



A Comparison of the Sensitivity and Performance Characteristics of Melt-pour Explosives with TNT and DNAN Binder^{*)}

Waldemar A. TRZCIŃSKI, Stanisław CUDZIŁO*,
Sławomir DYJAK, Marcin NITA

*Military University of Technology,
Kaliskiego 2, 00-908 Warsaw, Poland*

**E-mail: scudzilo@wat.edu.pl*

Abstract: Some sensitivity and performance characteristics for pure 2,4-dinitroanisole (DNAN) and 2,4,6-trinitrotoluene (TNT), as well as for melt-pour composites containing 40% of DNAN or TNT, 20% of RDX, and 40% of NTO were determined (under the same conditions) and compared.

Keywords: insensitive explosives, thermal analysis and performance

1 Introduction

Melt-pour explosives are commonly used in large caliber munitions, because of the ease of the shell filling process, the possibility of recovery of the explosive from demilitarized warheads, a comparatively low cost and good performance. Currently melt-pour formulations incorporate 2,4,6-trinitrotoluene (TNT) or 2,4-dinitroanisole (DNAN) as the melting ingredients [1]. The former is used, for example, in the XF[®] explosive family developed at Nexter Munitions in France in the 1990s. These compositions contain 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 3-nitro-1,2,4-triazole-5-one (NTO) to improve the detonation performance. Aluminum powder can also be added when an enhanced blast effect is preferred. XF[®] explosives meet all of the criteria for insensitive munitions (IM) and one of their applications is in the 155 LU211 artillery shell that is now

^{*)} Some results in this paper were presented at the 15th Seminar on New Trends in Energetic Materials, Pardubice, Czech Republic, 2012.

under mass production for the French army [2-5].

In the USA a family of melt-cast DNAN based explosives containing RDX or 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), nitroguanidine (NQ), ammonium perchlorate (AP), NTO and aluminum powder was developed and introduced into service. For example IMX-101 containing DNAN, NTO, and NQ was selected as a common TNT replacement and was qualified by the U.S. Army as the main fill explosive in the 155 mm M795 Artillery Projectile. IMX-104 contains DNAN, NTO, and RDX. It is being evaluated as a replacement for Composition B in mortar systems. OSX-12, an aluminized version of IMX-104, offers high blast energetic output. All of the explosives have been shown to reduce the response of munitions to external threat stimuli in all kinds of tests for insensitive munitions [6-12].

In Poland insensitive compositions based on NTO or FOX-7 (1,1-diamino-2,2-dinitroethylene) have been investigated [13-15]. The detonating performance of new explosive compositions containing NTO, TNT, RDX, and HMX was investigated in Ref. [13]. The detonation properties and energetic characteristics of TNT/RDX/NTO and TNT/HMX/NTO formulations are higher than or comparable with those of TNT/RDX (40/60) composition. The impact and jet sensitivity of the tested formulations is lower than the sensitivity of the TNT/RDX mixture. Low sensitivity mixtures containing NTO and NQ were tested in work [14]. The measured detonation velocity and brisance of the chosen mixtures are higher than those measured for TNT and phlegmatized RDX. FOX-7 and its mixtures with HMX, phlegmatized with Viton, were prepared and their detonation properties were investigated in Ref. [15]. It was shown that the FOX-7-based compositions have detonation parameters comparable to or even higher than RDX phlegmatized with wax. The sensitivity of phlegmatized FOX-7 to mechanical stimuli (shock, impact and friction) is comparable or even less than the sensitivity of TNT. The composition of FOX-7 and HMX with the particles covered properly by a phlegmatizing agent is less sensitive than phlegmatized RDX.

DNAN has been proposed as a less sensitive substitute for TNT. Moreover the solubility of RDX in liquid DNAN is several times greater than RDX in TNT, and this causes the dynamic viscosity of suspensions of crystalline fillers in molten DNAN/RDX to be lower than that containing TNT. As a result, it is easier to achieve a workable viscosity at the cast/pour temperature, even for compositions with a high content of solid phase. On the other hand DNAN exhibits a much lower crystal density, detonation velocity and acceleration capability (by 20-25%). What is more, DNAN is also a much more expensive alternative [16].

