



Effect of Coated Ammonium Dinitramide on the Properties of Nitrate-ester Plasticized Polyether Solid Rocket Propellants

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Abstract: Several industrial and research types of nitrate-ester plasticized polyether (NEPE) solid propellants were experimentally analyzed. In general, their compositions differed in the mass fraction of ammonium dinitramide (ADN), which was used as a promising highly energetic filler, as an alternative to ammonium perchlorate (AP). ADN exhibits high performance, low signature and non-polluting characteristics. The propellant composition without ADN, but with AP, was used as the reference. The microstructure and granularity distribution of the uncoated and coated ADN particles were experimentally analyzed. It was found that uncoated ADN particles exhibited irregular shape, while the ADN particles after coating are spherical. Because of their irregular shape, uncoated ADN particles caused inferior processability of the propellant slurry when added to the propellant formulation. Consequently, the NEPE propellants with coated ADN were studied in further detail. The rheological properties, energetic properties, mechanical sensitivities and combustion properties (burning rate and pressure exponent) of the NEPE propellants with coated ADN were studied and compared with the reference NEPE propellant. The addition of ADN particles to the propellant formulations increased the standard theoretical specific impulse and heat of explosion of the propellants, while decreasing the density. The propellants containing ADN particles were much more sensitive to impact and friction compared to the reference sample. Moreover, increasing the ADN mass fraction in the propellant formulation can significantly affect the combustion behaviour and increase the burning rate and pressure exponent compared to of the reference

formulation. However it appears that ADN is a very promising candidate as a new energetic material in compositions of NEPE propellants, although several important questions concerning ADN's suitability, especially in the context of its sensitivity to friction and impact, remain to be answered.

Keywords: energetic materials, NEPE composite solid propellants, ADN, hazardous properties, combustion characteristics

Nomenclature

ADN	Ammonium dinitramide
Al	Aluminum powder
AP	Ammonium perchlorate
BTTN	1,2,4-Butanetriol trinitrate
CL-20	Hexanitrohexaazaisowurtzitane
DNTF	3,4-Dinitrofurazanfuroxan
HMX	Cyclotetramethylenetetranitramine
N-100	polyisocyanate
NEPE	nitrate-ester plasticized polyether
NG	Nitroglycerine
RDX	Cyclotrimethylenetrinitramine
PET	Ethylene oxide/tetrahydrofuran co-polyether
SEM	scanning electron microscope
SSA	specific surface area, $\text{m}^2 \cdot \text{g}^{-1}$
d_{10}	particle diameter corresponding to 10% of the cumulative undersize distribution, μm
d_{50}	median particle diameter, μm
d_{90}	particle diameter corresponding to 90% of the cumulative undersize distribution, μm
Span	$(d_{90}-d_{10})/d_{50}$
C^*	characteristic exhaust velocity, $\text{m} \cdot \text{s}^{-1}$
T_c	temperature of combustion products, K
Q_v	heat of propellant combustion at constant volume, $\text{kJ} \cdot \text{kg}^{-1}$
I_{sp}	standard theoretical specific impulse, $\text{N} \cdot \text{s} \cdot \text{kg}^{-1}$
a	pre-exponential factor of burning rate law
\bar{M}	the average molecular weight of combustion products, $\text{g} \cdot \text{mol}^{-1}$
r	strand burning rate, $\text{mm} \cdot \text{s}^{-1}$
ρ	density, $\text{g} \cdot \text{cm}^{-3}$
n	pressure exponent in strand burning rate law
p	pressure, MPa
P_c	pressure of combustion chamber

P_0	atmospheric pressure
P	friction sensitivity, N
σ_m	maximum tensile strength, MPa
ε_m	elongation at maximum tensile strength, %

1 Introduction

High energy solid propellant formulations play an essential role in propulsion for space exploration [1-3]. The specific impulse or density specific impulse of propellants can be increased by the inclusion of certain high-energy materials (HEMs), such as CL-20, ADN, DNTF and others [4-6]. Moreover, the development of environmentally friendly propellants with lower toxicity, low smoke signature characteristics and highly energetic properties has also been of great interests for researchers [7-11]. ADN, compared with nitramines such as RDX and HMX, is a new kind of highly energetic material and a promising oxidizer with a high density ($1.82 \text{ g}\cdot\text{cm}^{-3}$), and high oxygen content (+ 25.79%). The absence of chlorine in ADN implies that it burns without the formation of hydrochloric acid. For these reasons ADN has been widely studied and used in the field of solid propellants and high explosives for space applications [12-14]. It was found experimentally that one advantage of ADN over AP (the common oxidizer in HTPB composite propellants) is the clean production of ADN and its higher heat of formation [15-20]. Though the development of ADN based solid propellants has faced a number of challenges, research has continued, motivated by ADN's high potential. Due to the incompatibility of ADN with many widely used components of solid propellants, such as NC, TDI, HDI and MAPO *etc.*, it is difficult to find suitable formulations on which to analyze the properties of propellants containing ADN. In recent years, many technical problems have been solved, such as ADN's synthesis, stability, compatibility *etc.* [21-26]. There are some reports on the synthesis, spectroscopy, combustion characteristics, and thermal behaviour of ADN, and a large number of papers have been published on the combustion properties of ADN and ADN based propellants [27-31]. Nitrate-ester plasticized polyether (NEPE) solid rocket propellants, which combine the advantages of double-base propellants and composite propellants, are some of the most important highly energetic propellants to meet tactical missile engine requirements. NEPE propellants have become one of the key research goals for the next decade. However, the combustion, hazardous and mechanical properties of NEPE solid rocket propellants based on a high mass fraction (50 wt.%) of ADN particles have almost never been discussed in the open

