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Combustion Performance of Spherical Propellants Deterred by Energetic Composite Deterring Agents

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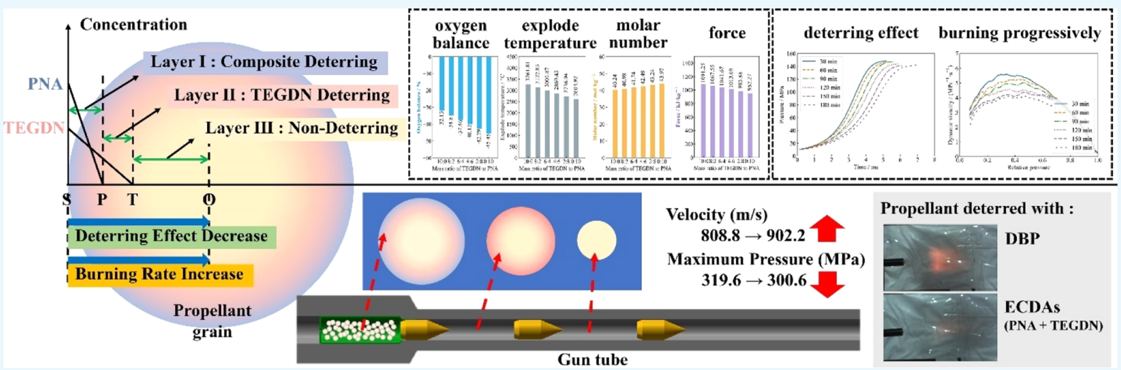

ABSTRACT: In order to achieve ideal burning progressivity and reduce harmful phenomena such as muzzle flame and smoke, energetic composite deterring agents (ECDAs) deterring spherical propellants were designed and prepared. The combustion performance of ECDA-deterred propellants was characterized by a closed vessel, and the interior ballistic performance was studied by a ballistic gun. High-speed photography and a smoke box were employed to capture muzzle flames and smoke. The results showed that triethylene glycol dinitrate (TEGDN) had a slight deterring effect weaker than that of poly(neopentyl glycol adipate) (PNA) on the propellants. The maximum pressure in the closed vessel bore of the ECDA-deterred propellants was 2.29 MPa higher than that of the dibutyl phthalate (DBP)-deterred propellants, though the *L*−*B* curve of the ECDA-deterred propellants was slightly lower and its combustion time was 0.44 ms longer. For ECDA containing 5 wt % PNA and 3.2 wt % TEGDN, 80 °C and 150 min are the best deterring conditions. The average velocity of the bullet propelled by ECDA-deterred propellants was increased by 93.4 $m \cdot s^{-1}$, while the average maximum pressure in the gun bore was decreased by 19 MPa, compared with the original propellants. The muzzle flame and smoke of the ECDA-deterred propellants were significantly reduced compared with the DBP-deterred propellants, where the smoke concentration was reduced by up to 44.5%.

■ INTRODUCTION

According to the theory of interior ballistics and propellant charge, improving the propellant energy and producing propellants that can burn progressively are two effective ways to improve the force and comprehensive properties of guns.[1] The burning progressivity of propellants means that the burning area or the burning rate gradually increases during the process of combustion. Improving the burning progressivity of propellants can improve the energy efficiency, increase the initial velocity of projectiles, and reduce the maximum bore pressure.[2]

The burning progressivity is classified as burning area progressivity and burning rate progressivity. The combustion process of propellants follows the law of geometric combustion, so burning area progressivity is an effective method to cause the progressive burning of propellants and is widely applied in large caliber weapon propellants, such as 7-hole propellants, 19-hole propellants, foamed propellants, and so on.[3−5] In the field of medium and small caliber weapons, it is very difficult to prepare small-sized and complex-shaped propellants on an industrial scale. In this case, the method of burning rate progressivity is very suitable. Surface deterring is a simple and efficient technology for achieving burning rate progressivity.[6,7]

The surface deterring technology is to diffuse materials with relatively low energy into the surface layer of the propellants. Special gradient distribution forms there, which means that the concentration of deterring agents was decreasing from the surface to deeper sites of the propellants. Therefore, the burning rate and the gas formation rate of the deterred

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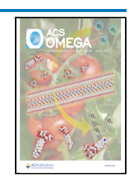

Table 1. Calculated Parameters of Basic Properties of Different Propellants[a]

component			properties			
NC/%	NG/%	additives (10%)	OB/%	M/(mole·kg^{-1})	f/(kJ·kg^{-1})	T_v/K
100			−31.84	39.55	1065.09	3238.83
90		TEGDN	−35.32	40.98	1054.89	3095.90
90		PNA	−48.63	44.63	903.95	2436.12
90		DBP	−51.07	44.95	903.93	2418.41
90	10		−28.30	38.74	1101.43	3419.29
81	9	TEGDN	−32.13	40.24	1091.25	3261.81
81	9	PNA	−45.45	43.97	952.27	2604.92
81	9	DBP	−47.89	44.34	953.20	2585.80

[a]OB, oxygen balance. [b]M, total molar number of generated gases. [c]f, force. [d]T_v, flame temperature. [e]Nitrogen content of NC, 13%.

