of energetic materials research. Advances in energetic materials have been made in all types of composite propellant ingredients, including binders, oxidizers, and metal additives [1,2]. Special processing techniques of functionally graded energetic materials have also been developed in recent years [3]. These developments have made significant performance

Report Documentation Page				Form Approved OMB No. 0704-0188	
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1. REPORT DATE 01 NOV 2006		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Effects of Nano-sized Energetic Ingredients in High Performance Solid Gun Propellants				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Army, Army Research and Development Engineering Center (ARDEC) Picatinny Arsenal, NJ 07806				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM002075.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

improvements in gun propellants that go beyond conventionally utilized modified double-base propellants, such as JA2. In view of these improvements, nitramine-based propellants have been suggested to be utilized rather than double-base propellants in certain gun propulsion applications. Nitramines utilized in this study are primarily cyclotrimethylenetrinitramine (RDX or $C_3H_6N_6O_6$) having T_{melt} around 204 °C with a small portion of energetic ingredients like hexanitrohexaazaisowurtzitane (CL-20 or $C_6H_6N_{12}O_{12}$) and hydrazinium nitroformate (HNF or $CH_5N_5O_6$) having $T_{melt} \approx 120$ °C considered for burning rate enhancement. RDX has been selected because it offers many advantages for advanced gun propulsion, such as improvement in performance (high energy content and high impetus), thermal stability (low sensitivity), and environmental friendliness. RDX is attractive also because of its low cost. CL-20 is a stable nitramine explosive ($T_{melt} \approx 167$ °C) and has been considered as a potential ingredient because of its high density (1.98 g/cc), which is an important physical property that couples directly to improved performance. CL-20 is also available for large-scale synthesis and qualification in propellant formulations. HNF has been utilized due to its high density (1.91 g/cc) and its positive oxygen balance (13.11%), which is beneficial for increasing the propellant burn rate.

The goal of this study is to develop a pair of layered propellants through a “materials-by-design”

approach for use in a fast-core gun propulsion application. A pair of baseline propellants was initially developed and named as ME (moderate energy) propellant with a relatively slow burning rate and HE (high-energy) propellant with a fast burning rate. Modifications of these propellants with different ingredients have been made such that the burning rate ratio between fast and slow burning propellants is suitable for use in applications requiring layered propellants (~3:1). Additional information on propellant formulations can be found in reference 4. The desired propellant combination should also have high-impetus (~1,300 J/g), low flame temperature (<3,400 K), and maintain conventional requirements of gun propellants.

2. EXPERIMENTAL APPROACH

The current study considers the energetic thermoplastic elastomer (TPE) binders BAMO-(BAMO/AMMO) (also called BBA) which allow the propellant to be melted ($T_{melt} \approx 80$ °C) and reprocessed. Reprocessing capability is advantageous for both propellant development and propellant disposal. New high-energy oxidizer materials (CL-20 and HNF) were considered to increase energy content over existing gun propellants. Nano-sized energetic particles such as aluminum and boron were selected because of their potential to increase the propellant’s burning rate by increasing the rate of energy feedback to the propellant surface. When fully reacted, these particles also have the ability to increase the propellant’s energy content. Nano-

sized aluminum particles (Alex[®]) with mean particle size of around 185 nm were obtained from Argonide Company. Boron particles (with 99.0% purity and particle size less than 150 nm) were obtained from SB Boron Corporation.

To develop the propellants through a “materials-by-design” approach that relates the ingredients to the properties and performance of the designed material, the energy content of the propellant formulations investigated in this study were predicted using thermochemical equilibrium computational codes (CHEETAH and NASA-CEA) using a constant-volume and constant-internal energy (uv) problem with a loading density of 0.2 g/cc. The CHEETAH code was developed by the Lawrence Livermore National Laboratory. CHEETAH has an advantage over NASA-CEA, in that it contains a built-in gun propellant analysis to compute the impetus performance directly. Pure aluminum (neglecting the oxide layer) was used in the thermochemical calculations due to the high percentage (~85 %) of active aluminum in the Alex[®] particles.

