New fusible binder additives for composite explosives

Marina Komarova, Aleksey Vakutin*, Nikolai Kozyrev, Gennady Sukhanov and Sergey Ilyasov

Institute for Problems of Chemical and Energetic Technologies, SB RAS, 1 Sotsialisticheskaya street, Biysk, 659322, Russia

Abstract. Occupational safety in manufacturing powerful melt-cast composite explosives requires replacement of conventional fusible binders, as trotyl and dinitrazapentane, by less sensitive compounds. To solve this challenge, insensitive 3-nitro-1,2,4-triazole derivatives (1-, 2-methyl, tert-butyl, ethoxymethyl) and their eutectic mixtures with furazanyl furoxane can be used in formulations with 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (octogen, HMX) and 6-nitrohexaazaisowurtzitane (CL-20). Our studies shows quite low sensitivity impact of the nitrotriazole derivatives (≥ 500 mm at a load weight of 10 kg), their melting temperatures (56…94 °C), and their eutectic temperatures with furazanyl furoxane (57…62 °C). For HMX-based composite explosives, the optimum options are ethoxymethyl-3-nitro-1,2,4-triazole and its eutectic melt with furazanyl furoxane (80/20 weight ratio), while for CL-20-based formulations, the appropriate additives were 1-methyl-3-nitro-1,2,4-triazole and its eutectic melt with furazanyl furoxane (80/20 weight ratio). Phase diagrams of the new fusible binder additives are also given. The data were obtained by differential scanning calorimetry (DSC).

1 Introduction

Application of more powerful explosives increases the risks associated with production, processing, storage, and application occupational hazards of composite explosives. Therefore, greater attention should be paid to the safety problems, especially when high-sensitivity powerful explosives such as octogen (HMX), furazanyl furoxane (BNFF) and hexaazaisowurtzitane (CL-20) are employed. Hence, the search for new solutions is a hot topic.

In composite explosives produced by the casting method to bond the filler (HMX, CL-20, etc.), fusible binder additives are utilized. The conventional fusible binders are trotyl (TNT) and dinitrazapentane (DNP) whose mechanical sensitivities are considered acceptable but not sufficient to design explosives with reduced sensitivity and enhanced power. Some derivatives of ploynitrogen heterocyclic compounds are promising. These compounds feature a high enthalpy of formation and a fairly high density, and contain energetic groups rich in nitrogen [1, 2].

Nitrotriazole derivatives have very low sensitivities to impact and friction, and an appropriate melting temperature for technological processing. For instance, 1-methyl-3-nitro-1,2,4-triazole is close to TNT in some properties (density, oxygen balance, detonation rate) but its melting temperature (~65 °C) is more appropriate for casting, and it is also highly safe.

The sensitivity level is lower than that of conventional fusible binders, which makes it possible to improve the energetic performance of nitrotriazole derivatives by means of powerful BNFF. Due to melting at 107…111 °C [3-8] BNFF can form eutectic mixtures with other ingredients of composite explosives, including TNT [4, 8, 9]. It was experimentally shown [8] that TNT/BNFF eutectic systems had better energetic and technical characteristics than TNT alone and lower sensitivities to impact and friction than BNFF. The regulating role of the variation of the TNT and BNFF ratio was also well shown. Thus, the replacement of TNT and DNP by nitrotriazole derivatives or by their eutectic mixtures with BNFF for use in HMX and CL-20 formulations is of interest in terms of designing new and optimizing the existing composite explosives.

The present study reports experimental results of developing new fusible binder additives and composite explosives on their basis.

2 Experimental part

2.1 Materials

To prepare fusible binder additives, we synthesized high-energy materials on the basis of nitrogen-containing heterocycles-nitrotriazole derivatives under laboratory conditions. 1-Methyl-3-nitro-1,2,4-triazole (Me3H) and 2-methyl-3-nitro-1,2,4-triazole (2Me3H) were synthesized by alkylating 3-nitro-1,2,4-triazole with methyl iodide and dimethyl sulfate in the presence of alkali [10, 11]. Ethoxymethyl-3-nitro-1,2,4-triazole (EOM) was synthesized by acid-catalyzed reaction between the corresponding heterocyclic and aliphatic alcohols. tert-Butyl-3-nitro-1,2,4-triazole (tBu3H) was prepared by alkylaition of 3-nitro-1,2,4-triazole with tert-butyl alcohol in the presence of catalytic amounts of sulfuric acid [12]. The said nitrotriazole derivatives

*Corresponding author: alex-wakutin@e-mail.ru

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under normal conditions are solids with a melting point below 94 °C (Table 1).