literature. Raw (uncoated) ADN particles obtained from commercial sources are of an irregular shape and therefore they are not appropriate for direct use. They could cause inferior processability of the propellant slurry when added to the propellant formulation. In order to modify the shape of the ADN particles, in order to increase the mass fraction of ADN in the propellant formulation, it is better to coat the ADN particles with polymers or other materials. In our study, polyurethane, one of the common polymer binders used in solid propellants, was chosen for coating the ADN particles. The characteristics of the uncoated and coated ADN particles were analyzed using SEM and laser granulation analysis diagnostic techniques. Three different NEPE propellant compositions were tested, *i.e.* two compositions with coated ADN and one composition with AP instead of ADN. This latter composition was treated as the reference one in the frame of theoretical calculations and experimental measurements. The focus of this paper is on how the coated ADN particles affect the combustion properties of NEPE propellants, placing emphasis on the investigation of their hazardous properties, which should be of critical importance for solid rocket motor applications.

2 Experimental

2.1 Materials and specimens

PET binder cured with N-100, NG/BTTN=1:1 (*wt/wt*), and micron-sized Al powder (30 μm , $\geq 99.8\%$) were used as the fuel components of the propellants. Two granulation types of AP were utilized in the propellant formulations. The first consisted of research grade AP (>99 wt.% pure) with an average particle size of 105-147 μm . The second was obtained by grinding AP in a fluid energy mill to an average particle size of around 1-5 μm . Coated ADN particles with $d_{50} = 23 \mu\text{m}$ were used. The coating process, forming spherical particles, was run in Xi'an Modern Chemistry Research Institute as described elsewhere [2]. The following mass percentages of the ingredients were used in the three different propellant formulations, as shown in Table 1.

Table 1. The mass percentages of main ingredients of the tested propellants

Sample	PET [%]	NG+BTTN [%]	Al [%]	AP [%]	ADN [%]	Additives [%]
PDN-1	10.2	12.8	25	50	0	2.0
PDN-2	10.2	12.8	25	25	25	2.0
PDN-3	10.2	12.8	25	0	50	2.0

Each propellant formulation was mixed in 500 g batches using a 2 L vertical planetary mixer. All the propellant samples involved in this investigation were prepared by the slurry cast technique at 50 °C and then solidified for 120 h (at 50 °C) in a water jacketed oven.

2.2 Equipment and experimentation

2.2.1 SEM and particle size distribution procedure for ADN powders

Electron microscopy was used to study the shape, size, morphology and defects of the ADN powders. The morphologies of the ADN particles were examined by SEM technology. Granulometric analyses (particle size and particle size distribution) of the samples were performed by laser scattering (Malvern Mastersizer 2000) using a dry dispersion unit. The specific surface area measurements were computed from the nitrogen adsorption isotherm obtained by static volumetric measurement at boiling liquid nitrogen temperature (77 K). The quantity of material *per* test was about 0.07 g to 0.10 g. Obscuration filtering was switched on and set to values in the range 0.5-10%.

2.2.2 Determination of the rheological properties of the tested propellants

The viscosity of the propellant slurry was determined using a HAAKE cylindrical rotational rheometer RS300. The samples were tested in the coaxial cylinder sensor system at a temperature of about 50 °C.

2.2.3 Determination of the heat of explosion for the propellant samples

The heat of explosion values can be measured by means of an isothermal method. A definite mass of propellant sample was placed in the calorimetric oxygen bomb, surrounded by a fixed mass of water. The propellant was ignited in the bomb, the heat of explosion of the sample was calculated according to Equation (1) after measuring the increase in the water temperature.

$$Q_v = (C\Delta T - q_1) / m \quad (1)$$

where Q_v is the heat of explosion, [J/g]; C is the thermal capacity of the calorimeter, [J/K]; ΔT is the temperature increase during combustion, [K]; q_1 is heat of explosion of the initiation wire, Joule [J]; m is the mass of the sample, [g].

2.2.4 Density test procedure for the propellant samples

The measurement of the density of the propellants was carried out on a Model AG 104 METTLER TOLEDO balance. The test samples of the propellants had a rectangular shape with dimensions of 30 mm × 30 mm × 10 mm. These test samples were immersed in liquid paraffin at 20 ± 2 °C.

2.2.5 Hazardous properties tests for the propellant specimens

The hazardous properties of the propellant compositions to impact stimuli were determined by applying the fall hammer method (2 kg drop weight) with 30 mg of propellant on the Bruceton Staircase apparatus in the Xi'an Modern Chemistry Research Institute, and the results were given in terms of the statistically obtained 50% probability of explosion (H_{50}) [18]. Friction sensitivity was measured using a Julius Peters apparatus in the Xi'an Modern Chemistry Research Institute by incrementally increasing the load mass from 0.2 kg to 36 kg, until ignition occurred or explosion occurrence in five consecutive test samples. All of the tested samples were prepared as powders, and the volumes of the samples tested in the friction and impact tests were 0.5-0.8 mL [19].