The purpose of the present paper is to determine and compare some sensitivity and detonation characteristics for domestically produced DNAN and

TNT, as well as for simple melt-pour composites containing 40% of DNAN or TNT, 20% of RDX and 40% of NTO.

2 Characterization of DNAN and TNT

2.1 Thermal analysis

TG/DTA traces for DNAN and TNT are shown in Figure 1. The sample mass was constant up to 160 °C, at which temperature DNAN and TNT begin to evaporate very fast; the sharp melting endotherms peak at 95.8 and 82.1 °C (respectively), indicating the high purity of the explosives. Both of them had completely evaporated by 270 °C.

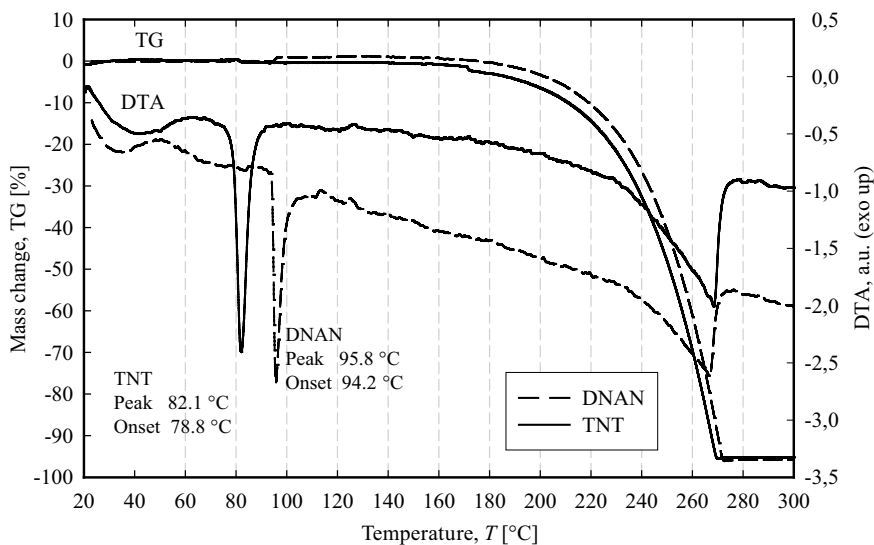


Figure 1. TG/DTA thermograms for DNAN and TNT, sample mass: 5.0 mg, heating rate: 5 °C/min, atmosphere: nitrogen.

TG/DTA thermograms for 50:50 mixtures of DNAN or TNT with NTO, FOX-7, RDX and HMX are shown in Figures 2 and 3. Each additive reduces the melting point of DNAN, and this depression is the most pronounced in the presence of RDX (by approx. 10 °C), because RDX dissolves in the DNAN melt [16, 17]. DNAN has quite a significant impact on the thermal decomposition profiles of RDX and HMX. There is no melting endotherm in the DTA trace of RDX, and its decomposition starts at approx. 180 °C. The decomposition of HMX in the presence of DNAN begins at approx. 225 °C, *i.e.* at a lower

temperature (by approx. 50 °C) than that of pure HMX. FOX-7 decomposes at temperatures higher than 200 °C, and it is a two-step process, as in pure FOX-7 [18]. The decomposition exotherm of DNAN/NTO mixture peaks at 250 °C. This temperature is lower, by approx. 20 °C, than in the case of pure NTO [19].