We also used commercial conventional fusible binders (Producer, Russia) as 2,4-dinitrazapentane (DNP) and 2,4,6-trinitromethylbenzene (trotyl, TNT). As the ingredient of the fusible binder additives, we used the powerful explosive 3,4-bis(4- nitrofurazanyl-3)furoxane (BNFF) prepared under laboratory conditions in a pilot setup [13].

The fusible binder additives were made as follows: the components were powdered and mechanically mixed in different weight ratios of 20/80, 40/60, 50/50, 60/40 and 80/20. The ready-made mixtures were placed into fluoroplastic cups, heated in a vacuum oven to a temperature close to the melting point of the high-melting ingredient BNFF (to 115 °C), and then held at this temperature until the mixtures turned into the liquid state. The resultant melts were cooled at ±24±1°C. The melts containing less than a half of BNFF easily crystallized under normal conditions. The melts containing more than a half of BNFF experienced difficulties, and such melts were put into a cooling chamber for 3 hrs to lower their temperature to 4°C. After being cured, all the samples were held at 24±4°C for 24 h to complete the process. The samples were then ground and poured into glass sample bottles with caps, and stored in a sealed package under normal conditions.

Commercially available octogen (HMX, Producer, Russia) and hexanitrohexaaazaisowurtzitane (CL-20) were used to make explosive formulations. The HMX and CL-20 crystals were mechanically mixed with the pulverized fusible binders in a weight ratio of 50/50. The mixtures contained in the fluoroplastic cups were heated to the final melting point of the binder additive (Table 2), stirred and cooled. The samples thus obtained were characterized by the methods described hereinafter.

### 2.2 Measurement methods

For prediction of the properties of materials and explosive formulations, we used a differential scanning calorimetry (DSC) by recording the energy required for temperature equalization of a test substance and a reference standard, depending on time and temperature [14]. The experiments were done on a Mettler Toledo DSC822e modular calorimeter (Switzerland) in a temperature range from -65 °C to +700 °C. The calorimeter was equipped with a heat flux sensor and an analog converter; the highest programmable sample heating rate was 250 °C/min and the measurement error was ± 0.2 °C. The instrument was part of the STAR™ complex measuring system (Thermal Analysis System Software). The instrument was calibrated against heat flux and melting temperature of indium (In, 99.999 % purity) and zinc (Zn, 99.998 % purity) by using dedicated test programs.

The samples of the high-energy materials and explosive formulations in the quantity of 0.7–3.5 mg were placed into aluminum melting crucibles with perforated lids and heated from + 25 °C to + 125 °C or to +350 °C, at a heating rate of 10 °C/min, in dynamic nitrogen atmosphere (nitrogen gas purge rate was 60 ml/min). The initial information acquired by the STAR™ measuring system was processed in the STAR™ software v. 14.00. Numerical values of the melting heat (Q_m) and decomposition heat (Q_d) were thus acquired. The heat effects were estimated from the area of the heat effect limited by the DSC graph and by the corresponding baseline (program option ‘Integration’). The following baselines were used: ‘Tangential Left’ – a tangent to the DSC curve, drawn from the left border (for integration of melting peaks with subsequent decomposition); ‘Spline’ – lines based on two tangents drawn from the left and right borders and connected by a smooth transition line (for overlapping effects). The temperature values of the heat effects were determined from the intercrossing of the tangents drawn to the peak (program option ‘Peak’) [15].

The morphological features of the starting materials and final composites (crystal surface and size, surface of melts, and so on) were visualized by optical methods. A Motic DMBA-300 Professional Series digital optical microscope (China) was employed with a built-in video camera, computer interface and Motic Images Plus 2.0 image processing software. Zooms were x100, 400 and 1000. The crystal sizes were determined from the plane projections of their images. A comparative analysis of the crystal surface images was used to pre-check the compatibility (no reaction) with the nitrotriazole derivatives and fusible binder additives.

To determine the chemical stability of the high-energy compounds, a Crystal-2000M instrument (gas chromatograph, Russia) and a standard ampule-chromatographic procedure were used [16, 17]. The procedure was performed as follows: a 2–3 g test sample was placed into an ampule; the air medium was replaced by vacuum; the ampule was sealed and held at +80 °C for 24 h. The ampule was then opened and the released gaseous products were analyzed in order to identify the qualitative and quantitative composition of the gases. The sample was considered stable if the gas volume did not exceed 0.08–0.1 cm³/g. The same procedure was employed to determine the chemical compatibility of the ingredients of the composite explosives.