2.2.6 Strand burning rate test for the propellant specimens

A nichrome fine wire with 0.1 mm in diameter was threaded through the top of the propellant strand, with an alternating voltage of 100 V to ignite the strand (diameter = 5-6 mm, length = 140 mm) at an initial temperature of 20 °C. The samples were placed vertically on the combustion rack in the sealed chamber which was filled with a nitrogen atmosphere. The burning rates of the propellant strands were determined in the pressure range between 1.0 MPa < P < 15.0 MPa by means of the fuse-wire technique [15-17]. The burning rates were computed from the combustion time that was recorded for the tests conducted at each pressure, for each pair of fuse wires, separation distance 10 mm, and each pressure, and were tested 5 times.

2.2.7 Combustion flame structure tests and apparatus

The combustion flame structures were registered by a high-speed and high resolution camera. The tested propellant specimens were rectangular sticks as 2 mm × 5 mm × 5 mm, placed/mounted in a quadoptic transparent combustion chamber in a nitrogen atmosphere at pressures of 1 MPa and 3 MPa.

2.2.8 Mechanical properties tests and apparatus

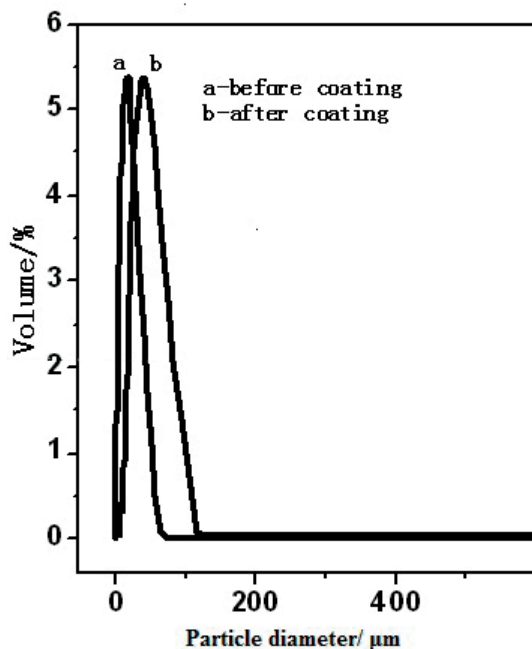
The mechanical properties of the propellants were determined with an Instron 4505 tensile tester. Cured propellants were cut into slices, from which JANNAF

dog bones were stamped (length = 100 mm, width = 40 mm, height = 20 mm). The tests were carried out at 20 °C with 100 mm·min⁻¹ cross-head speed.

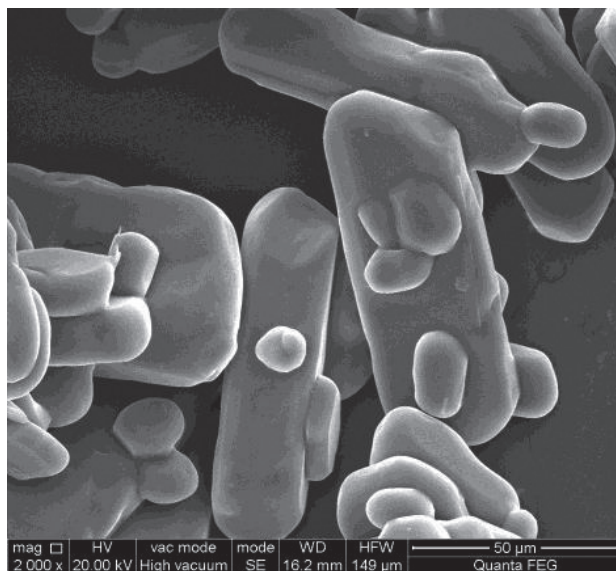
3 Results and Discussion

3.1 ADN particles, SEM and grain size distribution analysis

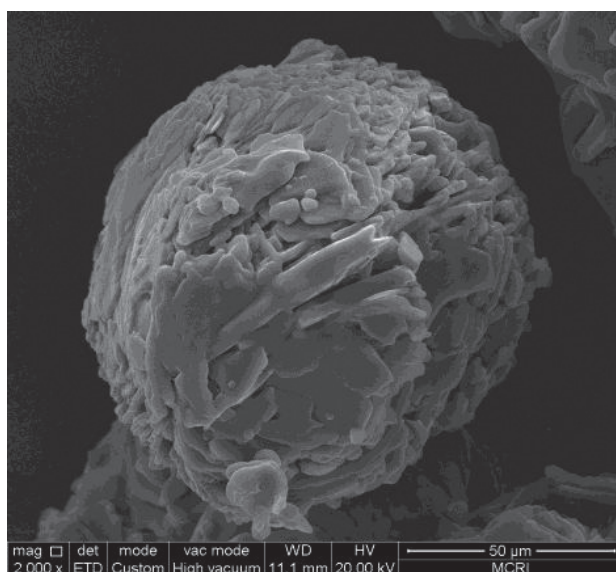
Detailed morphological information concerning the ADN powders was collected by running a series of advanced diagnostic techniques. The well-dried ADN particles were free of fluid; the microstructure and grain size distributions of the ADN powders are shown in Figure 1 and Table 2.



(a)



(b)



(c)

Figure 1. Particle size distribution (a) of the tested unprilled/uncoated (b) and coated (c) ADN particles

Table 2. Characteristics of ADN particles

ADN sample	d_{10} [μm]	d_{50} [μm]	d_{90} [μm]	Span	Vol. weighted mean [μm]	SSA [$\text{m}^2\cdot\text{g}^{-1}$]	P [$\text{g}\cdot\text{cm}^{-3}$]
Uncoated*	2.65	12.76	34.10	2.47	15.93	1.13	1.812
Coated	5.65	22.99	54.37	2.12	26.97	0.70	1.814

* - the diameter of unprilled/uncoated ADN particles was $d = (d_1+d_2)/2$, d_1 is the long diameter distance, d_2 is the short diameter distance.