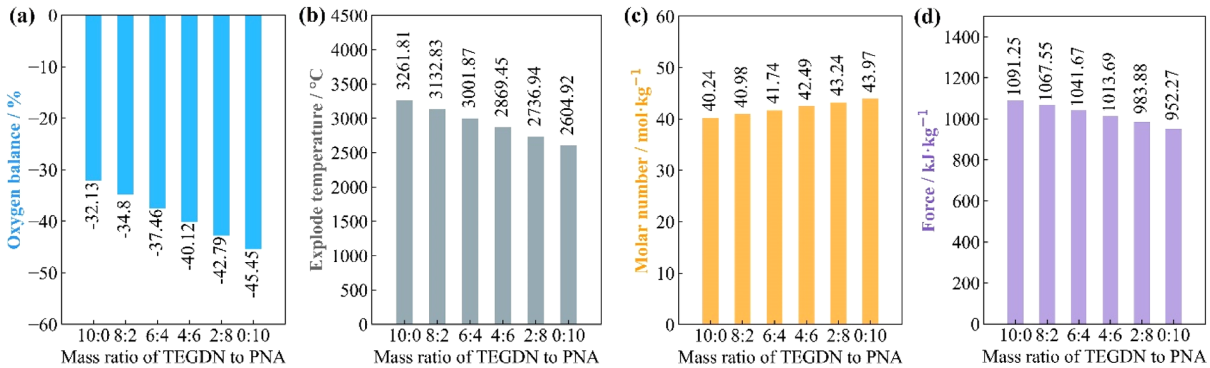

Figure 1. (a) Oxygen balance, (b) explosion temperature, (c) molar number, and (d) force of 90 wt % double-base matrix (81 wt % NC and 9 wt % NG) and 10 wt % ECDAs with different mass ratios of TEGDN to PNA.

propellants are low in the initial stage of combustion, but increase gradually as the combustion proceeds.

Traditional deterring agents include camphor, dibutyl phthalate (DBP), dinitrotoluene (DNT), and other substances.[8,9] Among them, DBP is the most widely applied deterring agent in medium and small caliber weapon propellants. However, DBP is a toxic compound that can cause functional changes in the central and peripheral nervous systems and other harmful effects.[10,11] In the process of gun shooting, it leads to many unfavorable phenomena such as strong flame, severe smoke, residues, and unstable ballistic properties.[12] The reason is that DBP is a nonenergetic inert compound, aggravating the negative oxygen balance of propellants and making the unfavorable phenomena more severe.[13]

The oxygen balance of the propellant components is an essential factor that determines the combustion adequacy of propellants and the unfavorable phenomena such as smoke, flame, residue, and so forth. It means that increasing the oxygen balance can directly improve the combustion properties of propellants and meanwhile reduce the harmful phenomena.[14,15] Polyester is a new deterring agent which is obtained by polycondensation reaction between polyacid and polyol. It has characteristics of a higher oxygen content and less combustion smoke compared with DBP. Switzerland has successfully applied polyester as deterring agents into extruded impregnated propellants (EI propellants), achieving good performance such as low temperature coefficients and stable ballistic results.[16] Remarkably, polyester is also a nonenergetic material, with an oxygen balance still at a negative level, though slightly higher than DBP.

Triethylene glycol dinitrate (TEGDN) is a commonly used energetic plasticizer for propellants, as it can improve the comprehensive properties, especially the mechanical property at low temperatures.[17,18] It should be noted that the energy of TEGDN is still lower than nitrocellulose (NC) and nitroglycerin (NG), indicating that TEGDN can exert a weak deterring effect on propellants.[19] Therefore, a composite deterring agent consisting of energetic TEGDN and nonenergetic polyester is expected to achieve a good deterring effect, with fewer unfavorable phenomena.

Based on the above mentioned facts, an attractive structure is desired to achieve progressive burning of propellants and reduce harmful phenomena. Because of the significant molecular weight contrast of polyester and TEGDN, polyester is distributed in the shallow position from the propellant surface and has a strong deterring effect, while TEGDN is distributed in the deep position and has a weak deterring effect. This special distribution realizes the burning progressivity of propellants. At the same time, the composite deterring improves the oxygen balance of propellants compared with the traditional single inert deterring agent. It is effective to reduce the flame and smoke within the period of the propellants burning. This work made the first attempt at mixing energetic TEGDN with a nonenergetic polyester by emulsification to form an energetic composite deterring agent (ECDA). Then, the TEGDN/polyester ECDA was diffused into propellants to achieve the deterring function. The combustion performance of the spherical propellant deterred with ECDAs at different process conditions was investigated with a closed vessel. Also, the interior ballistic, muzzle flame, and smoke of the ECDAs-deterred propellant were characterized.

Principle of Energetic Composite Deterring. *Basic Energy Properties of ECDAs.* TEGDN is a nitrated alcohol ester of triethylene glycol, and it has always been regarded as

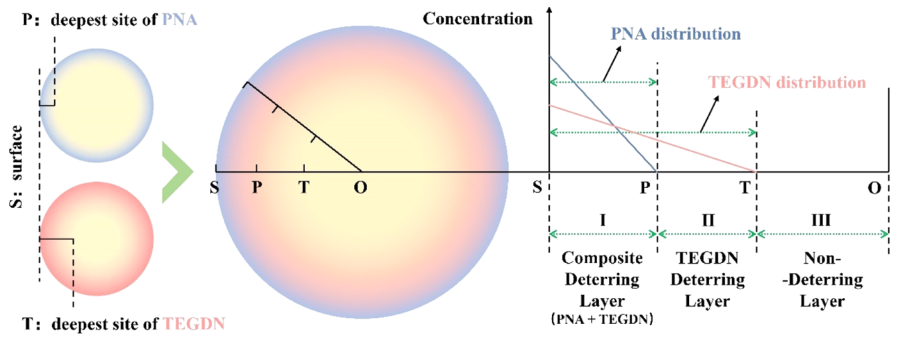

Figure 2. Composite structure of the TEGDN/PNA composite-deterred propellants.

an energetic plasticizer for propellants in traditional research. Table 1 gives the basic properties of propellants with different additives calculated by the method of minimum Gibbs free energy using REAL software.

