

## Research Article

# **Compatibility Study of 1,1-Diamino-2,2-Dinitroethene** (FOX-7) with Some Energetic Materials

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1,1-diamino-2,2-dinitroethene (FOX-7) is a novel explosive with low sensitivity and high performance. The compatibility of FOX-7 with nine common energetic materials including hexanitrohexazaisowurtzitane (CL-20), cyclotetramethylenetetranitramine (HMX), cyclotrimethylenetrinitramine (RDX), 3,4-dinitrofurazanfuroxan (DNTF), 3-nitro-1,2,4-triazol-5-one (NTO), hexanitrostilbene (HNS-II), 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105), 2,4,6-triamino-1,3,5-trinitrobenzene (TATB), and 2,4,6-trinitrotoluene (TNT) were tested by differential scanning calorimetry (DSC) and the vacuum stability test (VST) as the thermal technique and X-ray diffractometry (XRD) as a nonthermal technique. DSC measurements showed that the binary systems of FOX-7/CL-20, FOX-7/HMX, FOX-7/NTO, and FOX-7/TNT were compatible in grade of A, the systems of FOX-7 with heat-resistant explosives including HNS-II, LLM-105, and TATB were compatible as well in grade of A-B, and the binary systems of FOX-7/DNTF and FOX-7/RDX had poor compatibility. VST results indicated that FOX-7 was compatible with nine energetic materials. Besides, the compatibility results of the thermal analysis were confirmed by the XRD technique.

## 1. Introduction

1,1-diamino-2,2-dinitroethene (FOX-7) is a novel explosive combining comparatively high performance and low sensitivity [1]. Since it was reported in 1998 [2], it has quickly been the subject of explosives research in various countries of the world. Many researchers have focused on the theoretical calculation, synthesis, thermal properties, and nanostructure of FOX-7 [3–10]. Previous results on the physical and chemical characterization of FOX-7 have demonstrated that it possesses good thermal and chemical stability. It is expected that FOX-7 will be a new important explosive ingredient with potential application.

Compatibility is one of the most important indicators to measure the safe use of explosives and is a decisive factor in the long-term normal storage of energetic materials. It is well-known that the single explosive system fails to meet the actual requirements in modern weapons, and mixed explosives are often the ultimate way to achieve weapon damage. So, the compatibility of FOX-7 is a key issue and has to be investigated entirely prior to its actual use in composite explosives.

Due to the thermal effects of energetic material interactions, the DSC method can be used to quickly and accurately measure the amount of heat generated [11], which has been widely used as a rapid screening method for compatible material since it is simple and safe [12–15]. The vacuum stability test (VST) is another method for chemical compatibility judgment [16]. The test conditions are closer to the real environment, which can provide more valuable data for the practical application of energetic materials. Besides the thermal techniques, nonthermal techniques such as NMR, FTIR, and XRD have been employed to provide structural information on the particle dispersed and analysis of chemical characteristics or interactions between components [17–19]. Fu [20], Van Der Heijden et al. [21], and Zhao et al. [22] have studied the compatibility of FOX-7 with some potential ingredients, but failed to evaluate the compatibility of FOX-7 with some conventional energetic materials. In order to expand the application of FOX-7, its compatibility with nine energetic materials including CL-20, HMX, RDX, DNTF, NTO, HNS-II, LLM-105, TATB, and TNT were tested, which lay the foundation for its further application in modern weapons and ammunition.

#### 2. Materials and Methods

2.1. Materials and Samples. FOX-7 was provided by Xi'an Modern Chemistry Research Institute, whose purity was more than 99%, and the average particle size was  $20 \,\mu$ m. The molecular structure is shown in Figure 1.

The nine selected explosives including hexanitrohexazaisowurtzitane (CL-20 > 99%, 100  $\mu$ m), cyclotetramethylenetetranitramine (HMX > 99%, 50  $\mu$ m), cyclotrimethylenetrinitramine (RDX > 99%, 45  $\mu$ m), 3,4-dinitrofurazanfuroxan (DNTF > 99%, 80  $\mu$ m), 3-nitro-1,2,4-triazol-5-one (NTO > 99%, 50  $\mu$ m), hexanitrostilbene (HNS-II > 99%, 30  $\mu$ m), 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105 > 99.5%, 25  $\mu$ m), 2,4,6-triamino-1,3,5-trinitrobenzene (TATB > 99.5%, 25  $\mu$ m), and 2,4,6-trinitrotoluene (TNT > 99%, 40  $\mu$ m) were provided by Gansu Yinguang Chemical Industry Group Co., Ltd.

A binary system of FOX-7 with each selected explosives was prepared in the 1:1 (m/m) ratio by grinding in an agate mortar with pestle for 5 min.

#### 2.2. Thermal Techniques and Nonthermal Techniques

2.2.1. DSC. DSC curves were obtained using a TA Q2000 instrument (TA Instruments, New Castle, DE, USA) with closed stainless steel crucibles and about 1 mg of samples. The measurements were performed under a dynamic atmosphere of nitrogen at a flow rate of 50 mL min<sup>-1</sup> with a heating rate of  $10^{\circ}$ C min<sup>-1</sup>. Tests were carried out individually for pure FOX-7 and selected explosives and then for prepared mixtures. Prior to the DSC test, we screened each sample using a 400 mesh sieve to achieve a uniform particle size distribution.