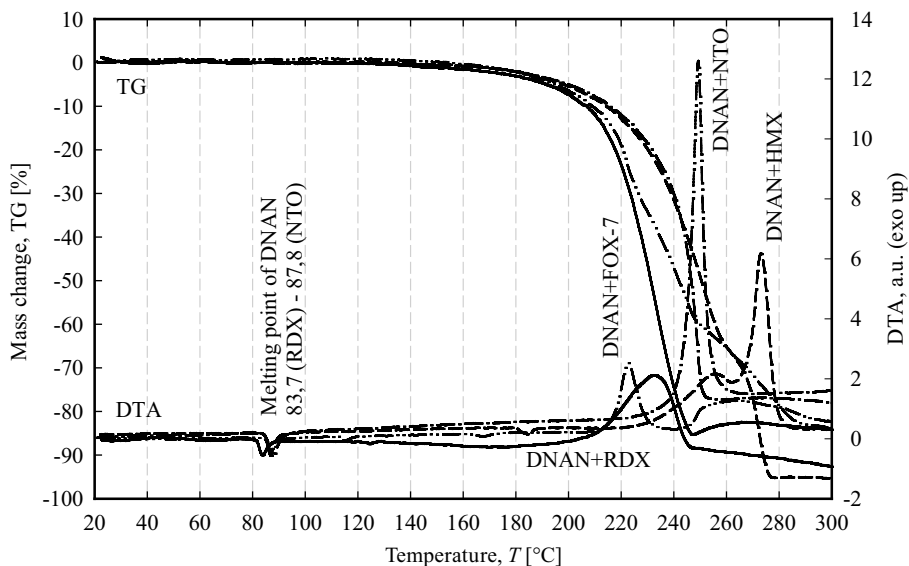


Figure 2. TG/DTA thermograms for mixtures of DNAN with NTO, FOX-7, RDX and HMX, sample mass: approx. 5.0 mg, heating rate: 5 °C/min.

Exothermic reactions in mixtures of TNT with FOX-7 and HMX begin at temperatures higher than 200 °C. The thermal decomposition of the mixtures proceeds in two steps. Both of them are accompanied by heat release. Only in the case of TNT-NTO, is the first step (mass loss) an endothermic one. This indicates that liquid TNT does not react with NTO, but just evaporates.

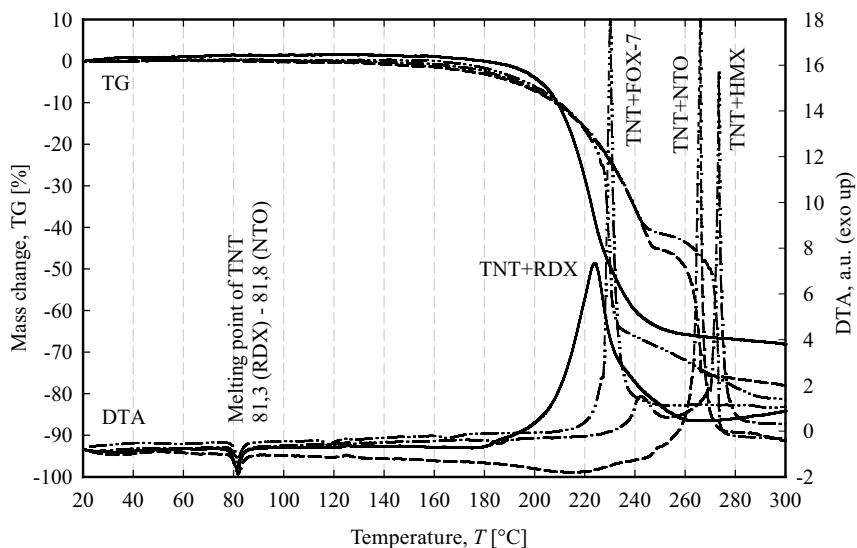


Figure 3. TG/DTA thermograms for mixtures of TNT with NTO, FOX-7, RDX and HMX, sample mass: approx. 5.0 mg, heating rate: 5 °C/min.

RDX suspended in the TNT melt has the lowest thermal stability. Exothermic reactions occur at approx. 180 °C.

In summary, TNT-NTO mixtures are the most thermally resistant, whereas RDX containing compositions are characterized by the lowest thermal stability.

2.2 Explosive properties of DNAN and TNT

The impact and friction sensitivity of DNAN and TNT was tested according to BAM methods. DNAN, purified by crystallization from methanol, is insensitive to friction (no reaction up to 360 N). The impact sensitivity was determined by the use of a testing apparatus with 5 kg hammer. The highest drop height (h_0) was determined at which no reaction was observed (the highest limit of insensitivity – [20]). Six trials were conducted at consecutive heights that were changed in intervals of 1 cm. DNAN is insensitive up to the value of h_0 corresponding to an impact energy of 200 J. The first reaction of flaked TNT to impact was recorded at an energy of 16 J. The sensitivity of TNT to friction was found to be higher than 360 N.

