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Application Characteristics of Ammonium Dinitramide to HTPB Composite Propellants

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In order to reduce signal and increase energy of HTPB composite propellants, ammonium dinitramide (ADN) was applied to this formulation. Using SEM, vacuum stability test (VST) and other standard methods, mechanical sensitivity, thermal stability and combustion properties of HTPB/ADN propellant were tested. Results show that the mechanical sensitivity of HTPB/ADN propellants increase for higher friction sensitivity and impact sensitivity of ammonium dinitramide, while effect of ammonium dinitramide on mechanical sensitivity of propellants is less by replacing part of RDX. The amount of gas produced by ammonium dinitramide is greater than ammonium perchlorate (AP) in vacuum stability test, which reduce thermal stability of HTPB/ADN propellants. Under the pressure of 4-15 MPa, the pressure exponent of burning rate (n) of this propellants reach 0.70, which is higher than that of HTPB/AP propellants, while after adding iron-based catalyst, burning rate can be reduced to 0.60 or less. The combustion wave structure of this propellants is same as that of HTPB/AP propellants, but the slope of T-t curves increase more with pressure increasing.

Keywords: Ammonium dinitramide, HTPB/ADN propellant, Mechanical sensitivity, Thermal stability, Combustion wave structure.

INTRODUCTION

Ammonium dinitramide (ADN) is a non-chlorine, high enthalpy oxidant and can increase solid propellants energy substantially, reduce smog significantly with a replacement of ammonium perchlorate (AP). When the content of ammonium dinitramide is 70 %, the specific impulse of propellants is higher than that of ammonium perchlorate by 100 N s/kg, simultaneously, which can reduce the propellant characteristic signals and environmental pollution. It is especially applied to tactical missiles, less polluting transport shuttle boosters and space power systems. Therefore, ammonium dinitramide is the most promising high-energy materials to produce low signal and green composite propellants.

Synthesized ammonium dinitramide is flaky and needle-like crystals and this kind of crystal morphology ammonium dinitramide is easy to absorb moisture, with great sensitivity, low decomposition temperature,which also affected the process performance, combustion performance and safety performance of propellants with ammonium dinitramide. Even ammonium dinitramide samples is spherodized, its sensitivity is still higher. Although a literature reported that the sensitivity of ammonium dinitramide is small and safety to application[1]. There are also significant accidents reported in Russia about ammonium dinitramide application process, and there are accidents on ammonium dinitramide synthesis process in China. So the major problem of ammonium dinitramide application is to choose the right propellant system.

According to reports of ammonium dinitramide propellants, as a new oxidant, ammonium dinitramide (ADN) was applied to the second stage engine of Soviet SS-24 strategic missile in the 1980s and the loading amount of each engine is 3474 kg, which is roughly composed by HTPB/AP/ADN/Al/HMX/ferrocene derivatives[2]. In recent years, there are many applied research on ammonium dinitramide based on the binder system, compatibility of components and propellant formulations[3-8]. The authors had carried out a study on HTPB propellant system and founded mechanism of forming pore[9]. In order to further explore the ammonium dinitramide application to composite propellant system, the paper discussed the mechanical sensitivity, thermal stability and combustion properties of HTPB/ADN propellant.

EXPERIMENTAL

Spherical ammonium dinitramide is made by Xi'an Modern Chemistry Research Institute with purity of 99.5 %, storaged in vacuum desiccator. HTPB is prepared by Liming Research Institute of Chemical, hydroxyl value is 0.68 mmol/g, number-average molecular weight is 3100. Al, AP, RDX and other component are industrial products. Composite propellant samples with ammonium dinitramide were made by Casting process.

The surface morphology of ammonium dinitramide and ammonium dinitramide propellant were tested by Japanese JSM-5800 scanning electron microscopy (SEM).

According to Chinese GJB770A-97, method 501.2, Vacuum stability test was carried out in pressure sensor method at 100 °C, with sample quality of 5 g. When gas volume (V_0) produced in tests is less than 2 mL/g, the stability of sample is good.

Friction sensitivity of ammonium dinitramide propellants were tested using GJB770A-97 Method 602.1, at 20 °C, under 2.45 Mpa, with a swing angle of 66º and samples quality of 20 mg. Explosion probability (%) is used to represent results in frictionation tests. Impact sensitivity of samples were tested using GJB770A-97 Method 601.2, at 20 °C, with a drop hammer of 2 kg and samples quality of 20 mg Drop height (H_{50}) is used to represent results in impact tests.