The results show that TEGDN, poly(neopentyl glycol adipate) (PNA), and DBP all have deterring effects on the NC matrix or NC−NG mixed matrix, which were manifested in the variation of the oxygen balance, force, heat of explosion, and molar number of generated gases. For example, when the TEGDN content was 10 wt % in NC, the oxygen balance of propellants dropped by 11.6%, and the $\sum n$ value of gas products increased by 3.8%. The descending order of deterring effects on the propellant matrix is DBP, PNA, and TEGDN. Note that both DBP and PNA are nonenergetic materials, and they have strong deterring effects on propellants. TEGDN still had a weak deterring effect, though it is an energetic material because its energy level is relatively lower than the propellant matrix.

One strong deterring agent PNA and one weak deterring agent TEGDN were chosen. The basic properties of the 90% double-base matrix (81 wt % NC and 9 wt % NG) and 10 wt % ECDAs with different mass ratios of TEGDN to PNA were determined, as shown in Figure 1.

It was revealed that with the increase of PNA and decrease of TEGDN, the negative oxygen balance of the propellants became serious, the force declined, the explosion temperature decreased, and the total molar number of combustion gas products increased. It can be concluded that replacing a small part of nonenergetic PNA with energetic TEGDN can both achieve the deterring goal and increase the oxygen balance of propellants, which would reduce harmful phenomena such as emission of smoke and flame.

Composite Deterring Structure. The diffusion process in polymers is governed by extremely complicated physical and chemical principles. The diffusion rate is between those in liquid and solid, and it depends largely on the internal structure and swelling degree of the polymer. In addition, the diffusion of the solvent in the polymer is related to the physical properties of the polymer network and the interaction between the polymer and the solvent itself.

When the temperature is higher than the glass transition temperature T_g of the polymer, the network structure of the polymer is in a high elasticity and fluidity state. In this situation, the solvent is easy to enter the polymer and the diffusion rate is high, which is in accordance with the classical Fickian diffusion model.[20] The non-Fickian diffusion phenomenon of the polymer mainly occurs when the polymer temperature is lower than T_g, the polymer network structure is tight and cannot move sufficiently, and the solvent is difficult to diffuse.[21−24]

Current research suggests that the deterrent−propellant system is a typical agent−polymer diffusion system.[25] Trewartha et al. studied the diffusion spectrum of DNT-deterred small-caliber weapon propellants by confocal Raman spectroscopy. It was concluded that the spectral distribution of the propellants was consistent with the non-Fickian diffusion law.[26]

The deterring process is to make nonenergetic or low-energetic deterring agents diffuse into the surface of propellants. The deterring agents exhibit a gradient distribution from the outside to the inside of the propellants. That special structure allows for the propellants to have the characteristic of progressive burning. There are many factors affecting the diffusion rate of deterring agents in propellants, including the polymer structure, the deterring temperature, and the molecular weight of deterring agents. When the molecular weight of the deterring agents is high, the diffusion rate of the deterring agents in the propellants is low.

Two different deterring agents, that is, a small-molecule energetic plasticizer TEGDN and a large-molecular high viscosity inert polymer PNA, which have different diffusion laws in the propellants, were used in the composite deterring process of propellants in this paper. This difference in the diffusion law allows for the propellants to form a composite deterred structure with a gradient from the outside to the inside, with a schematic diagram as shown in Figure 2.

Because the molecular weight of PNA is much higher than that of TEGDN, PNA is distributed in the shallow position from the propellant surface and has a strong deterring effect, while TEGDN is distributed in the deep position and has a weak deterring effect. This special structure realizes the burning progressivity of propellants. Compared with the traditional single inert deterring agent, the composite deterring improves the oxygen balance of propellants while achieving good burning progressivity. It is expected to effectively reduce the flame and smoke within the period of the propellant burning.

We had tried to use a laser microscopic confocal Raman spectrometer to acquire the distribution property of the deterrents. The samples were prepared by frozen embedding and Leica semi-thin slice machine, which is shown in Figure S1. The results showed that PNA is distributed within 10 μm of the propellant surface, while DBP is distributed within 60 μm of the propellant surface (see the analysis process in Supporting Information). Through distribution depth contrast of the PNA and DBP, we can clearly see the influence of molecular weight of deterrents on diffusion capacity. Yet, there are still some difficulties to study the distribution property of ECDAs accurately by a Raman spectrometer: (1) the shape and size of the propellant grains vary greatly, and the sample measured is not representative of the whole samples. (2) The hardness of grains is high, so the samples sliced by the Leica slice machine were not quality enough. Also, the contrast of each slice was conspicuous. (3) The Raman signal of TEGDN is similar to that of the propellant matrix; therefore, the distribution of TEGDN is very difficult to obtain at present. (4) Because of the impurity in the propellant, the sample has more heteropeaks and the signal-to-noise ratio was not high enough. In addition, a strong fluorescence signal appeared in some samples.