It can be seen from the results in Figure 1 and Table 2 that the microstructure of the ADN particles, after coating with polyurethane binder, was more oval shaped with a rough surface, whereas ADN before coating exhibited more elongated, irregular shapes; the coated ADN particles were more uniform than the uncoated ones. The median diameters d_{50} of the coated ADN particles (22.99 μm) was much larger than that of the uncoated ADN particles (12.76 μm). Although the d_{50} values for coated ADN were larger, the specific surface area of coated ADN was 0.70 $\text{m}^2\cdot\text{g}^{-1}$, much less than that of uncoated ADN particles (1.13 $\text{m}^2\cdot\text{g}^{-1}$). The span of coated ADN particles was 2.12, which is much lower than that of uncoated ADN particles (2.47).

3.2 Effects of ADN particles on NEPE propellant slurries

The viscosities and yield stress of NEPE propellants, with and without ADN particles, were determined and the rheological results of the propellant slurry in 1 h are listed in Table 3. The flow properties and a cured propellant sample are shown in Figure 2.

Table 3. Effect of ADN particles on the rheological properties of NEPE solid propellants (shear rate: 1 s^{-1})

Sample	Viscosity [$\text{Pa}\cdot\text{s}$]	Yield stress [Pa]	Flow properties of propellant slurry ^{a)}
PDN-1	187.5	76.7	A
PDN-2	477.8	123.2	C
PDN-3	949.0	333.2	D

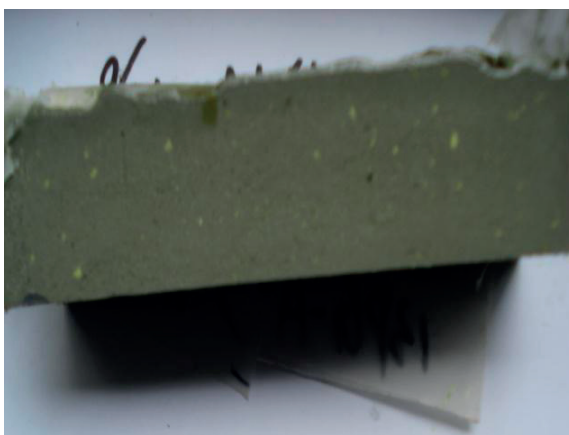
^{a)} A - D - represents the flow properties (qualitative assessment, the slurry is easy or difficult to flow) of a propellant slurry, from A to D corresponds to good to bad

It was found that the rheological properties of the propellant slurry exhibited the behaviour of a pseudo-plastic, non-Newtonian fluid. The ADN particles, when added to the propellant, can significantly increase the viscosity of the slurry. The viscosity and yield stress of the propellant slurries without ADN

particles (sample PDN-1) were significantly lower than those of propellant slurries (PDN-2 and PDN-3). Unfortunately, the processing ability of propellant slurry PDN-3 was the worst, resulting in this propellant slurry being very difficult to be successfully cast in vacuum.



(a)



(b)

Figure 2. Solidification stages of the solid propellant with 25% ADN: a flowing propellant slurry (a) and a well cured propellant sample (b)

3.3 Theoretical and experimental properties of the NEPE solid propellants

3.3.1 Theoretical energetic, physical and ballistic properties

The energetic properties of the NEPE propellants with a solid mass content of 75% were computed in our computer programs using the criterion of minimum free energy. Table 4 summarizes the results.

Table 4. Theoretical energetic, physical and ballistic properties of tested NEPE solid propellant compositions at 6.86 MPa

Sample	I_{sp} [N·s·kg ⁻¹]	Q_v [J·g ⁻¹]	C^* [m·s ⁻¹]	ρ [kg·m ⁻³] ($\times 10^3$)	T_c [K]	\bar{M} [g·mol ⁻¹]
PDN-1	2627.4	6054	1600.2	1.846	3715.6	36.34
PDN-2	2671.5	6345	1631.8	1.813	3706.8	37.90
PDN-3	2713.6	6573	1662.4	1.786	3698.3	39.47

Note: The standard theoretical specific impulse (I_{sp} , the combustion chamber pressure was 6.86 MPa, P_c/P_0 was 70:1), characteristic exhaust velocity (C^*), combustion temperature (T_c) and the average molecular weight of the combustion products (\bar{M}) were theoretical values, the density (ρ) and heat of explosion (Q_v) were measured data.

It can be seen from the calculated results (Table 4) that the standard theoretical specific impulse and heat of explosion of the solid propellant sample PDN-1 were 2627.4 N·s·kg⁻¹ and 6054 J·g⁻¹, respectively. These values are lower than those of propellants with ADN particles replacing an equal content of AP particles. Thus, it can be said that the addition of ADN particles to the propellant formulations increases the energetic properties, which is in agreement with references [6, 9]. The density of the propellant without ADN particles (1.846 g·cm⁻³) was larger than those of propellants with ADN particles (1.786-1.813 g·cm⁻³), which may be attributed to the density of ADN (1.82 g·cm⁻³) being lower than that of AP (1.94 g·cm⁻³). The density of the propellant with ADN particles may be increased by means of different shapes and particle size distribution of ADN, which will be investigated in the future.

