Studies on NTO-, FOX-7- and DNAN-based Melt Cast Formulations

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Abstract: In the present paper, 2,4-dinitroanisole (DNAN) has been evaluated as a melt cast explosive in comparison to the widely used 2,4,6-trinitrotoluene (TNT). The detonation failure diameter of a bare DNAN charge is greater than 100 mm and about 44 mm with 1.5 mm steel confinement. Comparative studies of two sets of formulations were carried out. The first set comprised formulations containing 60% of NTO, FOX-7, HMX or RDX and 40% of DNAN or TNT. The second set comprised formulations containing 30% of NTO, FOX-7, TATB or RDX and 70% of DNAN or TNT. The studies were mainly concentrated on characterization of the formulations, which included determination of the sensitivity parameters and the velocity of detonation (VOD). The study confirmed that DNAN and DNAN-based formulations are relatively insensitive compared to TNT and the analogous TNT-based formulations respectively. The rate of the detonation reaction of DNAN is enhanced in the presence of the high energy ingredients RDX, HMX, FOX-7 and NTO to varying degrees. The VODs of the FOX-7/TNT and RDX/TNT formulations match closely with the proportions of FOX-7 and RDX under study. The VOD and shock sensitivity of the FOX-7/DNAN formulations decrease rapidly compared to the RDX/DNAN formulations, with increases in the proportion of FOX-7 or RDX. The combinations of NTO with TNT, and NTO with DNAN, are more shock insensitive than TNT or DNAN alone. NTO-based compositions are more insensitive than FOX-7-based compositions.

Keywords: melt cast, DNAN, TNT, FOX-7, NTO, RDX/TNT, VOD, sensitivity

1   Introduction

Trinitrotoluene (TNT) is the preferred and widely used melt cast explosive for filling munitions. Although TNT is a low performance explosive, it is an ideal base and acts as an energetic binder as well as a desensitizer for relatively sensitive high energy explosives like RDX, HMX, PETN *etc*., in melt cast compositions like Comp B [RDX/TNT (60/40)], Octol [HMX/TNT (75/25)], Pentolite (50/50), Torpex, *etc*., which are used as fillings in munitions [1]. These munitions are vulnerable to unintended accidental initiation, resulting in huge loss of personnel and property. The design of safer insensitive munitions (IMs) reduces the risks of accidental initiations. One of the aspects in realizing an IM is to use less sensitive explosives and their formulations, with performances similar to the existing munitions [2]. Plastic bonded explosives (PBXs) are categorized as low vulnerability explosives due to their high thermal stability, improved insensitivity and good mechanical strength, compared to TNT-based formulations, attributed to their rubbery nature in addition to their high-energy output [3]. Despite these qualitative advantages, PBXs have some major limitations, such as manufacture and filling, which require specialized facilities, and are batch processes, which are costly compared to melt cast explosive filling, and due to their inherent physical stability are difficult to demilitarize after the expiry of their shelf life. Thus, TNT or TNT-based mixtures are still preferred due to the ease of processing in the existing standard melt-cast facilities all over the globe. The following, inherently insensitive materials offer an attractive approach, adoptable for mass production of low vulnerability ammunition/warhead fillings at economical cost, using existing production facilities for melt-cast compositions.

2,4-Dinitroanisole (DNAN), a Hazardous Division (HD) Class 4.1 flammable solid with a melting point of 94.6 °C is reported as a possible low vulnerability alternative to TNT [4], with a performance marginally lower (~10%) compared to TNT. Van Alphen [5] observed dimorphism of DNAN, with melting points of 86.9 °C and 94.6 °C, suggesting that the latter form is the thermodynamically stable form. Davies *et al*. [6] have reported the use of DNAN during World War II in Amatol 40 (50% DNAN, 35% AN, 15% RDX) for filling the warheads of V-1 bombs. Doll *et al*. [7] have also reported that DNAN-based melt-cast compositions are relatively less sensitive to impact, shock and thermal stimuli. Furthermore, Wilson [8] observed that DNAN and DNAN-based compositions solidify in a shorter time, with less shrinkage, than TNT-based compositions. Samuels *et al*. [9] have observed irreversible growth, in the form of dimensional changes of up to 15%, of cast DNAN test samples subjected to 30 or more temperature cycles between –54 °C and +71 °C. Ward *et al*. [10] identified six

polymorphs during studies of controlled irreversible growth of DNAN during cycling between –54 °C and +71 °C, using crystal doping of DNAN with 2,4-dinitrotoluene (DNT) or 1,3-dinitrobenzene (DNB). Walsh *et al*. reported toxicity of DNAN during characterization of PAX-21 insensitive munition detonation residues [11] and energetic residues from the detonation of IMX-104 insensitive munitions [12].