The sensitivity of the nitrotriazole derivatives towards mechanical stimuli was measured by the standard techniques [18, 19] using a K-44-II impact-testing machine and a K-44-III friction-testing machine (Russia). The sensitivity measurement methods consisted in initiating a chemical reaction by impact or friction. For the impact stimulus, the Kozlov’s K-44-II impact-testing machine was used. The impact tester consisted of a massive slab located on a solid concrete foundation and three guide supports between which there was a load weight fixed at a certain height. The load weight was intended to impact a test specimen. The test specimen was 0.05–0.1 g and was fixed in a special clutch. The standard technique involved the measurement of the so-called lower limit of sensitivity by dropping a 10-kg weight from a height of 250 mm. Ten to twenty five tests were done and the number of explosions were documented. Next, the relative incidence rate (%) of explosions was estimated [18, 20].
The friction sensitivity was determined by the standard method for friction measurement under impact shear on a K-443-3 friction tester (the Kozlov’s pendulum testing machine). The method was based on measuring the so-called lower limit of sensitivity being defined by the maximum application pressure under which the test specimen did not detonate. The test specimen was fixed between two steel plates moving by 1.5 mm relative to each other in 25 tests [19, 20]. Test specimens were 0.02–0.05 g. The pressure was defined from special tables, depending on the angle (28–108°) of the diversion of the instrument lever with the load weight [19].

The Excel and Mathcad universal mathematical programs were employed for the approximation of experimental data [21].

3 Results and discussion

The sensitivity of high-energy materials is one of the most essential characteristics because it determines the production and application safety levels of composite explosives. For instance, the impact sensitivity of 2,4,6-trinitromethylbenzene (TNT) is 4–8 % [22] with a weighed portion of 0.05 g, a drop height of 250 mm, and a drop weight of 10 kg; the friction sensitivity is 300 MPa [23]. 2,4-Dinitrazapentane (DNP) has similar characteristics: 5–10 % at the same drop height and weight [24]. The probability of explosion due to impact for 3,4-bis(4-nitrofurazanyl-3)furoxane (BNFF) is 80–96 % at a height of 250 mm and a load weight of 10 kg, and the friction sensitivity is 44–60 %. [25]. Hence, TNT is the least sensitive and BNFF is the most sensitive among these compounds.

In comparison with TNT, the nitrotriazole derivatives (EOM, 2Me3H, Me3H and tBu3H) are practically safe. The experimental data corroborate this statement: no explosion occurred in 25 tests (i.e. 0%) and the lower limit of the friction sensitivity was therefore 10000 kgf/cm² (980.66 MPa). The impact sensitivity was ≥ 500 mm at a drop weight of 10 kg. So, the addition of some BNFF to the nitrotriazole derivatives should not have a considerable influence on the sensitivity of the binary fusible binder.

Besides the sensitivity, it is necessary to determine other basic characteristics of the starting components. The melting temperature of the binder additive is of great importance because it has a bearing on the production process and storage of a finished explosive formulation. In some researchers’ opinion [8], the melting temperature must be in the range from +80 to +100 °C. Our experience shows that the temperature of +50–60 °C is enough.

According to DSC tests (Table 1) samples were heated to +125 °C and the following parameters were determined: onset temperature of heat effect (T_b), melting temperature (T_m), endset temperature of heat effect (T_e), melting heat (Q_m). The sign ‘-’ (minus) stands for heat absorption (endothermic effect).

The results in Table 1 demonstrate that the melting point of 2Me3H is close to that of TNT, and the melting point of EOM is close to that of DNP. The compound tBu3H is more high-melting than the conventional fusible binders TNT and DNP. The compound Me3H is a medium variant with T_m = 65.9 °C. For BNFF, the melting point is 110.3 °C, which is in agreement with the literature data [6, 8, 26].

Since binary eutectic mixtures have a significantly lower melting point than each of the components, it is fair to expect that fusible binder additives based on BNFF will turn to the liquid state at a temperature below 90 °C. Thus, a fusible additive can be obtained with an improved energetic performance and desirable technological properties. The optimum component ratio can be determined after the measurement of T_b and T_m required for building a phase diagram. Below is shown how it can be achieved.