Burning rate of propellants were tested by target wire method. The combustion mechanism of HTPB/ADN propellants were investigated by means of the single color frame amplification photography, Π mode miniature thermocouple. Flame structures were obtained by a high-speed camera with rectangular sticks as 2 × 5 × 15 mm samples in a quad-optic transparent combustion chamber in nitrogen atmosphere.

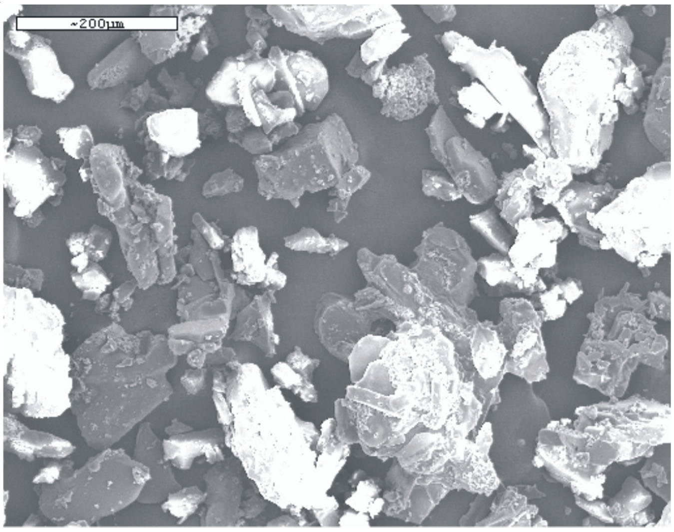
RESULTS AND DISCUSSION

Security properties of ammonium dinitramide (ADN): Thermal sensitivity, friction sensitivity and impact sensitivity of spherical and refined ammonium dinitramide samples are compared, results are shown in Table-1. The picture of spherical and refined ammonium dinitramide samples are shown in Fig. 1.

TABLE-1
SECURITY PROPERTIES OF SPHERICAL AND REFINED AMMONIUM DINITRAMIDE (ADN)

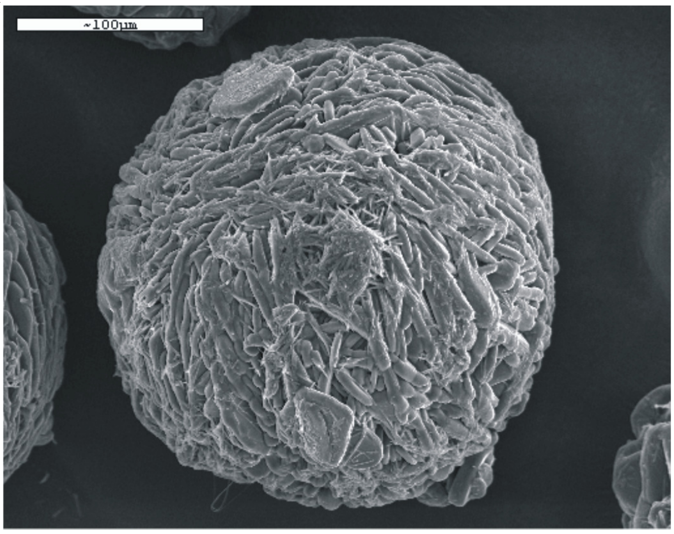
Sample name	Explosion temperature (5 seconds delay)	V_0 (mL)	H_{50} (cm)	P (%)
Refined ADN	-	1.8 mL/g	24	20
Spherical ADN	200 °C	1.7 mL/g	33.5	10