Burning characteristics of solid propellant strands, processed at ARDEC, were conducted at the Pennsylvania State University. A Solid Propellant Strand Burner (SPSB) was utilized to determine the burning rates of the samples up to a pressure of 66 MPa. A non-optical Ultra High Pressure Strand Burner (UHPSB) was used to measure the burning rates between 66 – 190 MPa. The propellant strands were burned under

constant-pressure conditions and the burning rates were deduced either from video images.

3. DISCUSSION OF RESULTS

In this section, the results of the advanced energetic propellants are presented and compared with those of two baseline propellants mentioned above as the ME and HE propellants, with the assumption that the combined fast-core propellant is made of 75% faster-burning propellant and 25% slower-burning propellant.

3.1 Results of burning the baseline propellants

The HE propellants utilized a certain percentage of CL-20 to increase the flame temperature, while the lower energy ME formulation was developed by the addition of nearly equivalent percentage of nitroguanadine (NQ) with reported T_{melt} from 232 to 257 °C and oxygen balance of -30.75%. The dependence of the burning rate on the pressure for the baseline propellants HE and ME was examined up to a pressure of 190 MPa at an initial temperature of 300 K. Figure 2 illustrates the measured burning rate versus pressure on a log-log plot. The results show a straight line with a slope break at around 49.6 MPa and 62.1 MPa for the HE and ME propellants, respectively. The burning rate (r_b) equations in the form of Saint-Robert's law for the HE propellant were found to be

$$r_b \text{ (m/s)} = (2.02 \times 10^{-7}) [P \text{ (Pa)}]^{0.674} \quad \text{for} \\ P < 49.6 \text{ MPa} \quad (1a)$$

and

$$r_b(\text{m/s}) = (1.49 \times 10^{-10})[P(\text{Pa})]^{1.08} \quad \text{for} \\ P \geq 49.6 \text{ MPa} \quad (1b)$$

For the ME propellant, the burning rate equations were obtained as

$$r_b(\text{m/s}) = (7.35 \times 10^{-7})[P(\text{Pa})]^{0.589} \quad \text{for} \\ P < 62.1 \text{ MPa} \quad (2a)$$

and

$$r_b(\text{m/s}) = (6.09 \times 10^{-12})[P(\text{Pa})]^{1.24} \quad \text{for} \\ P \geq 62.1 \text{ MPa} \quad (2b)$$

Figure 2 also shows the calculated ratio between the burn rates of HE and ME propellants. The maximum value of the burning-rate ratio between HE and ME propellants was found to be only about 1.4 at 62.1 MPa, which is less than half of the demanded value of this study. On the other hand, the calculated values of the flame temperature of the HE propellant, ME propellant and their combination reveal that the temperature of the combined propellant was relatively low. Since the impetus value is directly proportional to the flame temperature, the impetus of the combined propellant pair is found to be much lower than the demanded value.

Because of the unsuitable values obtained for the burning rate ratio, the flame temperature and the impetus of the baseline propellants, several modifications were investigated, and the first modified versions were named as intermediate propellants. These modifications include the addition of nano-sized aluminum, nano-sized boron, and the higher energy oxidizer, HNF.

3.2 Effect of nano-sized aluminum particle addition

Addition of nano-sized aluminum particles as an energetic ingredient is highly desirable in propellant formulations because their small dimensions and high surface area-to-volume ratio enables the propellant to achieve the higher burning rates and impetus. Aluminum has a relatively high gravimetric heat of oxidation (31.06 kJ/gm) and high volumetric heat of oxidation (83.86 kJ/cm³). Aluminum also has a high density of 2.7 gm/cm³. One advantage of utilizing Al particles in nanoscale dimension is that they have a short ignition delay and combustion time. If the particles burn close to the propellant surface, the heat feedback rate into the propellant surface can be increased, causing an increase in the burning rate. However, addition of nano-sized Al particles to the HE propellant did not modify the burning rate as expected. Figure 3 shows a comparison between the burning rates of the HE and HE/Al propellants as a function of pressure. The addition of nano-sized Al particles slightly decreased the propellant burning rate at pressures below 41.4 MPa while it exhibited almost no effect on the burning rate above this pressure. This unexpected effect can be attributed to the lack of the oxidizer environment in the nitramine-base propellant compared to the AP-based propellant.