3.3.2 Hazardous properties

ADN particles, with its reactive groups, especially on the particle surfaces, and its highly energetic characteristics, are very sensitive to friction and impact [4, 15]. Thus, it is necessary to study the hazardous properties of propellants containing ADN particles. The results of the hazardous properties experiments are listed in Table 5.

Table 5. Effect of the presence of ADN particles on the hazardous properties of NEPE solid propellants

Sample	Friction sensitivity (P) [N]	Confidence interval of 95%*	Impact sensitivity [J]	Standard deviation S (logarithmic value)
PDN-1	32.4	(55%, 91%)	8.32	0.11
PDN-2	19.8	(69%, 98%)	4.57	0.07
PDN-3	14.6	(86%, 100%)	2.14	0.18

Note: * - the confidence interval refers to the estimation interval of the overall parameters constructed by the sample statistics, that is the confidence level "probability" of the measured values of these parameters.

The data above indicate that the propellant formulations containing ADN particles were more sensitive to impact and friction compared to the reference formulation, *i.e.* without ADN, and the friction and impact sensitivities increased with increasing mass content of ADN particles in the propellant formulation. The sensitiveness may be attributed to the different particle sizes, particle shapes and the number of reactive sites on the ADN particles surfaces compared with the conventional filler (AP particles). The result revealed that the use of ADN particles in solid propellants leads to an increase in the impact and friction sensitivities of the loaded propellants.

3.4 Effects of ADN particles on the properties of NEPE propellants

3.4.1 Solidified surface microstructures of NEPE propellants

Coated ADN particles have a significant influence on the solidified morphology and physical structure of NEPE solid propellants. The microstructures of the propellants with coated ADN and without ADN, are shown in Figure 3.

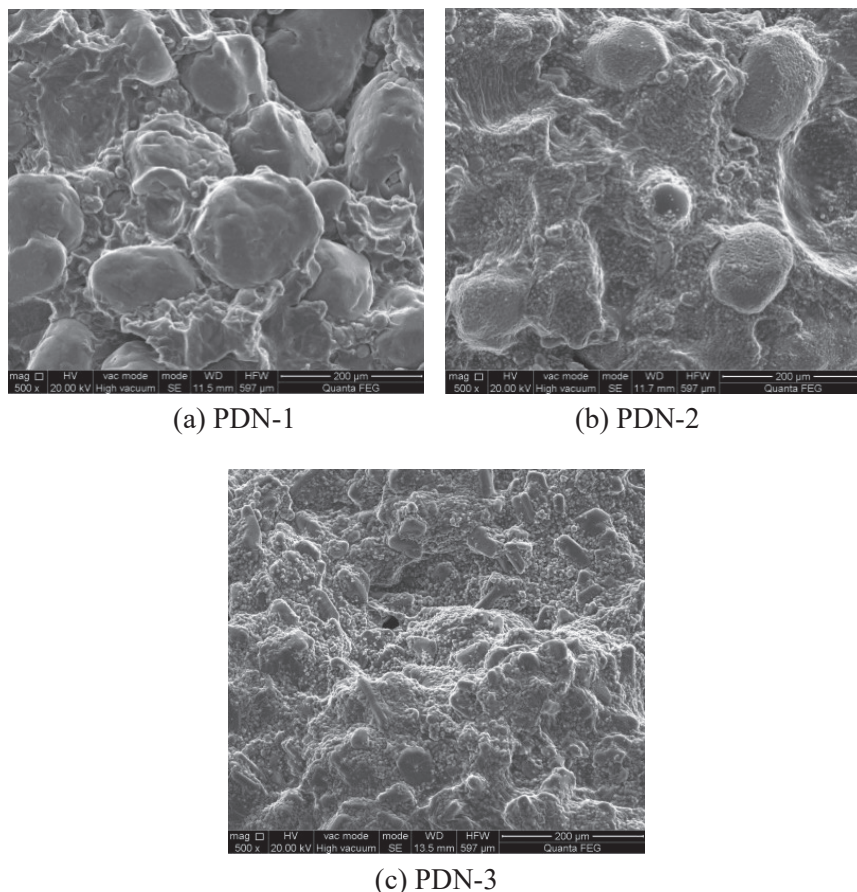


Figure 3. Microstructure surface of NEPE solid propellants with and without ADN

Figure 3 indicates clearly that there are many approximately oval and granulated particles on the surfaces of the cured NEPE solid propellants. Granulated particles of greater size, are fewer in NEPE propellants containing ADN. The propellant PDN-3 shows the lowest particle granulation. Granulated particles with smaller diameters can fill the spaces between the larger grains.

3.4.2 *Burning rate and pressure exponent*

Propellant burning rates determine the rate of gas generation, which determines the pressure inside the rocket motor and the overall thrust [22-25]. Burning rates

herein were obtained experimentally by burning small propellant strands and measuring the time needed to travel between two nichrom wires embedded into the propellant strand. Various factors, such as the particle diameter, oxidizing species, pressure, and temperature, affect the burning rate of the particles. The burning rate data of the NEPE propellants, with and without ADN, obtained under different pressures are shown in Figure 4.