Note: "-" Indicates no such a test

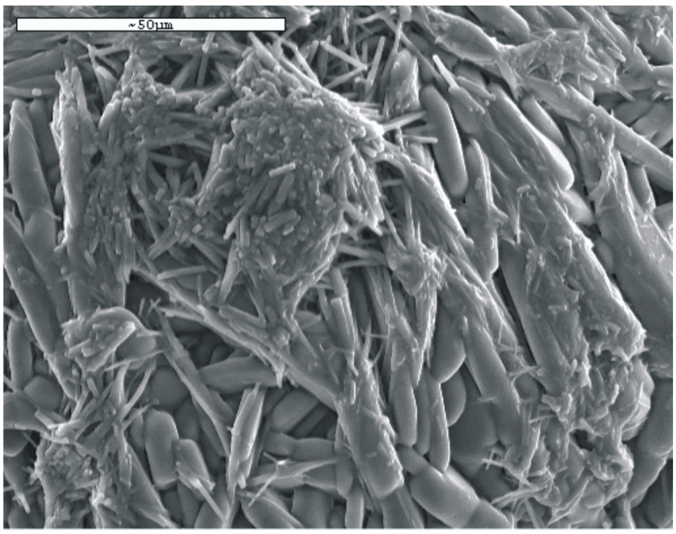


(a) 600 times SEM photo of refined ammonium dinitramide (ADN)

(b) Picture of spherical ammonium dinitramide (ADN)



(c) 350 times SEM photo of spherical ammonium dinitramide (ADN)



(d) 1000 times SEM photo of spherical ammonium dinitramide (ADN)

Fig.1. Picture of spherical and refined ammonium dinitramide (ADN)

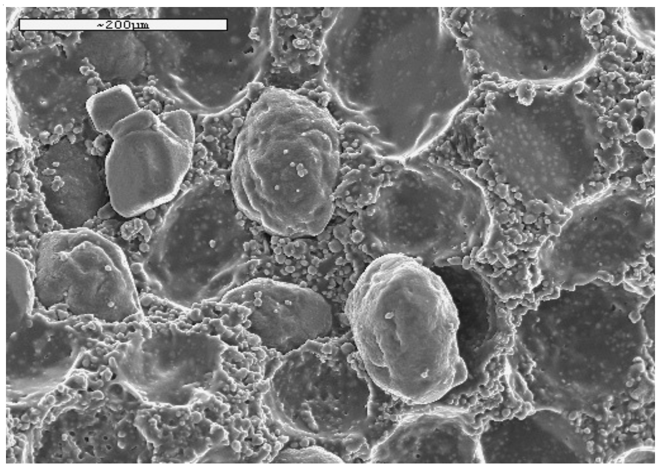
The results show that before and after sphered, ammonium dinitramide samples have a good thermal stability, but the explosion temperature of spherical ammonium dinitramide is lower, close to its exothermic peak temperature. 5 seconds delay and VST test indicate that, because decomposition products of ammonium dinitramide have little effect on the self-catalytic reaction of ammonium dinitramide in VST with low heating rate, so spherical ammonium dinitramide show a good thermal stability. But for sensitization of inside hole of ammonium dinitramide in 5 seconds delay test with rapid heating, this interaction leads to explosion of ammonium dinitramide at the lower temperature. Compared with other materials, explosion temperature (5 seconds delay) of RDX is 230 °C, that of HMX is 327 °C. Therefore, according to the measure standard of explosives, thermal sensitivity of spherical ammonium dinitramide is so higher than other explosives that the process of appling ammonium dinitramide to propellant formulations must be strictly controlled, and to avoid violent thermal decomposition of ammonium dinitramide.

Results of friction sensitivity and impact sensitivity show that the sphericity of ammonium dinitramide can greatly reduce the sensitivity of ammonium dinitramide and improve application security. As the microscopic point of view, spherical surface of the ammonium dinitramide particles still is irregular, and ammonium dinitramide particles are interconnected with spiculate crystal, which may result in increase of sensitivity. On the whole, sphericity of ammonium dinitramide can distribut spiculate crystal of particle surface from disorder into order, reduce the surface energy and improve stability of ammonium dinitramide.

Security properties of HTPB/ADN propellants: Effect of spherical ammonium dinitramide on mechanical sensitivity of HTPB composite propellant slurry and powder were tested and compared with HTPB/AP propellants at the same condition. Results is shown in Table-2.

Base on forementioned investigation, effect of spherical ammonium dinitramide on mechanical sensitivity of AP/nitramine HTPB composite propellant were tested and compared with HTPB/AP/RDX composite propellants at the same condition. Results is shown in Table-3.