It is well known that under hot-gas environments, the nano-sized Al particles have much shorter ignition delay and combustion time than the micron-sized particles. If nano-sized Al particles are contentiously supplied in an oxidizing environment, they

could react to a high degree of completion in the close vicinity to the propellant surface. However, nitramine-based propellants have much less oxygen available for aluminum oxidation than do AP-based propellants. Both RDX and CL-20 have negative oxygen balance ($OB_{RDX} = -21.61\%$ and $OB_{CL-20} = -10.95\%$) while AP has a positive oxygen balance of ($OB_{AP} = +34.04\%$). Also, the AP-based propellants decomposed to generate oxygen-rich species that diffuse into the fuel-rich region, while RDX decomposition does not generate an oxygen-rich region around the reacting particles. Thus, in the nitramine-based propellant flame, the nano-sized Al particles combustion would be delayed until conventional aluminum oxidizing species, H_2O and CO_2 , are produced. Furthermore, when Alex[®] powder was added to the already fuel-rich RDX-based propellant, the equivalence ratio will be increased and thus the N_2O and NO production rates are reduced. This reduction can result in lower oxidation rate of Al by the reactions with these two species. This production is known to occur at modest rates since the initial RDX decomposition steps are thermodynamically neutral. The low rate of H_2O and CO_2 production resulted in aluminum particles being significantly distant from the propellant burning surface when the heat release occurs. As a consequence, aluminum particle oxidization provides no additional heat flux into the burning propellant surface, and hence no increase in burning rate was detected.

3.3 Effect of nano-sized boron particle addition

Boron has a high gravimetric heat of oxidation (58.74 kJ/gm) and high volumetric heat of oxidation (137.45 kJ/cm^3)—the highest of all common fuels. Boron also has a density of 2.34 gm/cm^3 , which is lower than aluminum and should increase the mass burning rate of the propellant. In a hybrid rocket motor, using 13 % of nano-boron particles in HTPB-based solid fuels, Risha et al. observed an increase of mass burning rate of 44 % for nano-sized boron particles and 111 % for nano-sized B_4C particles [4].

Figure 4 illustrates the burning rate of the HE/B propellant as a function of pressure. The effect of addition of boron nano-particles to the HE propellant is similar to what was observed in the case of nano-sized aluminum particle addition that there is a noticeable decay of the burning rate rather than an enhancement of the burning rate. This can be explained by the same “energy-sink” effects introduced by the nano-sized aluminum. However, a comparison between Fig. 3 and Fig. 4 reveals that boron particles have stronger effect on the reduction of the burning rate of the HE propellant than the nano-sized aluminum particles. This can be attributed to three reasons. First, the specific heat capacity of boron is greater than that of aluminum on a mass basis. Therefore, boron particles are a more effective thermal energy sink than aluminum particles. Second, the boron particles are harder to ignite than aluminum particles, thus the energy release due to their combustion occurs at even larger distances away from

the propellant surface. Third, the HE/B propellant is more fuel-rich than the HE/Al propellant with the same weight percentage of B and Al in the propellant. This results in less oxidizing species for the boron oxidation reactions. This is due to the fact that the product distribution favors HOB formation versus liquid B_2O_3 . The formation of HOB instead of liquid B_2O_3 in the products results in a reduction of the heat release from ideal conditions.