A cylinder expansion test was performed to estimate the acceleration capability of the tested explosives. They were placed inside a copper tube, 250 mm long with an inner diameter and wall thickness of 25 mm and 2.5 mm, respectively. The expansion of the tube, driven by the detonation products, was

recorded using a SANDIFLASH X-ray apparatus. Images were recorded when the detonation front was 5 mm from the end of the charge. The detonation velocity (D) of the charges was simultaneously measured using short circuit sensors. The test was performed for pressed DNAN charges with a density of approx. 1.52 g/cm^3 ($D = 5960 \pm 50 \text{ m/s}$) and for a melt DNAN charge with a density of 1.45 g/cm^3 ($D = 5690 \text{ m/s}$). For comparison, TNT charges, pressed to a density of 1.59 g/cm^3 ($D = 6910 \text{ m/s}$), were also tested under the same conditions.

A detailed procedure for determining the cylinder velocity is given in [21]. It uses the dependence of the position of the cylinder's external surface on the axial coordinate, as recorded in a cylinder test. The examined range of the axial co-ordinate was limited to the value for which the volume of detonation products was 9 times larger than the initial volume. The calculated dependencies of the cylinder velocity and the Gurney energies on the relative volume of the detonation products are presented in Figure 4.

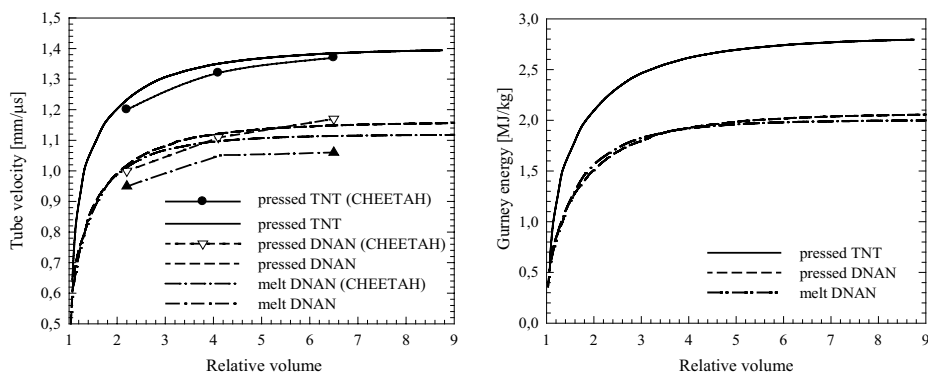


Figure 4. Tube velocity and Gurney energy versus relative volume of detonation products.

The tube velocities at three different volumes of the expanding tube, calculated with CHEETAH using the BKWC set of the BKW equation of state [22], are also shown in Figure 4. In the case of DNAN, the measured and calculated tube velocities are almost the same, but for TNT there is not such good agreement. In any case, both the calculated and experimental tube velocities for TNT are higher than those of DNAN (by approx. 250 m/s at the final stage of expansion). Of course, the final value of the Gurney energy of TNT is also much greater than that of both types of DNAN (cast and melt), *i.e.* 2795 versus 2060 and 2000 J/g, respectively. This means that the acceleration capability (performance) of DNAN is lower by approx. 25% than that of TNT.

3 Characterization of DNAN/RDX/NTO and TNT/RDX/NTO formulations

3.1 Preparation of the explosives

Simple test formulations comprising 40% DNAN or TNT, 20% RDX, and 40% NTO were prepared by addition of the crystalline ingredients to the DNAN or TNT melt, at 94 °C. NTO was recrystallized from a water-N-methylpyrrolidinone mixture ($H_2O/NMP = 60/40$ v/v, cooling rate 1 K/min). The NTO particles obtained were spherical with diameters in the range 50-500 μm . Only two fractions (shown in Figure 5) were used in the formulations, namely 125-160 μm and 250-300 μm . The viscosity of the formulations containing only coarse NTO particles was too low and their sedimentation in the DNAN or TNT/RDX solutions was observed upon cooling.