Results of Tables 2 and 3 indicate that sensitivity of ammonium dinitramide samples are higher than that of HTPB composite propellants. In order to analysis the reason why sensitivity of ammonium dinitramide samples are so high, the surface morphology of ADN-2 propellant were tested by SEM, and results is shown in Fig. 2. For improving surface bonding



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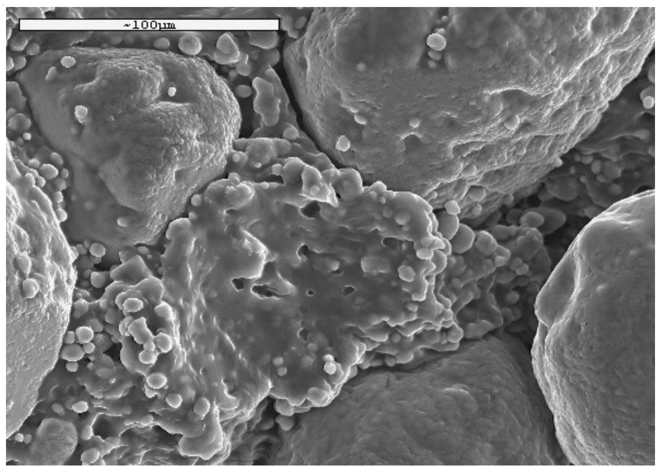

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Fig. 2. SEM photo of propellants ammonium dinitramide-2 (ADN-2)

TABLE-2
EFFECT OF SPHERICAL AMMONIUM DINITRAMIDE (ADN) ON MECHANICAL SENSITIVITY OF HTPB PROPELLANT

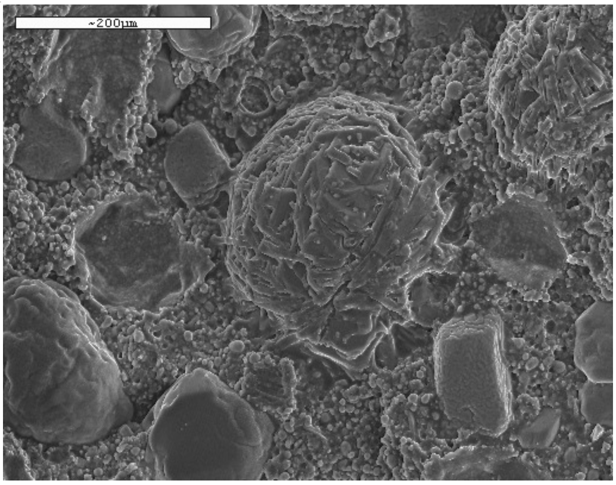
Name	P (%)	H_{50} (cm)	V_0(mL)	Note
AP-1	10	110.2	-	Slurry, Al 18 %, AP 67 %, HTPB system 15 %
AP-1	36	120.2	-	Propellant particles, Al 18 %, AP 67 %, HTPB system 15 %
ADN-1	56	44.7	-	Propellant particles, Al 15 %, AP 50 %, 15 % ADN, HTPB system 20 %
ADN-2	32	97.7	-	Slurry, Al 18 %, AP 52 %, ADN 15 %, HTPB system 15 %
ADN-2	80	74.1	3.5	Propellant particles, Al 18 %, AP 52 %, ADN 15 %, HTPB system 15 %
ADN-3	68	86.2	-	Propellant particles, Al 18 %, AP 52 %, ADN 15 %, HTPB system 14.8 %, 0.2 % bonding agent

– = Represent no testing

TABLE-3
EFFECT OF SPHERICAL ADN ON MECHANICAL SENSITIVITY OF AP/NITRAMINE HTPB PROPELLANT

Name	P (%)	H_{50} (cm)	V_0 (mL)	Note
RDX-1	47	88.4	-	Slurry, Al 18 %, AP 52 %, RDX 15 %, HTPB 5 %
AR-1	32	97.7	-	Slurry, Al 18 %, AP 52 %, ADN 15 %, HTPB 15 %
RDX-2	64	-	-	Particles, Al 10 %, AP 30 %, RDX 20 %, HTPB 40 %
AR-2	38	-	-	Particles, Al 10 % AP 30 %, ADN 20 %, HTPB 40 %
RDX-3	-	-	0.36	Particles, Al 10 %, AP 52 %, RDX 20, HTPB 18 %
AR-3	-	-	5.82	Particles, Al 10 %, AP 37 %, RDX 20,15 % ADN, HTPB 18 %

of ammonium dinitramide particles with binders, a kind of bonding agent was added to ammonium dinitramide propellants ammonium dinitramide-3 (ADN-3), SEM photo of ADN-3 is shown in Fig. 3.