![Fig. 1. DSC curves of binary eutectic melts: 1 – 60/40 EOM/BNFF; 2 – 40/60 EOM/BNFF.](image-url)
20/80, 50/50 and 80/20 refer to DSC curves resembling those of 40/60 EOM/BNFF, i.e. to the curves having two melting effects. Hence, the melting of EOM/BNFF can take place in two different temperature ranges (Table 2).

<table>
<thead>
<tr>
<th>Compound</th>
<th>BNFF content, %</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td>T_{b1}, °C</td>
<td></td>
</tr>
<tr>
<td>T_{m1}, °C</td>
<td></td>
</tr>
<tr>
<td>T_{b2}, °C</td>
<td></td>
</tr>
<tr>
<td>T_{m2}, °C</td>
<td></td>
</tr>
<tr>
<td>Q_m, J/g</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Parameters of fusible EOM/BNFF binder additives

The analysis of the results listed in Table 2 showed that the onset melting (T_{b1}) values were close; whichever the BNFF content was, the T_{b1} parameter differed by no more than ±1.7 °C. The melting points (T_{m1}, the first peak) differed by no more than ±0.5 °C. The mean value of T_{m1} was 46.8 °C. This temperature is eutectic. The ongoing melting process and its onset temperature (T_{m1} and T_{b2}, the second peak), as well as the Q_m heat effect values, were significantly distinct and depended on the BNFF content.

![Fig. 2. Phase diagram of EOM/BNFF](image)

Thus, the DSC technique was able to determine the temperatures of the binary eutectic composites and the approximate ratio of the starting components required to form a pure eutectic system. To refine the parameters of the pure eutectic mixture, more detailed experiments can be done with a greater diversity of the fusible EOM/BNFF additive. This can also be achieved by using the values of the heat effects to build a plot of Q_m versus the BNFF content (Table 2). The third-degree polynomial approximation of the experimental data makes it possible to find the coordinates of the extremum whose abscissa corresponds to a more accurate content of the ingredients in the eutectic mixture. For the EOM/BNFF additive, this ratio is 58.5/41.5.

By using the algorithm described above, all the binary fusible binders such as tBu3H/BNFF, Me3H/BNFF, 2Me3H/BNFF, TNT/BNFF and DNP/BNFF were studied. The results are summarized in Tables 3 and 4.

Phase diagrams of DNP/BNFF (Fig. 2) and 2Me3H/BNFF (Fig 3) were constructed from the data in Tables 3 and 4. Table 5 lists characteristics of eutectic systems for all the fusible additives. The T_{b2} parameter for each type of binder additives was obtained by averaging the corresponding melting temperatures in five experiments; the component ratios were calculated mathematically. The results obtained for TNT/BNFF are on a par with those of other researchers [8].

The data in Table 5 show that in order to form pure eutectic systems, it is required that the nitrotriazole derivatives be mixed with a sufficiently larger amount of furazanyl furoxane (41.5–52.8 %); moreover, the melting temperatures of pure eutectic systems based on Me3H and EOM are below 50 °C, which is undesirable. The TNT/BNFF and DNP/BNFF eutectic mixtures contain a less amount of BNFF (37.6 % and 36.4 %), but they must have a higher sensitivity than TNT and DNP. Besides, the DNP/BNFF eutectic system has a too low melting point (35 °C), which is absolutely unacceptable.
Table 4. $Q_m$ of fusible binder additives, J/g.

<table>
<thead>
<tr>
<th>Compound</th>
<th>BNFF content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td>tBu3H</td>
<td>-98.3</td>
</tr>
<tr>
<td>Me3H</td>
<td>-92.1</td>
</tr>
<tr>
<td>2Me3H</td>
<td>-78.3</td>
</tr>
<tr>
<td>TNT</td>
<td>-61.9</td>
</tr>
<tr>
<td>DNP</td>
<td>-69.1</td>
</tr>
</tbody>
</table>

Fig. 3. Phase diagram of DNP/BNFF

Fig. 4. Phase diagram of 2Me3H/BNFF

In the storage of composite explosives, the stability of finished materials is of significant importance. Therefore, when designing composite explosives, it is necessary to examine the chemical compatibility of ingredients. It is known [8] that TNT is compatible with BNFF and HMX but is poorly compatible with CL-20 [27]. Initially, the compatibility can visually be checked by optical microscopy from the change in the surface morphology of HMX and CL-20 crystals.

Table 5. BNFF content and $T_b$ of eutectic systems.