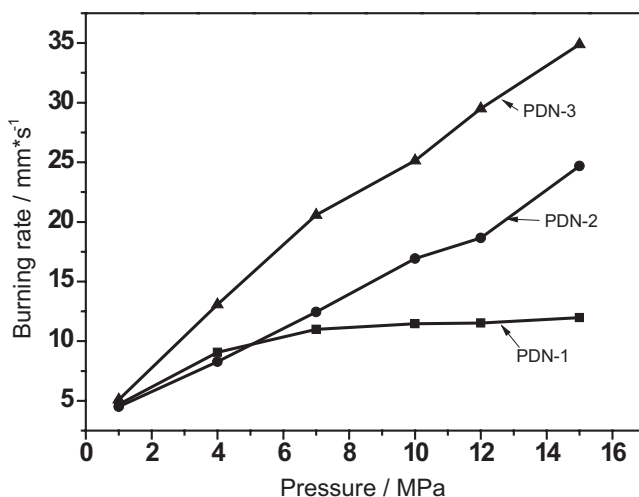


Figure 4. Burning rate results of NEPE solid propellants with and without ADN over the pressure range 1-15 MPa

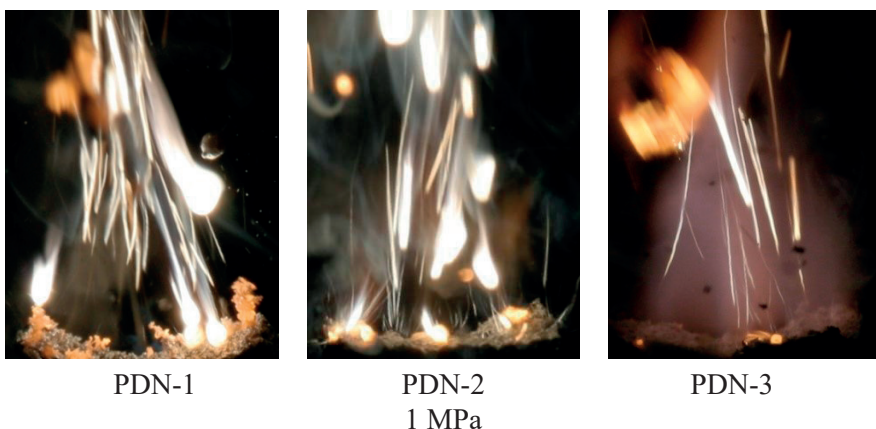
Table 6. Effects of ADN content on the combustion properties of NEPE solid propellants (pressure range: 1-15 MPa; initial temperature: $T_0 = 298$ K)

Sample	Strand burning rates, r [mm·s ⁻¹], at different pressures					
	1 MPa	4 MPa	7 MPa	10 MPa	12 MPa	15 MPa
PDN-1	4.70	9.07	10.98	11.46	11.52	11.97
PDN-2	4.50	8.27	12.44	16.92	18.66	24.69
PDN-3	5.09	13.07	20.58	25.13	29.51	34.88
Sample	Burning rate pressure exponent n					
	1-4 MPa	4-7 MPa	7-10 MPa	10-12 MPa	12-15 MPa	1-15 MPa
PDN-1	0.47	0.34	0.12	0.03	0.17	0.35
PDN-2	0.44	0.73	0.86	0.54	1.26	0.61
PDN-3	0.68	0.81	0.56	0.88	0.75	0.71

It may be seen from the curves in Figure 4 and the data in Table 6 that the ADN content affects the combustion behaviour and changes the burning rate and pressure exponent. The burning rate (r) and pressure exponent (n) of the propellant increase with an increase in the content of ADN particles in the formulations. However, for the PDN-3 propellant, the pressure exponent does not change much over the experimental pressure ranges. The pressure exponent of PDN-1 was 0.35 (1-15 MPa), which was the lowest among the tested formulations. Moreover, the extent of the burning rate increase for the PDN-1 propellant over the pressure range of 1.0-7.0 MPa is obviously higher than that over the pressure range 7.0-15 MPa. It was reported [6-9] that with an increase in the mass fraction of ADN, the decomposition heat for the first peak of the decomposition stage of NEPE propellants with ADN particles described by DSC curves, increases, and the main decomposition peak temperature advances until it disappears. When the same content of AP is replaced by ADN, the first decomposition peak temperature (T_1) moves backwards and the second decomposition peak temperature (T_2) advances, so the temperature difference between T_2 and T_1 ($\Delta T = T_2 - T_1$) increases. It was found that the decomposition of NEPE propellants can be greatly catalyzed by the addition of ADN particles and the burning rate of ADN is controlled by reactions in the condensed phase and a multi-zone flame structure has been established, which is in agreement with the burning rate results for these propellants.

3.4.3 Combustion flame structures

In order to understand the effects of ADN particles on the combustion flame structure, images of NEPE propellant flames with and without ADN particles at 1 MPa and 3 MPa are shown in Figure 5.



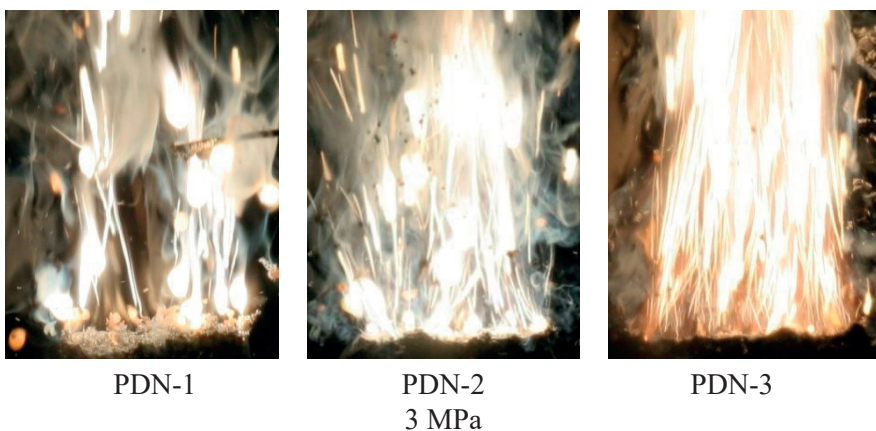


Figure 5. Combustion flame structures of NEPE solid propellants with and without ADN particles