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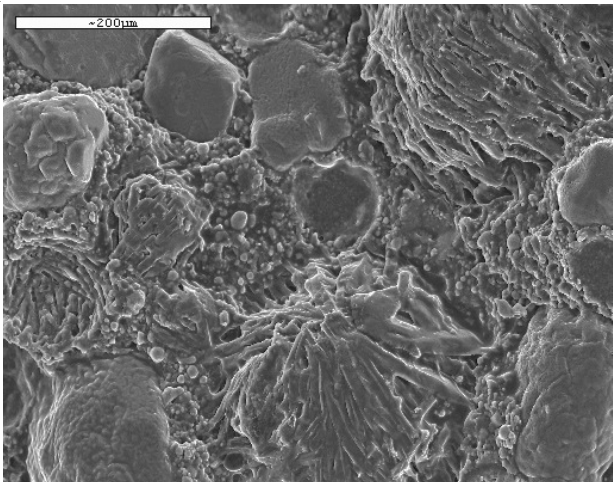

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Fig. 3. SEM photo of propellants ammonium dinitramide-3

Results show that: (1) After curing, friction sensitivity and impact sensitivity of HTPB composite propellants containing ammonium dinitramide increase, but when ammonium dinitramide is part alternative with RDX, whether curing or not, friction sensitivity and impact sensitivity of propellants containing ammonium dinitramide is lower than that of AP/nitramine HTPB composite propellant. Becsuse HTPB/Al/AP/RDX propellants has been applied in security, HTPB/ADN propellant slurry also can be mechanically mixed safely.

(2) After curing, mechanical sensitivity of ammonium dinitramide propellant increases. Compared with ammonium dinitramide, after ammonium dinitramide is coated by HTPB prepolymer binder, impact sensitivity of ammonium dinitramide propellant slurry reduces greatly and friction sensitivity increases slightly. Before binders in HTPB slurry cure, it has a certain passivation on ammonium dinitramide particles. In the process of impact, HTPB binder chains is compressed, which increase its storage modulus and weaken part of impact energy of the drop hammer acting on ammonium dinitramide particles. Therefore, impact sensitivity of ammonium dinitramide propellant slurry decreases.

In addition, the impact sensitivity and friction sensitivity of propellant particles of ammonium dinitramide are higher than that of slurry, which is relate to voids on the surface of the ammonium dinitramide. Since there are weak chemical bonding between ammonium dinitramide particles and HTPB binder network, ammonium dinitramide particles are easy to Dewetting from HTPB binder network and forming voids. It can be clearly observed that there are voids around particles of spherical ammonium dinitramide in SEM images, which is easy to foming "hot spots" under the action of the external energy and exploded. Therefore, impact sensitivity of ammonium dinitramide propellant increases.

(3) Compared Fig. 3 with Fig. 2, results indicated that ammonium dinitramide particles is so closely coated by HTPB binders, that there is no voids existing among ammonium dinitramide particles surface. Therefore, the impact sensitivity and friction sensitivity of Propellant ADN-3 are improved significantly.

(4) With solid content of HTPB composite propellant increasing, friction sensitivity of ammonium dinitramide propellant increases slightly. Compared with HTPB composite propellant without ammonium dinitramide, friction sensitivity and impact sensitivity of ammonium dinitramide propellant increased significantly.

(5) Since gas volume of ammonium dinitramide propellants produced in vacuum stability test are significantly greater than that of conventional composite propellants, thermal stability of ammonium dinitramide propellants decreases, but it is still safety to applications. Compared with ammonium perchlorate and RDX, gas volume of ammonium dinitramide is 1.8 mL/40 h at 100 °C, that of RDX is 0.7 mL/40 h and that of ammonium perchlorate is only 0.13 mL/40 h. Results indicate that thermal stability of ammonium dinitramide is so low that the thermal stability of ammonium dinitramide propellants decrease. Because ammonium dinitramide decomposes at low temperature, at the same time, there is a certain interaction between RDX and ammonium dinitramide, both of materials decompose and generate NO_2, which has a certain self-catalytic function on the decomposition of ammonium dinitramide[10]. This leads to the increase of gas generation, and reduce thermal stability of propellants.

Combustion characteritics of HTPB/ADN propellants: Effect of ammonium dinitramide on burning rate (u_r) and burning rate pressure exponent (n) were investigated, and results are shown in Table-4.