2.2.2. VST. The VST test was performed using a pressure transducer according to STANAG 4147. A single and mixture system were heated at a constant temperature of  $100^{\circ}$ C for 40 h in an initial vacuum. Based on the volume of additional gas produced by the contact between the two components in the mixture, the compatibility was judged.

2.2.3. XRD. DX-2700 X-ray diffraction (XRD, Dandong Haoyuan Corporation, Liaoning, China) was used to analyse the crystal form of as-prepared samples at a voltage of 40 kV and a current of 30 mA using Cu-K $\alpha$  radiation at  $\lambda = 1.5418$  Å. Data were drawn by means of the software Origin version 8.5.



FIGURE 1: Diagram of the FOX-7 molecular structure.

#### 3. Results and Discussion

3.1. DSC Observations. The DSC curves at a heating rate 10°C/min for the single and binary systems measured are presented in Figure 2. It can be seen that neat FOX-7 has an obvious endothermic peak at 116.30°C, and two exothermic peaks are at 233.51°C and 276.65°C, respectively, which is similar to previous DSC investigations [6]. The first exothermic peak at 233.51°C was chosen to calculate the differences between a single and mixture system when the temperature is lower than the lowest decomposition peak temperature of another single system. The obvious endothermic peak at 116.30°C is due to the crystal transformation from  $\beta$  to  $\gamma$ , and the thermal decomposition of FOX-7 consists of two stages: the first stage may be due to the intramolecular reaction of denitrification, and the second stage is caused by the intermolecular reaction of the rupture of the molecular skeleton [6, 23, 24].

According to the evaluated standards of compatibility for explosive [25], which are listed in Table 1, the maximum exothermic peak temperatures of systems obtained from the thermal curves are summarized in Table 2. From Figure 2 and Table 2, the following observations can be obtained.

In the FOX-7/CL-20 (Figure 2(a)) system, there was no obvious endothermic peak, and only a very strong endothermic peak appeared. The peak temperature of this system was 9.25°C higher than that of FOX-7, indicating that the presence of CL-20 makes thermal stability better. Similarly, the maximum exothermic peak of the FOX-7/HMX (Figure 2(b)) and FOX-7/NTO (Figure 2(e)) mixture system was postponed by 18.58°C and 6.73°C, respectively. The exothermic process of FOX-7/HMX consists of two stages, 252.09°C and 283.84°C, respectively, with only one exothermic peak in the FOX-7/NTO system to release energy completely. It was shown that the effects of HMX and NTO delayed the decomposition of FOX-7 in different degrees, played a stabilizing role of FOX-7, and improved the thermal stability. There was a weak exothermic peak at 231.83°C and an exothermic strong peak at 262.01°C in the FOX-7/TNT mixture system, which suggested that the introduction of TNT accelerated the thermal decomposition process of FOX-7 and made the second exothermic peak in advance. Consequently, the FOX-7/CL-20, FOX-7/HMX, FOX-7/ NTO, and FOX/TNT binary systems are compatible, indicating they are safe for use in explosive design.

As we can see from Figures 2(f)–2(h), the exothermic processes of the mixture systems of FOX-7 with heat-resistant explosives including HNS-II, LLM-105, and TATB are similar, and three exothermic peaks exist consisting of their respective exothermic peaks. The values of  $\Delta T_p$  between FOX-7 and its mixture with HNS-II, LLM-105, and TATB were 1.22°C, 2.87°C, and 2.63°C, respectively. Evaluation of







FIGURE 2: DSC curves of mixture systems.

TABLE 1: Evaluation standards of the compatibility for explosives and contact materials.

Criteria $\Delta T_{\rm p}$ (°C)	Rating	Note
Less than or equal to 2	A, compatible or good compatibility	Safe for use in any explosive design
		Safe for use in testing, when the device will be used in
3-5	B, slightly sensitized or fair compatibility	a very short period of time; not to be used as a binder
		material; or when long-term storage is desired
6-15	C, sensitized or poor compatibility	Not recommended for use with explosive items
Above 15	D, hazardous or bad compatibility	Hazardous. Do not use under any conditions

TABLE 2: Decomposition temperatures of binary systems obtained by DSC.