From the above images, it may be seen that the combustion of NEPE propellants with and without ADN particles exhibit multi-flame structures. It is clear that all of the combustion surfaces of the propellants are regular, with some spark pieces, during the combustion process, and lots of bright dots and the combustion flame of the propellants are luminous with a red or yellow periphery, which can be attributed to the presence of the aluminum metal particles in the propellant formulation. It may also be found that although the metal (Al) oxidation process follows a common set of events, aggregation/agglomeration phenomena near the burning surface are noticeably different, depending on the enforced operating conditions and details of the solid propellant formulation.

The combustion mechanism could be explained by the heat transfer and release principle: from the point of view of heat transfer, the presence of ADN in the propellant can effectively increase the heat transfer and feedback to the combustion surface during the combustion process. Also, the heat released and heat feed back to the combustion surface for ADN propellants are higher than those of the reference formulation over the experimental pressure range. Thus, the burning rate and pressure exponent values for NEPE propellant depend on the mass content of ADN in the propellant formulations. An understanding of these effects opens the path to improved ballistic performance, and the influence of ADN particle size on the properties of a propellant should be investigated in future work.

3.5 Mechanical properties of NEPE propellants with and without ADN

ADN particles not only have important effects on the combustion properties of NEPE propellants, they also have a significant influence on the mechanical properties of the propellants. The mechanical properties of NEPE propellants with and without ADN particles are shown in Table 7.

Table 7. The mechanical properties of NEPE solid propellants with and without ADN (+20 °C)

Sample	σ_m [MPa]	ϵ_m [%]
PDN-1	0.71	20.4
PDN-2	0.27	54.6
PDN-3	0.19	45.5

It may be seen from Table 7 that the mechanical properties, *e.g.* maximum tensile strength (σ_m), is affected. The reference propellant sample PDN-1 (0.71 MPa) had a higher σ_m than those of the compositions with ADN particles. By contrast, the elongation (ϵ_m) of the reference propellant was only 20.4%, much lower than those of the others (54.6% and 45.5%).

4 Conclusions

Some preliminary conclusions can be withdrawn from this investigation:

(1) Uncoated ADN particles are irregularly shaped, while spherical particles were obtained after coating/prilling. The addition of ADN particles to the propellant formulations can increase the standard theoretical specific impulse and heat of explosion of the propellant, while the density of a propellant with ADN particles is lower than that of propellants without ADN particles.

(2) The addition of ADN particles cannot only increase the burning rate but also increase the pressure exponent of NEPE propellants compared with the referenced composition without ADN particles.

(3) The formulations containing ADN were more sensitive to impact and friction compared to the formulation without ADN, and the sensitivities to friction and impact increase with increasing mass fraction of ADN particles in the formulation.

(4) Taking into account the above mentioned advantages and disadvantages of propellants containing ADN, even though ADN is one of the most promising candidates for a new energetic material, further investigation needs to be done,

especially for its industrial application.

Acknowledgement

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References

- [1] Menke, K.; Heintz, T.; Schweikert, W. Formulation and Properties of ADN/GAP Propellants. *Propellants Explos. Pyrotech.* **2009**, *34*: 218-230.
- [2] Xu, H.-x.; Liao, L.-q.; Liu, Q. Properties of Prilled Ammonium Dinitramide (ADN) Coated by Polyurethane Binders. (in Chinese) *Chinese Journal of Energetic Materials* **2008**, *16*(6): 525.
- [3] Teipel, U.; Heintz, T.; Krause, H. Crystallization of Spherical Ammonium Dinitramide (ADN) *Propellants Explos. Pyrotech.* **2000**, *25*: 81.
- [4] Johansson, M.; de Flon, J.; Petterson, A. Spray Prilling of ADN and Testing of ADN - based Solid Propellants[C]. *International Conferences: 3rd, Green Propellant for Space Propulsion and 9th, Hydrogen Peroxide Propulsion*, Poitiers, France, **2006**.
- [5] Zhang, L.-y.; Liu, Z.-r.; Heng, S.-y. Interaction of ADN with Nitrate Oxidizer. (in Chinese) *Journal of Solid Rocket Technology* **2007**, *30*(6): 518.
- [6] Pang, W.-q.; Fan, X.-z.; Zhang, W. Effect of Ammonium Dinitramide (ADN) on the Characteristics of Hydroxyl Terminated Polybutadiene (HTPB) Based Composite Solid Propellant. *JCST* **2013**, *2*(2): 53-60.
- [7] Sinditskii, V. P.; Egorshv, V. Y.; Levshenko, A.I. Combustion of Ammonium Dinitramide, Part 1: Burning Behavior. *J. Propul. Power.* **2006**, *22*(4): 769-776.
- [8] Liu, Z.-r. *Thermal Analyses for Energetic Materials*. National Defense Industry Press, BeiJing, **2008**.
- [9] Pang, W.-q.; Xu, H.-x.; Li, Y. Characteristics of NEPE Propellant with Ammonium Dinitramide (ADN) [J]. *Adv. Mater. Res.* **2012**, *399-401*: 279-283
- [10] Ostmark, H.; Wingborg, N.; Langlet, A. ADN: A New High Performance Oxidizer for Solid Propellants. In: *International Symposium, 16th*, San Francisco, USA, **1996**, 285-294.
- [11] Zhang, Z.; Ji, Y.; Wang, B.; Liu, Z. Application of Ammonium Dinitramide in Propellants and Explosives. (in Chinese) *Chinese Journal of Explosives and Propellants* **2004**, *27*(3): 36-41.
- [12] Yue, P.; Heng, S.-y.; Han, F. Compatibilities of ADN with Five Kinds of Binders [J]. (in Chinese) *Chinese Journal of Energetic Materials* **2008**, *16*(1): 66-69.
- [13] Kubota, N. *Propellants and Explosives: Thermochemical Aspects of Combustion*. 2nd ed., Wiley-VCG Verlag, Weinheim, **2007**; ISBN 978-3-527-31424-9.