3.4 Effect of HNF addition

HNF is an energetic oxidizer, which has a molecular weight of 183.08 and a heat of formation of -72 kJ/mol. Figure 5 shows the burning rate of the HE/HNF propellant as a function of pressure, and the ratio between the burning rates of the HE/HNF and HE propellant. It can be observed that the replacement of CL-20 with HNF increased the burning rate of the propellant by 200-250% over the entire range of pressure. This enhancement of the burning rate can be attributed to the positive oxygen balance of HNF. HNF decomposes quickly with a surplus of oxidizing species (H_2O and CO_2). These oxidizing species can further react with fuel-rich species near the propellant surface. The exothermic reactions of these oxidizing species with the fuel-rich species can increase the heat flux into the propellant burning surface and thus increase the burning rate. Also, the presence of oxygen-rich products near the propellant's surface can accelerate RDX decomposition by attacking nitramine fragments. HNF may also

augment Al particle combustion as it adds oxidizing species near the propellant surface. The replacement of CL-20 with HNF increases both the flame temperature and impetus when compared to the HE propellant.

3.5 Effect of addition of both HNF and nano-sized Al particles:

Based on the discussions in Sections 3.2 and 3.4, it is expected that further enhancement in the burning rate can be achieved when a combination of HNF and nano-sized Al particles are added to the HE propellant rather than the addition of HNF particles alone. A formulation pair containing both additives was developed to satisfy the criteria for the fast-core propellant. This formulation consists of two propellants, an Advanced High Energy (AHE) propellant and an Advanced Moderate Energy (AME) propellant. Addition of aluminum to the AME propellant is meant to increase the propellant impetus and not to increase the burning rate since no enhancement in the burning rate was noted in the HE/Al propellant (see Section 3.2). It can be observed that the combustion of a combination of 75% AHE and 25% AME achieves both the temperature and impetus values required for the fast-core propellant.

Figure 6 shows the burning rate of both AME and AHE propellants as a function of pressure, as well as the ratio between the burning rates of AHE/AME propellants for the entire pressure range. Both propellants have a slope break around 55.2 MPa. At a pressure of 189.6 MPa, the ratio between the burning

rates of AHE and AME propellants reaches 2.7. This relatively high ratio is attributed to the presence of the HNF oxidizer which has a surplus of oxidizing species for enhancing the combustion of the BBA, RDX and nano-sized aluminum particles.

4. SUMMARY AND CONCLUSIONS

High performance propellants have been developed using a “materials-by-design” approach, and their burning rate and impact sensitivity properties characterized. The materials were designed using higher energy ingredients (CL-20 and HNF), as well as nano-sized aluminum particles. To design the formulations, their properties and performance were computationally predicted using CHEETAH and NASA-CEA thermochemical equilibrium codes.

The desired features for the Advanced HE (AHE) and Advanced ME (AME) propellant combination (25% AME / 75% AHE) achieved in this study are the high propulsive performance with average impetus very close to 1,300 J/g, average flame temperature $\leq 3,400$ K, and high burn rate ratio ($r_{b,AHE} : r_{b,AME} = 2.7:1$) at a pressure of 190 MPa.

For propellants with oxygen deficient oxidizers (such as RDX, CL20), the addition of nano-sized energetic Al and B particles cannot increase the burning rate of the propellant because the reaction of these fuel particles can only occur at distances far from the propellant burning surface. However, for propellants containing oxidizers with positive oxygen balance (such

as HNF), the addition of nano-sized energetic Al particles can greatly enhance the propellant burning rate because the reaction of the particles can occur in close proximity to the propellant’s burning surface. Therefore, the burning rates of aluminized propellants (containing nano-sized aluminum particles) can be substantially increased when HNF or other oxidizer-rich crystals are added to the propellant formulation. The AHE propellant was observed to increase the burning rate by nearly 2.7 times over that of AME propellant.

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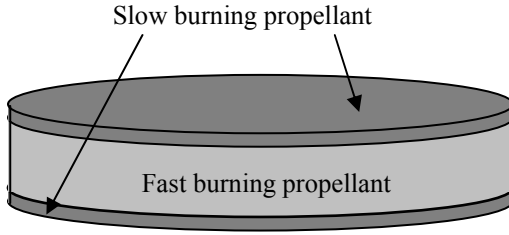