Binary system	Single system	Peak temperature			
		$T_{p1}$ (°C)	$T_{p2}$ (°C)	$\Delta T_{\rm p}$ (°C)	Rating
FOX-7/CL-20	FOX-7	233.51	242.76	-9.25	А
FOX-7/HMX	FOX-7	233.51	252.09	-18.58	А
FOX-7/RDX	FOX-7	233.51	220.20	13.31	С
FOX-7/DNTF	FOX-7	233.51	228.27	5.24	B-C
FOX-7/NTO	FOX-7	233.51	240.24	-6.73	А
FOX-7/HNS-II	FOX-7	233.51	232.29	1.22	А
FOX-7/LLM-105	FOX-7	233.51	230.64	2.87	A-B
FOX-7/TATB	FOX-7	233.51	230.88	2.63	A-B
FOX-7/TNT	FOX-7	233.51	231.83	1.68	А

Note. Binary system, 1/1-FOX-7/energetic material binary system; single system, system of the single energetic material, in which exothermic peak temperature is smaller of the two components;  $T_{p1}$ , the maximum exothermic peak temperature of the single system;  $T_{p2}$ , the maximum exothermic peak temperature of the mixture system;  $\Delta T_p = T_{p1} - T_{p2}$ .

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TABLE 3: Gas evolved (mL/g) of the VST test for the mixture system.



(e)

(f)



FIGURE 3: XRD diffraction patterns of mixture systems.

the DSC curves of the FOX-7/heat-resistant explosives system confirmed that there was no interaction obviously between heat resistant explosives and FOX-7. According to the evaluated standards of Table 1, the rating of the FOX-7/ HNS-II, FOX-7/LLM-105, and FOX-7/TATB are A, A-B, and A-B, correspondingly.

However, during the exothermic processes of the FOX-7/DNTF (Figure 2(d)) mixture system, one endothermic peak and two exothermic peaks are observed, and DNTF activated the FOX-7 when they released the heat, making the decomposition peaks 5.24°C lower than that of the FOX-7. There was an increase in reactive ability and a decrease in the thermal stability of the mixtures. Thus, the rating of the FOX-7/DNTF is B-C.

Notably, we can see a clear exothermic peak accompanied by a "step peak" from the DSC curves of FOX-7/RDX (Figure 2(c)). The decomposition peak temperature at 220.20°C is 13.1°C lower than the neat system. This may be due to the effect of FOX-7 which caused the RDX to melt ahead of time and to undergo a strong thermal decomposition reaction, implying a possible chemical interaction between FOX-7 and RDX, and the mixture therefore has poor compatibility. 3.2. VST Results. The vacuum stability test is another method to evaluate compatibility, which was used especially to confirm the incompatible measurements obtained by DSC. Test criteria of compatibility of the VST test are based on the additional gas volume evolved from the mixture tested under the same conditions relative to the pure product, and the mixture is considered as compatible if the volume is less than 5 mL. The gas evolved of each binary system showed in the Table 3 is lower than 5 mL, indicating that FOX-7 is compatible with nine kinds of explosives, which is consistent with prior works [20–22].

3.3. XRD Analysis. Brostoff et al. [26] and Chadha and Bhandari [27] have found that XRD is a direct measure for revealing unique diffraction patterns that contain the fingerprints of individual components. So, we employed it as a supplementary analytical technique for the detection of possible changes induced in the FOX-7/explosive mixtures. The XRD diffraction patterns of the mixture system are shown in Figure 3. In all systems, it is obvious that the diffraction intensity of the binary system is weakened in varying degrees compared with the corresponding single system. The characteristic peak of FOX-7 is at 14.90°, 19.95°, 26.80°, 29.90°, and 31.10°.

As shown in Figures 3(a)–3(e) and 3(i), the XRD patterns of the FOX-7/CL-20, FOX-7/HMX, FOX-7/RDX, FOX-7/ DNTF, FOX-7/NTO, and FOX-7/TNT were the combination of characteristic peaks of each component, accompanied by a decrease in strength. For example, the peaks at 26.95° and 32.35° of RDX in the FOX-7/RDX mixture are reducing significantly. Also, the results indicated that there was no interaction between them and they are compatible, which is somewhat different with the DSC results, but consistent with VST results.

The XRD patterns of FOX-7/HNS-II in Figure 3(f) manifest that the important diffraction peaks attributed to the characteristics of FOX-7 and HNS-II, except for the peaks of HNS-II at 8.35° and 34.10° that diminished, remain practically unchanged in this binary system. In the binary system of FOX-7/LLM-105 and FOX-7/TATB, the characteristic peak of FOX-7 at 29.90° overlaps continuously with broadening of the peaks with that of TATB at 28.35° and LLM-105 at 28.45°, respectively. It is shown that in the presence of LLM-105 and TATB, the interaction may be responsible for the enhanced thermal stability of FOX-7.

#### 4. Conclusions

The compatibility of FOX-7 with a selection of explosives, including CL-20, HMX, RDX, DNTF, NTO, HNS-II, LLM-105, TATB, and TNT, was explored by DSC and VST thermal techniques and supplementary nonthermal techniques of XRD. From the DSC results, it was found that the values of  $\Delta T_{\rm p}$  between FOX-7 and its mixture were all less than 6°C, except for FOX-7/RDX, suggesting that FOX-7 is compatible with the selected energetic materials. A further study through the VST indicated that all mixture systems possess good compatibility. Moreover, the results of XRD were in agreement with the thermal analysis results of VST.

#### **Data Availability**

The data used to support the findings of this study are available from the corresponding author upon request.

### **Conflicts of Interest**

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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