RESULTS AND DISCUSSION

Static Combustion Performance. The closed vessel was a device that effectively reflected the static combustion performance of the propellants. The NC powder was ignited by an electrode and produced flames and high-pressure gases, which ignited the propellants further. The pressure in the closed vessel bore (p) as a function of the corresponding time (t) was recorded by a pressure sensor. Then, the dynamic vivacity (L) and the relative pressure (B) could be calculated as

$$L(t) = \frac{\mathrm{d}p(t)/\mathrm{d}t}{p(t)\cdot p_{\mathrm{m}}} \tag{1}$$

$$B = \frac{p(t)}{p_{\mathrm{m}}} \tag{2}$$

L represents the combustion status of propellants. B is the ratio of the pressure to the maximum pressure (p_{m}). Therefore, L_{m} is the maximum value of L and B_{m} is the corresponding value of L_{m}.

The trend of $L-B$ curves reveals the burning progressivity of the propellants and the weapon type for which the propellants are suitable. The ideal burning progressivity is reflected in these aspects. The lower the L in the early stage, the higher is the L in the later stage, the more suitable the L_{m} is, and the larger the B_{m} is.

Effects of TEGDN Deterring. For the purpose of researching how TEGDN influences the combustion performance of propellants, 8 wt % TEGDN-deterred propellants and 6 wt % PNA-deterred propellants were prepared as described above. Their combustion properties were compared, through $L-B$ curves, with the original propellants without deterring. The result is shown in Figure 3.

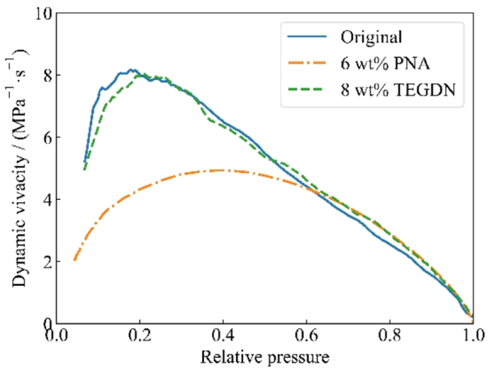

Figure 3. $L-B$ curves of propellants deterred by PNA or TEGDN in a closed vessel tester.

The $L-B$ curve of TEGDN-deterred propellants was slightly lower than that of the original propellants, especially in the initial stage. On the contrary, the initial dynamic vivacity of PNA-deterred propellants was nearly half of the original propellants. That was because TEGDN is also an energetic material, and its energy is much higher than the nonenergetic deterring agent PNA. However, the energy of TEGDN is lower than the NC/NG matrix, making TEGDN an energetic deterring agent.

Effects of Composite Deterring. Based on the comparison of the deterring effects and diffusion rates, spherical propellants were prepared by deterring with ECDA containing 5 wt % PNA and 3.2 wt % TEGDN at 80 °C for 90 min. Its $L-B$ curves and closed vessel results were compared with 5 wt % DBP-deterred propellants prepared at the same deterring conditions, as shown in Figure 4 and Table 2, respectively.

As depicted in Figure 4, both ECDA and DBP can reduce the initial dynamic vivacity of the original propellants. What needs to be concerned is that the maximum pressure in the closed vessel bore of the ECDA-deterred propellants was 2.29 MPa higher than the DBP-deterred propellants, though the $L-B$ curve of the ECDA-deterred propellants was slightly lower and its combustion time was 0.44 ms longer. This reveals that the ECDA-deterred propellants have a better burning progressivity, and the higher oxygen balance makes the propellants burn more adequately. On the other hand, a better gradient structure of propellants was obtained by the combination of PNA and TEGDN, making the burning phenomena (burning slowly in the initial stage and then burning faster gradually) more obvious. This confirms the previously described assumptions about the energy properties and composite deterring structure of ECDA-deterred propellants.

Effects of Deterring Time. Deterring is a diffusion process in which deterring agents gradually spread into a propellant matrix, and thus the deterring time is an important factor influencing the combustion performance of ECDA-deterred propellants.

The spherical propellants were prepared by deterring with ECDA containing 5 wt % PNA and 3.2 wt % TEGDN at 80 °C for different times. Figure 5 and Table 3 show the $L-B$ curves and closed vessel results of the composite deterred propellants with different deterring times, at a time interval of 30 min.

In practical terms, the maximum pressure (p_{m}) in the bore of the closed vessel and the maximum dynamic vivacity (L_{m}) can partly reflect the deterrent content in propellants. The reason is that deterrents reduce the energy of propellants, the gas generated decreases, and the dynamic vivacity becomes slower. In addition, the relative pressure (B_{m}) at L_{m} represents the turning point of dynamic vivacity, which means that the depth comparison of deterrent in samples can be qualitatively analyzed by the comparison of B_{m}. As the deterring time increased, the whole stage of the $L-B$ curve of ECDA-deterred propellants moved down gradually. As the deterring time increased, the maximum pressure in the closed vessel bore decreased, the burning time increased, and the maximum dynamic vivacity decreased, respectively. This was because more and more ECDAs penetrated into the propellants over time. Among them, the propellants deterred for 150 min had the best burning progressivity and its dynamic vivacity dropped sharply only when the B_{m} was greater than 0.6.