- [14] Boschi Goncalves, R. F.; Rocco, J. A. F. F.; Koshun I. *Energetic Materials Research, Applications, and New Technologies*. 1st ed., IGI Global, **2017**, ISBN: 9781522529040.
- [15] Zhang, W.; Xie, W.-x.; Fan, X.-z.; Liu, F.-l.; Pang, W.-q.; Liu, X.-g.; Ji Y.-p. Energetic Characteristics and Comprehensive Properties of Propellants Containing ADN. (in Chinese) *Chinese Journal of Explosives and Propellants* **2015**, 38(2): 81-85.
- [16] Bergman, H.; Edvinsson, H.; Ostmark, H. Trends and Development of New Energetic Materials [C]. *Militarteknisk tidskrift* **2001**, 70(2): 26-28.
- [17] Jones, D. E. G. Characterization of ADN and ADN-based Propellants. *Propellants Explos. Pyrotech.* **2005**, 30(2): 526-528.
- [18] Pang, W.-q.; de Luca, L. T.; Xu, H. X. Effects of Dual Oxidizers on the Properties of Composite Solid Rocket Propellants. In: *Chemical Rocket Propulsion* (de Luca, L.; Shimada, T.; Sinditskii, V.; Calabro, M., Eds) 1st ed., Springer International Publishing, **2017**; ISBN 978-3-319-27746-2.
- [19] Yan, X.-t.; Xia, Z.-x.; Huang, L.-y. Experimental Study on Combustion Process of NEPE Propellant. *Proc., 7th, European Conference Aeronautics and Space Sciences (EUCASS), 2017*, 324.
- [20] Ostmark, H.; Bemm, U.; Langlet, A. The Properties of Ammonium Dinitramide (ADN): Part 1, Basic Properties and Spectroscopic Data. *J. Energ. Mater.* **2000**, 18(2-3): 123-138.
- [21] Korobeinichev, O. P.; Paletsky, A. A. Study of the Flame Structure of ADN/HTPB Composite Propellants. *Combust. Flame* **2001**, 127(3): 2059-2065.
- [22] Pang, W.-q.; Zhang, W.; Xu, H.-x. Effects of Different Nanometric Particles on the Properties of Composite Solid Propellants. *Propellants Explos. Pyrotech.* **2014**, 39(3): 329-336.
- [23] Kuibida, L. V.; Korobeinichev, O. P.; Shmakov, A. G. Mass Spectrometric Study of Combustion of GAP- and ADN-based Propellants. *Combust. Flame* **2001**, 126(3): 1655-1661.
- [24] Weiser, V.; Eisenreich, N.; Baier, A. Burning Behavior of ADN Formulations. *Propellants Explos. Pyrotech.* **1999**, 24(3): 163-167.
- [25] Chan, M. L.; Reed, R.; Turner, A. Properties of ADN Propellants. In: *Proc., 5th, International Symposium on Special Topics in Chemical Propulsion, Combustion of Energetic Materials*. (Kuo, K. K.; de Luca, L. T., Eds.), Begell House, New York, **2002**, pp. 492-501.
- [26] Ramaswamy, A. L. Energetic-Material Combustion Experiments on Propellant Formulations Containing Prilled Ammonium Dinitramide. *Combust. Explos. Shock Waves* **2000**, 36(1): 119-124.
- [27] Zhang W.; Liu F.-l.; Fan, X.-z. Interaction and Compatibility of ADN with Compositions of Propellant by Thermal Analysis Method. *Journal of Solid Rocket Technology* **2014**, 37(5): 666-671.
- [28] Teipel, U.; Heintz, T.; Krause, H. H. Crystallization of Spherical Ammonium Dinitramide (ADN) Particles. *Propellants Explos. Pyrotech.* **2000**, 25(2): 81-85.

- [29] Palmucci, I. *ADN-Based Double Oxidizer Solid Propellants Formulations*. Dissertation, Politecnico di Milano, Milan, Italy, **2014**.
- [30] Klapotke, M. T. *Chemistry of High-Energy Materials*. 3rd ed., De Gruyter, **2015**, ISBN 978-3-11-043932-8.
- [31] Korobeinichev, O. P.; Paletsky, A. A.; Tereschenko, A. G. Structure of Ammonium Dinitramide Flame at 4.0 MPa. In: *Combustion of Energetic Materials* (Kuo, K. K., Ed.), Begell House Inc., New York, Wallingford, **2001**, pp. 486-491

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