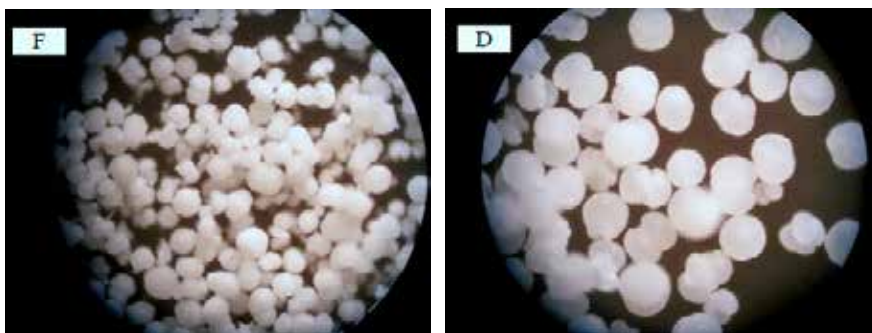


Figure 5. Photographs of the NTO particles used in the formulations.

3.2 Thermal analysis of the explosives

As shown in Figure 6, the masses of the DNAN/RDX/NTO and TNT/RDX/NTO samples do not change up to a temperature of 160 °C. The formulations begin to melt at approx. 80 °C and decomposition commences at approx. 180 °C. Thus the temperature delta between the pour and decomposition points is 100 °C, indicating a sufficient margin of safety during the cast process.

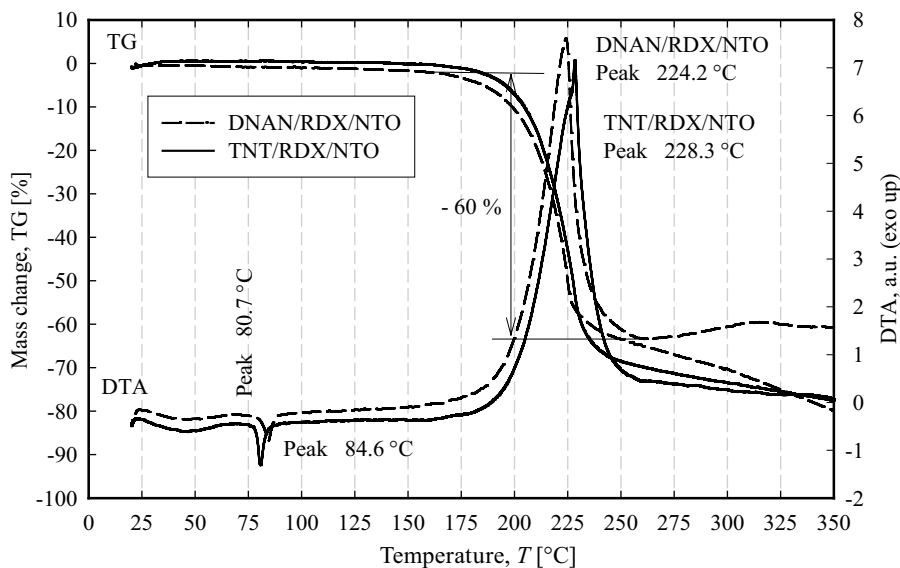


Figure 6. TG/DTA traces of (DNAN or TNT)/RDX/NTO, sample mass: 5.0 mg, heating rate: 5 °C/min.

The course of thermal decomposition of the DNAN or TNT based formulations is almost identical. It proceeds in two steps, and the mass change during the first step is 60-70%. This indicates that the decomposition course includes evaporation of DNAN or TNT, simultaneous decomposition of RDX, and subsequently decomposition of NTO (above 240 °C).

3.3 Explosive properties of DNAN/RDX/NTO and TNT/RDX/NTO formulations

The impact sensitivity of 40/20/40 formulations of DNAN/RDX/NTO and TNT/RDX/NTO was found to be 25 J and 14 J respectively, regardless of the NTO particle size distribution (125-160 μm or 250-300 μm). The sensitivity of pure NTO was 15 J, *i.e.* this energy corresponds to the highest drop height h_0 at which no reaction was observed in six trials.

The formulations comprising a bimodal NTO blend were poured into the copper tube used in the cylinder test (see Section 2.2 for experimental conditions). The average density of the charges obtained was 1.635 g/cm³ for the DNAN-based explosive and 1.660 g/cm³ for the one containing TNT. Under these conditions they detonated at a velocity of 7040 m/s and 7410 m/s, respectively. A cast TNT charge was also prepared and tested for comparison. It had a density of approx.