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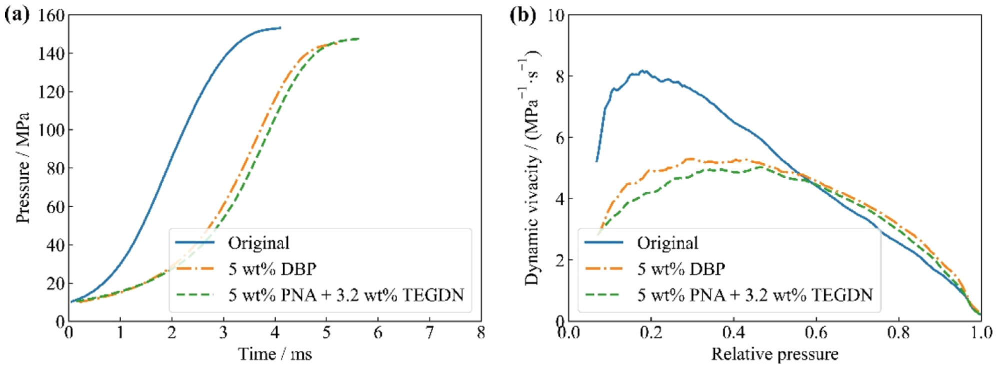

Figure 4. (a) $p-t$ curves and (b) $L-B$ curves of propellants deterred with ECDAs and DBP.

Table 2. Closed Vessel Results of Composite Deterred Spherical Propellants

sample	p_m/MPa	t_m/ms	L_m/MPa^{-1}·s^{-1}	B_m
original	153.09	4.065	8.177	0.178
5 wt % DBP (80 + 90)	145.23	5.160	5.294	0.297
5 wt % PNA + 3.2 wt % TEGDN (80 + 90)	147.52	5.600	5.027	0.468

Table 3. Closed Vessel Results of ECDA-Deterred Propellants with Different Deterring Times

sample (min)	p_m/MPa	t_m/ms	L_m/MPa^{-1}·s^{-1}	B_m
30	148.37	5.150	5.601	0.344
60	146.66	5.240	5.252	0.430
90	147.52	5.600	5.027	0.468
120	144.10	5.845	4.582	0.364
150	141.37	6.040	4.360	0.469
180	141.88	6.820	4.126	0.459

We firmly believe that the chemical/experimental characterization is very important for each sample to evaluate how much deterrent was incorporated into the propellant particles. The liquid chromatograph was used to study the content of deterrents in the propellants. There are still some difficulties in obtaining accurate and reproducible experimental data. Also, the main reason is that the storage life of standard solution containing energetic materials is not long. Sometimes, the standard solution of energetic materials was needed to be prepared temporarily. Therefore, the test conditions of samples were not strictly consistent.

Effects of Deterring Temperature. Temperature is one significant factor affecting the chemical reaction rate. Besides, temperature also has an obvious effect on the diffusion rate due to the fact that higher temperature contributes to the thermal motion of molecules.

The spherical propellants were prepared by deterring with ECDA containing 5 wt % PNA and 3.2 wt % TEGDN at different temperatures for 90 min. Figure 6 and Table 4 show the $L-B$ curves and closed vessel results of the composite deterred propellants with different deterring temperatures.

As the deterring temperature increased, the burning time and the maximum dynamic vivacity of propellants decreased slightly, while the whole burning process was not changed apparently. It is clear that the influence of deterring temperature on the burning property of the propellants is weaker than that of the deterring time.

Interior Ballistic Performance. The samples mentioned above deterring with ECDA containing 5 wt % PNA and 3.2 wt % TEGDN at 80 °C for 150 min were chosen for the interior ballistic, high speed photography, and smoke box tests.

The purpose of the interior ballistic test in this paper is to confirm the deterring effect of the ECDAs to original propellants. The interior ballistic performance of bullets filled with the ECDA-deterred propellants was investigated with one ballistic gun and compared with bullets filled with the original propellants. The results are listed in Table 5.

Remarkably, through replacement of the original propellants with the ECDA-deterred propellants, the average velocity of bullets was increased by 93.4 m·s^{-1}, while the average maximum pressure in the gun bore was decreased by 19 MPa. The key factor is that ECDAs change the combustion process of the propellants. In the early stage of propellant combustion, the bullet moves a short distance and the space

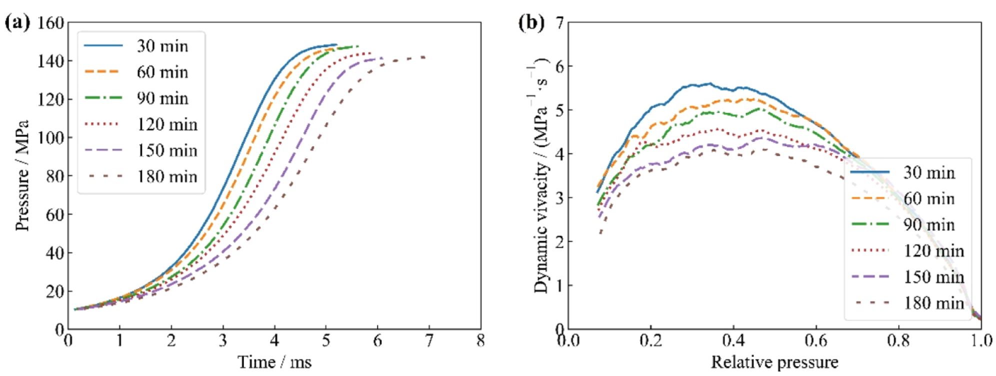

Figure 5. (a) $p-t$ curves and (b) $L-B$ curves of ECDA-deterred propellants with different deterring times.