<table>
<thead>
<tr>
<th>Compound</th>
<th>BNFF, %</th>
<th>$T_b$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>tBu3H</td>
<td>51.2</td>
<td>62.3</td>
</tr>
<tr>
<td>Me3H</td>
<td>52.8</td>
<td>46.7</td>
</tr>
<tr>
<td>2Me3H</td>
<td>52.6</td>
<td>58.3</td>
</tr>
<tr>
<td>EOM</td>
<td>41.5</td>
<td>46.8</td>
</tr>
<tr>
<td>TNT</td>
<td>37.6</td>
<td>56.0</td>
</tr>
<tr>
<td>DNP</td>
<td>36.4</td>
<td>35.0</td>
</tr>
</tbody>
</table>

Fig. 5 shows a photograph of CL-20 crystals, and Fig. 6 displays the crystals after they resided in the molten 2Me3H at 80 °C for 30 min. The images were taken at x400 zoom.

It is clearly seen in Fig. 5 that the crystals have a certain shape and a smooth surface. Fig. 6 illustrates how 2Me3H reacts with CL-20: the crystals lost their original shape and partially their volume. Hence, these ingredients are poorly compatible. A similar picture was observed after the HMX crystals were present in the 2Me3H melt. The HMX surface was highly damaged, although the crystals themselves retained the initial shape. The other nitrotiazole derivatives did not have such an effect on HMX and CL-20.

Sometimes, the chemical compatibility or its absence can be determined by the DSC technique. For instance, BNFF was shown to be incompatible with CL-20 [28]. However, this technique is not always effective. The reliable method in studying high-energy materials and their components is chromatography, which can provide a qualitative and quantitative outcome. The chromatographic study of the chemical compatibility between tBu3H, EOM, Me3H and HMX demonstrated that the gas release was 0.05 cm$^3$/g. This quantity suggests a good compatibility between the ingredients.

Table 6 summarizes the measurement data for composite explosives with conventional and new fusible binder additives. For the safety purpose, the binary fusible additives were prepared with a low amount of BNFF (20 %). The parameters $T_d$ (temperature extremum of decomposition) and $Q_d$ (heat effect value on the DSC curve; the sign ‘+’ (plus) stands for heat release) listed in Table 6 allow us to judge about the heat-generating capacity of the decomposition reactions taking place when the composites are heated up to $+350$ °C.
The amount of heat release during pyrolysis of a composite explosive is the most essential parameter that can preliminarily predict the performance capability of one composite explosive or another. The greater the heat release, the better. It follows from Table 6 that the highest heat release can be obtained if 2Me3H is used (Q_d = +1379.2 J/g with HMX; Q_d = +2226.3 J/g with CL-20). However, as is shown above, these components exhibited a poor chemical compatibility and their mixtures were unstable. The tBu3H and tBu3H/BNFF additives were very high-melting for processing (Table 2). The fusible 80/20 DNP/BNFF additive demonstrated a quite good result (Q_d = +1749.3 J/g) with CL-20 but its melting temperature was low (T_m = 45.6 °C), and it had a higher sensitivity than DNP. Thus, the following options are available: EOM, Me3H and their binary fusible mixtures with BNFF (20 %). The fusible EOM and 80/20 EOM/BNFF additives are suitable for composites with HMX, while Me3H and 80/20 Me3H/BNFF are appropriate for CL-20.

4 Conclusion

New insensitive fusible binder additives have been suggested herein for composite explosives. The experimental results demonstrated that for CL-20-based formulations, the optimum additives were 1-methyl-3-nitro-1,2,4-triazole and its eutectic melt with BNFF (20 %), while for HMX-based formulations, it was better to use ethoxymethyl-3-nitro-1,2,4-triazole and its melt with furazanyl furoxane (20 %). In future, the component database of insensitive fusible additives based on nitrotiazole derivatives needs to be diversified by means of conventional materials (TNT, DNP, etc.).

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References

15. M. Wagner Thermal Analysis in Practice (Mettler-Toledo AG, Schwerzenbach, 2009)
17. K.I. Sakodynskiy Analytical Chromatography (Khimiya Publisher, Moscow, 1993)
18. GOST RF 4545-88 Explosives, high. Sensitivity characteristics determination for impact (Standartpublishers, Moscow, 1988)
19. GOST R 50835-95 Explosives, high. Methods for determination of sensitivity characteristics to friction at impact displacement (Standartpublishers, Moscow, 1996)
23. L.V. Dubnov, N.S. Bakharevich, A.I. Romanov Industrial Explosives (Nedrapublishers, Moscow, 1988)