Results show that the burning rate (n) of HTPB/ADN propellants are higher than that of HTPB/AP at the same condition. When the more superfine ammonium perchlorate is added to HTPB/ADN propellants, the burning rate of propellants increases significantly, but n reduce little. When Fe_2O_3 is added to HTPB/ADN propellants, the burning rate of propellants increases, but n reduce more. Therefore, n of HTPB/ADN propellants can be reduced by combustion catalysts[11].

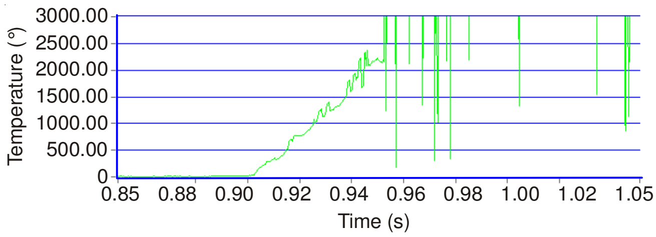
Combustion wave structure of HTPB/ADN propellants: The flame structure and combustion wave T-t curves of propellants ammonium dinitramide-3 burned at 4,7 MPa are shown in Figs. 4 and 5.

TABLE-4
EFFECT OF AMMONIUM DINITRAMIDE ON BURNING RATE (n)

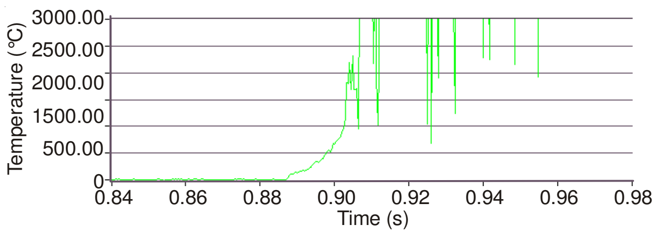
Name	u_r (mm/s)				n (4-15 MPa)	Remarks
	4 MPa	7 MPa	10 MPa	15 MPa		
AP-1	5.44	7.17	8.21	9.36	0.41	
ADN-3	6.61	9.35	11.88	15.64	0.66	Adding 15 % superfine AP
ADN-4	5.46	8.21	10.08	13.85	0.70	Adding 5 % surerfine AP
ADN-5	7.27	9.56	11.70	15.82	0.58	Adding 0.5 % Fe_2O_3

(a) at 4MPa (b) at 7MPa

Fig. 4. Flame structure of propellants ammonium dinitramide-3 (ADN-3)



(a) at 4MPa



(b) at 7MPa

Fig. 5. Combustion wave T-t curves of propellants ammonium dinitramide-3

In the flame structures, with the pressure increasing, the bright dots of Al particles reduce, flame zone is more bright. The flame is integrated and it is dark gradually far from combustion surface. From the combustion wave T-t curves, the temperature of surface reaction zone can be obtained, which is 400 and 500 °C, respectively, and the temperature of flame zone approximately is 2000 and 2500 °C, respectively. The slope of T-t curves at 4MPa is significantly bigger than that at 7MPa, this means that reaction rate increase with the pressure increasing. Therefore, the combustion wave structure of HTPB/ammonium dinitramide propellants is same as that of HTPB/AP propellants, and the main difference is that the slope of T-t curves in HTPB/ADN propellants increase more than that in HTPB/AP propellants,which result in the bigger burning rate pressure exponent.

Conclusions

• Sensitivity of refined ammonium dinitramide samples is high, in order to increase appling security in propellants, it must be sphericized to reduce friction sensitivity and impact sensitivity. Replacing with ammonium dinitramide, mechanical sensitivity of HTPB propellants will increase to some extent, but replacing some RDX, it affect little.

• Thermal stability of HTPB propellants decrease for the appling of ADN, so a right stabilizer must be choosed to reduce the self-decomposition of ammonium dinitramide .

• The burning rate pressure exponent of HTPB/ADN propellants is higher than that of HTPB/AP propellants, and some catalysts can reduce it. The combustion wave structure of HTPB/ADN propellants is same as that of HTPB/AP propellants.

• Although there are much problems of HTPB/ADN propellants, such as security, combustion and hygroscopicity, but for higher energy of HTPB/ADN propellants, much more research on HTPB/ADN propellants deserves to start.

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