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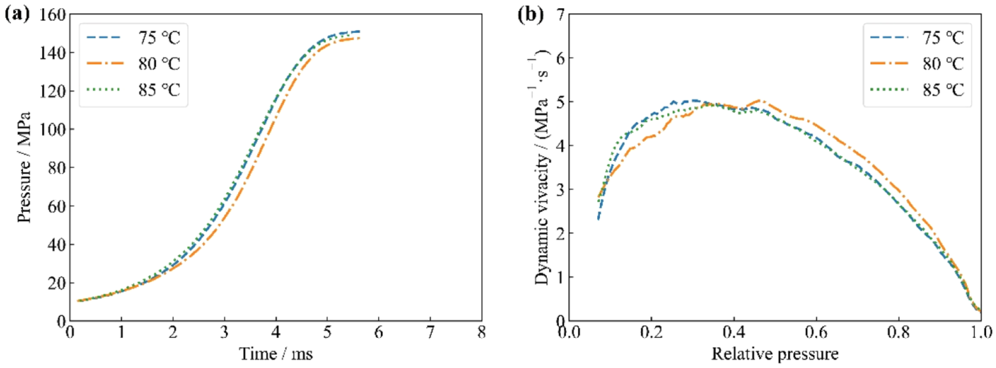

Figure 6. (a) p−t curves and (b) L−B curves of ECDA-deterred propellants with different deterring temperatures.

Table 4. Closed Vessel Results of ECDA-Deterred Propellants with Different Deterring Temperatures

sample	p_m/MPa	t_m/ms	L_m/MPa^{-1}·s^{-1}	B_m
75	151.12	5.645	5.029	0.303
80	147.52	5.600	5.027	0.468
85	149.14	5.385	4.952	0.354

Table 5. Interior Ballistic Performance of ECDA-Deterred Propellants

sample	charge/g	v/(m·s^{-1})	$\overline{v}$/(m·s^{-1})	p/MPa	$\overline{p}$/MPa
original propellants		808		319.2	
		804		318.1	
	1.2	813	808.8	320.3	319.6
		809		320.3	
		810		320.3	
ECDA-deterred propellants		901		304.9	
		904		291.6	
	1.6	912	902.2	306.2	300.6
		897		302.4	
		897		298.0	

behind the bullet is very small and the propellants burn slowly under the action of ECDAs, avoiding the extreme high pressure. This feature allows more propellants to be contained in bullets under safe pressure. As the combustion proceeds, the bullet moves a longer distance and the space behind the bullet becomes larger and the propellants burn faster due to the decrease of the ECDA concentration. More gas generated propels the bullet to gain a higher velocity. Also, the sample deterred with ECDAs achieves the same interior ballistic level as the traditional DBP-deterred propellants.

It is revealed that ECDAs have ideal deterring effects, providing the propellants with good burning progressivity and excellent interior ballistic performance. The most important thing is that the composite deterring reduced bad phenomena such as muzzle flame and smoke.

High Speed Photography. "Higher velocity with lower pressure" is an eternal goal of research on the barrel weapon. The deterrent can greatly achieve this goal, but it brings harmful phenomena at the same time. It is very important to achieve the coordination of various performances. The muzzle flame and smoke of the ECDA-deterred propellants were studied by a high-speed camera and compared with those of traditional DBP-deterred propellants. High-speed photographs of the two charges at different moments are shown in Figure 7, and their dynamic process comparison is shown in GIF S1.

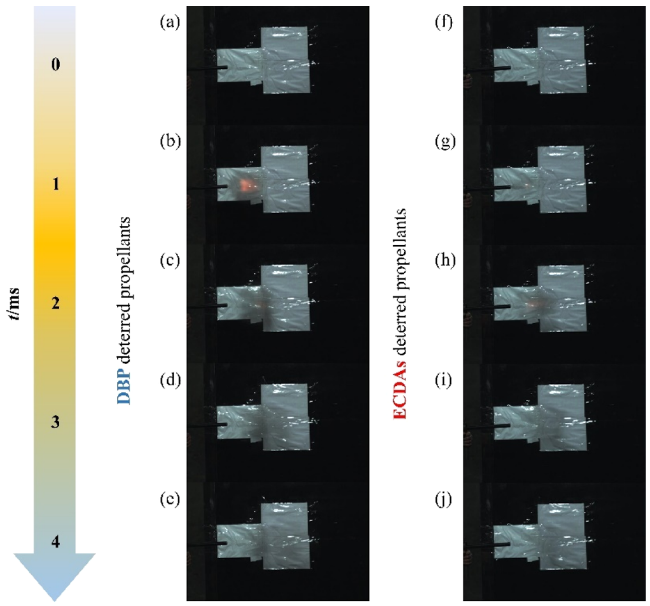

Figure 7. High speed photographs. The moment after shooting of the DBP-deterred propellant charges: (a) 0, (b) 1, (c) 2, (d) 3, and (e) 4 ms. The moment after shooting of the ECDA-deterred propellant charges: (f) 0, (g) 1, (h) 2, (i) 3, and (j) 4 ms.