Figure 1: Schematic Diagram of a Typical Layered Propellant Geometry

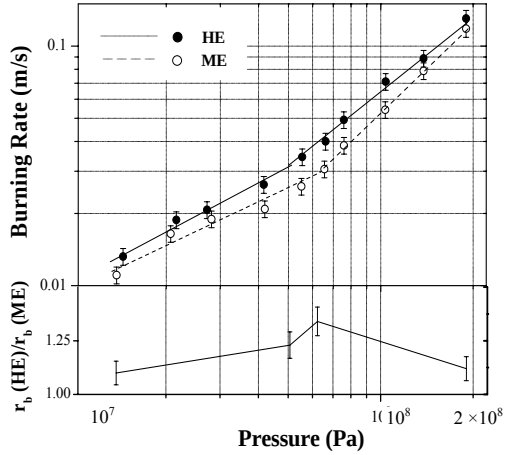


Figure 2: Burning Rates and Burning Rate Ratio of HE and ME Propellants

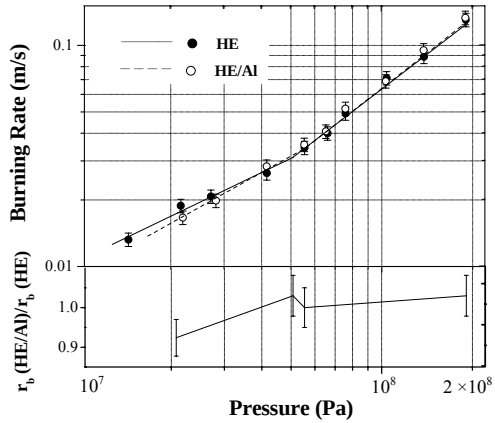


Figure 3: Burn Rates and Burning Rate Ratio of HE and HE/AL Propellant

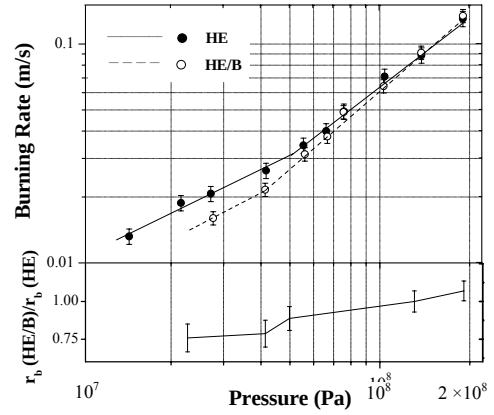


Figure 4: Burning Rates and Burning Rate Ratio of HE and HE/B Propellant

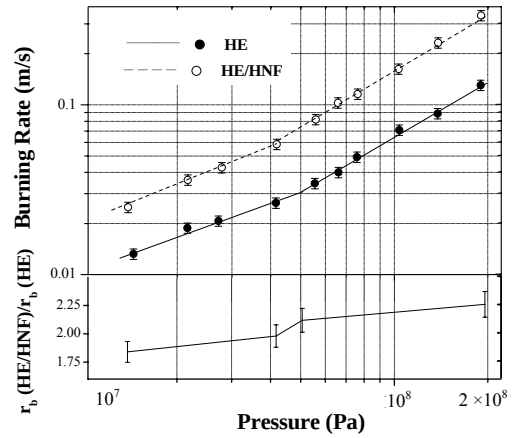


Figure 5: Burning Rates and Burning Rate Ratio of HE and HE/HNF Propellant

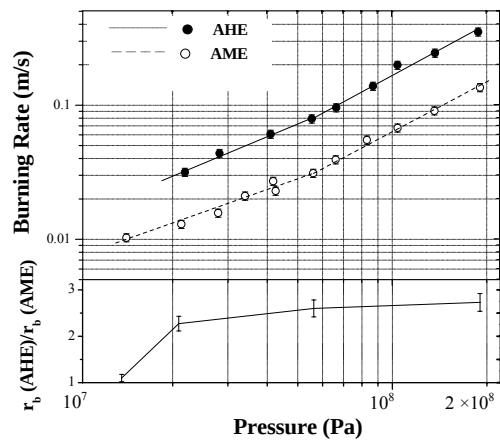


Figure 6: Burning Rates and Burning Rate Ratio of AHE and AME Propellant