1.60 g/cm³ and detonated in the copper tube at a velocity of 6730 m/s.

Experimental and calculated (CHEETAH) results of the cylinder test for (DNAN or TNT)/RDX/NTO and cast TNT charges are presented in Figure 7.

The TNT-based composition is the most effective in terms of the acceleration capability, but taking into consideration the density and detonation velocity, the Gurney energy is still too low if compared to that calculated for a cast TNT charge. The second composition tested produced an even worse result. The unexpectedly low tube velocity and Gurney energy for explosives containing NTO may be a result of a comparatively high value of the isentrope exponent of the NTO detonation products [23].

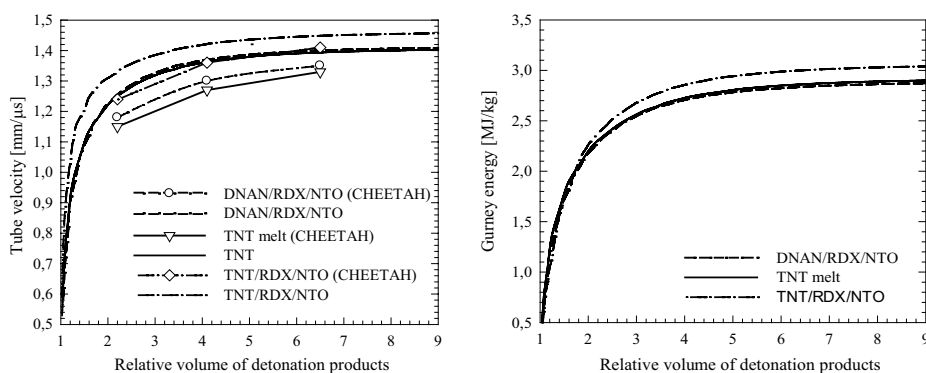


Figure 7. Tube velocity and Gurney energy versus relative volume of detonation products.

Indirect measurements of the detonation pressure were performed using a Plate Dent Test methodology. Steel plates with a hardness of 190 Brinell HB30 and dimensions of 150×150×50 mm were arranged in a stack consisting of four plates (Figure 8). Explosive charges with diameters of approx. 40 mm and a height of 200 mm were used in the tests. They were boosted by a 10-gram pellet of RDX/wax. The depth of the dent produced in the first plate was measured with a depth micrometer. In addition, four short-circuit sensors were placed in the charges to measure the detonation velocity. The first sensor was located 25 mm from the booster, and the distance between the sensors was 50 mm.

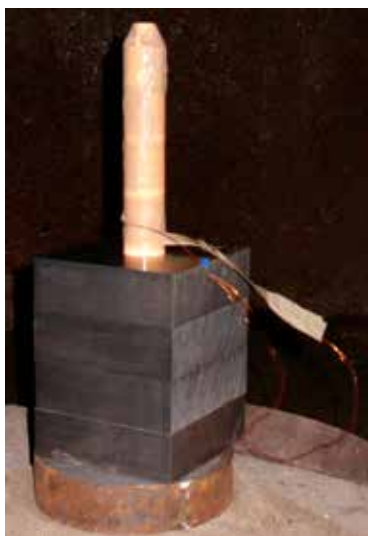


Figure 9. Photograph of the tested explosive charge on a stack of steel plates.

The relationship between the detonation pressure and the depth of the crater for the measuring system used is given by the relation:

$$p_{CJ} = 3.2455h + 0.4274 \quad (1)$$

where p_{CJ} [GPa] denotes the detonation pressure and h [mm] is the crater depth. The relative error of the method is about 5% for high explosives.

The results obtained are shown in Table 1. The table also contains values of the detonation pressure calculated with CHEETAH, and the detonation velocities measured during the tests.

Table 1. Detonation pressure and velocity for the explosives tested

Explosive	Density [g/cm ³]	Measured D [m/s]	Calculated D [m/s]	h [mm]	p_{CJ} [GPa]	Calculated p_{CJ} [GPa]
TNT/RDX/NTO	1.660	7500±100	7453	7.00	23.1	22.18
DNAN/RDX/NTO	1.635	7190±200	7143	6.64	22.0	19.92
Cast TNT	1.600	6750±200	6705	5.65	18.9	17.91

The brisance properties of the explosives tested are proportional to their density and detonation velocity. The highest detonation pressure was measured for TNT/RDX/NTO and the lowest for cast TNT. The calculated D and p_{CJ} values are consistent with the experimental ones.