It can be clearly seen from the figure that the muzzle flame of the ECDA-deterred propellants almost disappeared, compared with that of the DBP-deterred propellants, and the smoke concentration of the ECDA-deterred propellants was relatively low. This is consistent with the previous prediction. Based on the fact that ECDA-deterred propellants have a higher oxygen balance, the propellants burned more adequately; therefore, the muzzle flame and smoke reduced accordingly.

Smoke Box Result. It is difficult to clearly quantify the muzzle smoke based on the photograph from the high-speed camera. A smoke box was then used to gain the light transmittance of the muzzle smoke. The average light transmittance value of the DBP-deterred propellants and the ECDA-deterred propellants were 63.6 and 77.8%, respectively, as shown in Table 6.

The light transmittance of smoke can be converted into concentration by the Lambert Beer's law, as shown below:

$$A = \lg(1/T) = kbc \quad (3)$$

Table 6. Smoke Box Results of Composite-Deterred Spherical Propellants

formulas	light transmittance/%			average value/%
DBP-deterred propellants	65.2	64.2	61.3	63.6
ECDA-deterred propellants	76.9	79.8	76.7	77.8

where A is the absorbance, T is the transmittance ration, k is the molar absorption coefficient, b is the absorption layer thickness, and c is the concentration of smoke.

Furthermore, the equation of Lambert Beer's law for the two different propellants can be subjected to ratio treatment, and thus the muzzle smoke reduction percentage of the ECDA-deterred propellants compared with the DBP-deterred propellants can be determined as 44.5%. This further demonstrates that the energetic composite deterring technology can effectively reduce muzzle smoke.

■ CONCLUSIONS

The burning properties and harmful phenomena of the deterred propellants were improved by replacing traditional DBP with ECDAs. The special energy release regularity and the composite deterring structure provided the propellants with good burning progressivity and less muzzle flame and smoke, which were, respectively, confirmed by experiments.

The closed vessel test showed that TEGDN had a slight deterring effect that is weaker than that of PNA on the propellants. Compared with the DBP-deterred propellant, the ECDA-deterred propellant had a maximum pressure in the closed vessel bore of 2.29 MPa higher, though the L−B curve of the ECDA-deterred propellant was slightly lower and its combustion time was 0.44 ms longer. It is illustrated that the ECDA-deterred propellants have a better burning progressivity.

ECDA-deterred propellants under optimal conditions (80 °C and 150 min) were chosen for interior ballistic, high-speed photography, and smoke box tests. The average velocity of the bullet propelled by ECDA-deterred propellants was increased by 93.4 $m \cdot s^{-1}$, while the average maximum pressure in the gun bore was decreased by 19 MPa, compared with the original propellants. The muzzle flame and smoke of the ECDA-deterred propellants were significantly reduced compared with the DBP-deterred propellants, where the smoke concentration reduction rate reached 44.5%.

■ EXPERIMENT

Materials. Double-base spherical propellants had a diameter of 0.38 mm and contained 90 wt % nitrogen content (NC, 13.0%) and 10 wt % NG. PNA was a polyester prepared by polymerization reaction of neopentyl glycol and adipic acid. $H(C_{11}H_{18}O_4)_nOH$ had an average molecular weight of about 3000 g/mol. Double-base spherical propellants PNA and TEGDN were provided by Luzhou North Chemical Industry Limited Company. Gelatin was provided by Zibo Ouchang Gelatine Sales Limited Company, medical-grade, with a frozen force of 250 g bloom. Ethyl acetate was purchased from Sinopharm Chemical Reagent Co., Ltd.; it was chemically pure.

Deterring Process. The composite deterring process of propellants is shown in Figure 8 and mainly consisted of two steps.

The first step was the preparation of ECDAs. A total of 1 g of gelatin was dissolved in 100 mL of water and heated at 65 °C for 10 min with stirring to form a uniformly dispersed gelatin solution. Several deterring agents were added into the gelatin solution, and water was replenished to the solution to a volume of 400 mL. The mixed liquid was then emulsified at room temperature by a WIGGENS D-500 emulsifier. The working head of the emulsifier consisted of an S20F stator and an ER20 rotor. The speed of the emulsifier was 10000 rpm. The mixed liquid became a composite deterring emulsion which presented a milky look after being emulsified for 10 min.

The second step was a deterring process. A total of 400 mL of an ECDA emulsion and 100 g of the original propellants were put in a flask. Under heating in a 80 °C water bath with stirring at a 400 rpm speed, ECDA gradually diffused from the surface of original propellants into deeper sites. After drying in a water bath oven for 48 h, the composite-deterred propellants were prepared completely.

The deterring agents and deterring conditions for different propellants in the experiments are shown in Table 7. Among

Table 7. Formulation and Process Conditions of Different Samples

sample	deterring agent	deterring temperature/°C	deterring time/min
1	(original)		
2	6% PNA	80	150
3	8% TEGDN	80	150
4	5% DBP	80	90
5	5% PNA + 3.2%TEGDN	80	150
6	5% PNA + 3.2%TEGDN	80	30
7	5% PNA + 3.2%TEGDN	80	60
8	5% PNA + 3.2%TEGDN	80	90
9	5% PNA + 3.2%TEGDN	80	120
10	5% PNA + 3.2%TEGDN	80	180
11	5% PNA + 3.2%TEGDN	75	90
12	5% PNA + 3.2%TEGDN	85	90

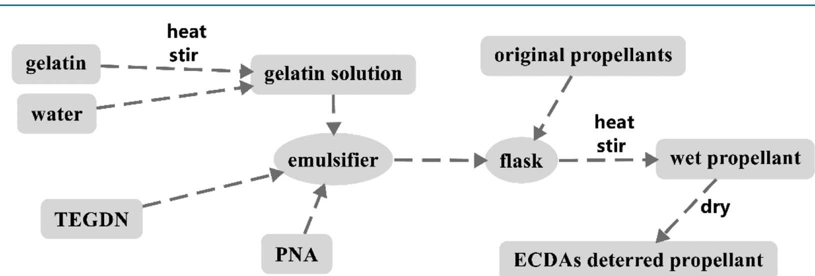

Figure 8. Flow chart of preparation of propellants deterred with ECDAs.

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them, the original propellants (1#) were the spherical propellants without deterring. The propellants deterred with ECDA containing 5 wt % PNA and 3.2 wt % TEGDN at 80 °C for 150 min (5#) were chosen for the interior ballistic, high-speed photography, and smoke box tests.

Closed Vessel Test. The static combustion performance of the composite deterring propellants was tested with a closed vessel, as shown in Figure 9. The testing temperature was 20 °C. The volume of the closed vessel was 50 mL. A total of 0.55 g NC (12.4%) was chosen as the ignition powder. The loading density of the propellants was 0.12 g/mL.

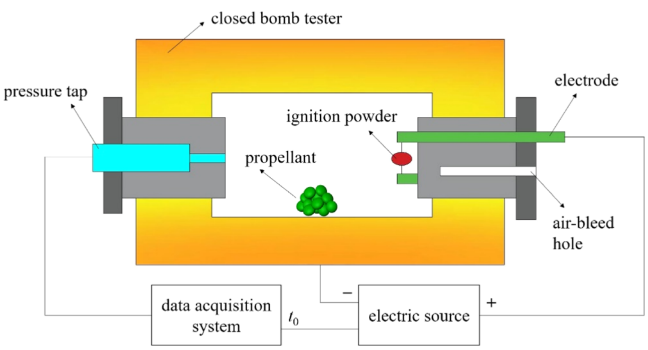

Figure 9. Schematic diagram of the closed vessel test.

Interior Ballistic Test. The interior ballistic performance of different propellants was investigated by one ballistic gun. A bullet velocity at the position 2 m away in front of muzzle was obtained by the distance between two photoelectric targets and the time during which the bullet passed through. The maximum chamber pressure was tested at the bottom of the gun tube by a copper cylinder pressure meter.

High Speed Photography. In order to determine whether the ECDA-deterred propellants can alleviate the harmful emission phenomena compared with the DBP-deterred propellant, the muzzle smoke and flame of different charges were recorded by a high-speed camera. The model of the camera was pco. dimax s4, with a frame rate of 1000 fps.

Smoke Box Test. The muzzle smoke can also be characterized by a device of a smoke box. The structure of the smoke box is shown in Figure 10. A visible light source and a photoelectric sensor were, respectively, placed on the sides of the smoke box with the protection of an optical glass window. After shooting, the hole through which the bullet passed was quickly coated by plasticine and thus muzzle smoke was collected. The light transmittance in the stable state can reveal the characteristics of the smoke.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00637.

Sample preparation for the laser microscopic confocal Raman spectrometer test; Leica slice machine and the sliced sample; analysis process of the Raman test result of the PNA deterred propellants; line scan path, Raman spectrometer at the site of edge/center, distribution of several characteristic peak intensities, and distribution of characteristic peak ratio of the PNA deterred propellants; analysis process of the Raman test result of the DBP deterred propellants; line scan path, Raman spectrometer at the site of edge/center, distribution of several characteristic peak intensities, and distribution of characteristic peak ratio of the DBP deterred propellants (PDF)

Dynamic process of the muzzle flame and smoke, the comparison between the DBP deterred propellants, and the ECDA-deterred propellants (ZIP)

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Notes

The authors declare no competing financial interest.

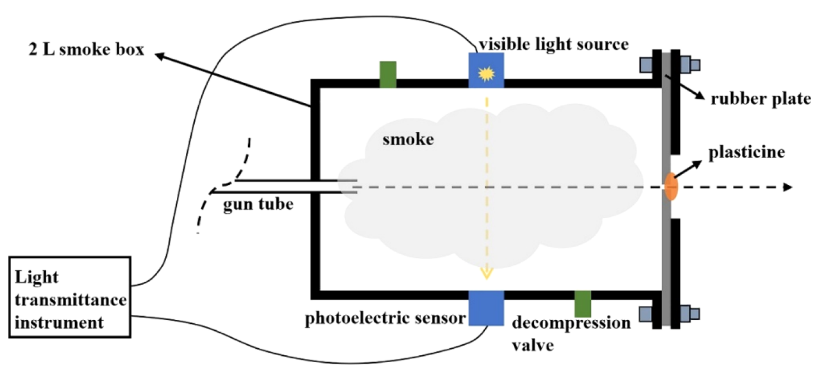

Figure 10. Schematic diagram of a smoke box.

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