4 Conclusions

TNT and DNAN lower the decomposition temperature of RDX, but exothermic reactions occur in the mixtures above 180 °C, *i.e.* at temperatures higher, by approx. 100 °C, than the melting point of the binders. A potential incompatibility of DNAN and TNT with HMX was also observed in the thermal analyses, however, fast decomposition of the mixtures starts at approx. 225 °C. Both TNT and DNAN are compatible with NTO.

Heavily confined (copper tube) DNAN charges of 25 mm in diameter, pressed to a density of 1.52 g/cm³, detonate at a velocity of 5960 m/s, and a melt with a density of 1.45 g/cm³ detonates at a velocity of 5690 m/s. The acceleration capability (Gurney energy) of DNAN is lower, by approx. 25%, than that of TNT pressed to a density of 1.59 g/cm³. DNAN is insensitive to mechanical stimuli, whereas the sensitivity of TNT to impact is 16 J.

Simple TNT- and DNAN-based formulations comprising 40% TNT or DNAN, 20% RDX and 40% NTO were developed. They have a suitable viscosity (no NTO sedimentation, but easily stirred, poured and cast). The formulations are reasonably sensitive to impact (14 J and 25 J, respectively for the TNT- and DNAN-based explosives) and start to decompose exothermically above 180 °C. Under typical casting conditions, the DNAN-based composition forms charges with a density of approx. 1.64 g/cm³, that detonate at a velocity of 7040 ± 50 m/s (25 mm in diameter, copper tube) and at 7190 ± 200 m/s (unconfined charge, 40 mm in diameter). The detonation pressure is 22.0 GPa, and the Gurney energy is equal to 2.85 MJ/kg (approx. 2.9 MJ/kg was evaluated for pure cast TNT). The measured detonation performances of TNT-based compositions are better – density: approx. 1.66 g/cm³, detonation velocity: 7410-7500 m/s, Gurney energy: 3.05 MJ/kg, detonation pressure: 23.1 GPa.

5 References

- [1] Ravi P., Badgujar D.M., Gore G.M., Tewari S.P., Sikder A.K., Review on Melt Cast Explosives, *Propellants Explos. Pyrotech.*, **2011**, *36*, 393-403.
- [2] Weckerle A., Coulouarn C., A Step Further for the XF[®] Explosive Family Dedicated to Insensitive Munitions (IM), *2010 Insensitive Munitions & Energetic Materials Technology Symposium – International Progress in Insensitive Munitions and Energetic Materials*, Munich, Germany, **2010** (CD).
- [3] Coulouarn C., Boulanger R., Bouchaud D., XP[®]: A Cost Effective Approach for Medium Calibre Insensitive Munitions (IM), *2010 Insensitive Munitions & Energetic Materials Technology Symposium – International Progress in Insensitive*

- Munitions and Energetic Materials*, Munich, Germany, **2010** (CD).
- [4] Aumasson R., Insensitive Munitions® Using Fusible and Pressable Explosives, *WAT – NEXTER – NitroChem Conference*, 15.03.2011 Warsaw (CD).
- [5] Spycykerelle C., Songy C., Eck G., IM Melt Cast Compositions Based on NTO, *2010 Insensitive Munitions & Energetic Materials Technology Symposium – International Progress in Insensitive Munitions and Energetic Materials*, Munich, Germany, **2010** (CD).
- [6] Rutkowski J., Cirincione R., Patel C., Common Low-cost Insensitive Munitions Explosive Program to Replace TNT and Comp B, *2010 Insensitive Munitions & Energetic Materials Technology Symposium – International Progress in Insensitive Munitions and Energetic Materials*, Munich, Germany, **2010** (CD).
- [7] Hummers W.B., The Insensitive TNT Replacement Explosive IMX-101 and IMX-104 Qualification, *2010 Insensitive Munitions & Energetic Materials Technology Symposium – International Progress in Insensitive Munitions and Energetic Materials*, Munich, Germany, **2010** (CD).
- [8] Fung V., Development and Manufacture of an Insensitive Composition B Replacement Explosive IMX-104 for Mortar Applications, *2010 Insensitive Munitions & Energetic Materials Technology Symposium – International Progress in Insensitive Munitions and Energetic Materials*, Munich, Germany, **2010** (CD).
- [9] Fung V., Price D., LeClaire E., Morris J., Tucker N., Carrillo A., Further Development and Optimization of IM Ingredients at Holston Army Ammunition Plant, *2010 Insensitive Munitions & Energetic Materials Technology Symposium – International Progress in Insensitive Munitions and Energetic Materials*, Munich, Germany, **2010** (CD).
- [10] Lee K.E., Balas-Hummers W.A., Di Stasio A.R., Patel C.H., Samuels J., Qualification Testing of the Insensitive TNT Replacement Explosive IMX-101, *2010 Insensitive Munitions & Energetic Materials Technology Symposium – International Progress in Insensitive Munitions and Energetic Materials*, Munich, Germany, **2010** (CD).
- [11] Pelletier P., Lavingne D., Laroche I., Cantin F., Phillips L., Fung V., Additional Properties Studies of DNAN Based Melt-pour Explosive Formulations, *2010 Insensitive Munitions & Energetic Materials Technology Symposium – International Progress in Insensitive Munitions and Energetic Materials*, Munich, Germany, **2010** (CD).
- [12] Zaloga D., Patel K., Travers B., Samuels P., Di Stasio A., Singh S., Initiation Trials of IMX-104 in 81mm Mortars, *2010 Insensitive Munitions & Energetic Materials Technology Symposium – International Progress in Insensitive Munitions and Energetic Materials*, Munich, Germany, **2010** (CD).
- [13] Trzciński W. A., Szymańczyk L., Detonation Properties of Low-Sensitivity NTO-Based Explosives, *J. Energ. Mater.*, **2005**, 23,151-168.
- [14] Bąk A., Maranda A., Nowaczewski J., Szerszeń M., Some Properties of High Explosive Mixtures of Low Sensitivity to External Stimuli, *Cent. Eur. J. Energ. Mater.*, **2006**, 3(3), 53-64.

-
- [15] Trzciński W.A., Cudziło S., Chyłek Z., Szymańczyk L., Detonation Properties and Thermal Behavior of FOX-7-Based Explosives, *J. Energ. Mater.*, **2013**, 31, 72-85.
- [16] Davies P.J., Provas A., *Characterization of 2,4-Dinitroanisole: an Ingredient for Use in Low Sensitivity Melt Cast Formulations*, Defense Science and Technology Organization, Edinburgh South Australia 5111, DSTO-TR-1904, Australia, **2006**.
- [17] Provas A., Wall C., Thermal Testing of 2,4-Dinitroanisole as a TNT Replacement for Melt-cast Explosives, *42nd Int. Annu. Conf. ICT*, Karlsruhe, Germany, **2011**.
- [18] Trzciński W.A., Cudziło S., Chyłek Z., Szymańczyk L., Detonation Properties of 1,1-diamino-2,2-dinitroethene (DADNE), *J. Hazard. Mater.*, **2008**, 157, 605-612.
- [19] Becuwe A., Delclos A., Low-sensitivity Explosive Compounds for Low Vulnerability Warheads, *Propellants Explos. Pyrotech.*, **1993**, 18(1), 1-10.
- [20] *Explosives for Civil Uses – High Explosives – Part 4: Determination of Sensitivities to Impact of Explosives*, Standard PN-EN 13631-4, Polish Committee for Standardization, Warsaw, **2004**.
- [21] Trzciński W.A., Application of a Cylinder Test for Determining Energetic Characteristics of Explosives, *J. Tech. Phys. (Warsaw, Pol.)*, **2001**, 42(2), 165.
- [22] Fried L.E., *CHEETAH 1.39 – User's Manual*, Manuscript UCRL-MA-117541 Rev.3, Lawrence Livermore National Laboratory, **1996**.
- [23] Cudziło S., Trzciński W.A., A Study on Detonation Characteristics of Pressed NTO, *J. Energ. Mater.*, **2001**, 19(1), 1-21.