Lochert [13] reported that 1,1-diamino-2,2-dinitroethene (FOX-7) is compatible with TNT and is also significantly less sensitive than RDX, particularly to impact and friction stimuli, and that the velocity of detonation and detonation pressure of FOX-7 charges are marginally higher than those for RDX charges. Wild and Teipel [14] have also reported that the performance of FOX-7 is close to that of nitramines with relatively insensitive characteristics. Mishra *et al*. [15] have also reported that FOX-7 is a potential replacement for RDX in TNT-based non-aluminized and aluminized melt-cast formulations, to achieve low vulnerability with little sacrifice in performance.

Lee *et al*. [16, 17] reported 3-nitro-1,2,4-triazol-5-one (NTO) to be relatively insensitive compared to RDX, with detonation performance comparable to RDX. Cliff *et al*. [18] carried out studies on NTO/TNT 50/50 formulations. Spyckerlle *et al*. [19] reported studies on NTO/TNT/RDX/Al formulations. Fung *et al*. [20] reported OSX-11 and OSX-12 formulations based on NTO, DNAN, Al, and NTO, DNAN, RDX, Al respectively, and studied their processing parameters and sensitivity characteristics. Radhakrishnan *et al*. [21] prepared spherical NTO of different particle sizes and determined the powder characteristics and also the viscosity behaviour of cast-cured PBXs. Trzciński *et al*. [22] characterized DNAN and studied melt-cast formulations containing 40% of DNAN or TNT, 20% of RDX and 40% of NTO.

TATB is reported to be a thermally stable compound which resists heating up to 300 °C, and is also insensitive to impact and friction. TATB is extremely shock insensitive and requires a large amount of booster to initiate it. Limited studies have been reported on melt cast TATB/TNT 50/50 and TATB/Al/TNT 40/20/40 formulations [23, 24].

Considering the exhaustive research work reported on low vulnerability explosives based on FOX-7, NTO, TATB and DNAN for IMs, we have undertaken studies to further explore these types of formulations for future applications. The present studies include comparative evaluation of melt-cast formulations based on NTO, FOX-7, TATB, HMX, and RDX and DNAN or TNT with respect to their sensitivities to different types of mechanical stimuli, and their explosive properties.

2 Experimental

2.1 Materials

The materials used for the preparation of the formulations are given in Table 1.

Table 1.   Materials used in the formulations

Sl. No.	Material	Melting point [°C]	Source
1	DNAN	95.2	Synthesized at HEMRL, Pune, India [4]
2	TNT	80.6	HE Factory, Pune, India
3	RDX	204	Ordnance Factory, Bhandara, India
4	FOX-7	264 (d)	Synthesized at HEMRL, Pune, India [25]
5	NTO	232	Synthesized at HEMRL, Pune, India [26]
6	TATB	350 (d)	Synthesized at HEMRL, Pune, India [27]
7	HMX	276	Synthesized at HEMRL, Pune, India

2.2 Formulations

The formulations prepared for characterization and evaluation were:
(i)   Characterization of DNAN used for the studies and its comparison with TNT.
(ii) Comparison of NTO/DNAN 60/40, FOX-7/DNAN 60/40, HMX/DNAN 60/40 and RDX/DNAN 60/40, analogous to TNT-based formulations: Set-1.
(iii) Comparison of NTO/DNAN 30/70, FOX-7/DNAN 30/70, TATB/DNAN 30/70 and RDX/DNAN 30/70, analogous to TNT-based formulations: Set-2.

2.3 Processing of the formulations

The standard melt-casting technique was used for the preparation of the charges. The general procedure adopted was to melt the TNT/DNAN in a jacketed vessel using steam. The required quantity of solid ingredient, RDX, FOX-7, NTO, HMX or TATB, was then incorporated into the molten mass with stirring at an appropriate speed and stirring was continued for about 20-30 min to form a homogenous mix. The melt, at a controlled temperature, was transferred into a suitable mould/test casing, followed by hot probing and compensation for shrinkage with additional melt. The cast charge was allowed to cool overnight under ambient conditions. The charge was machined to the required dimensions, stored and evaluated at temperatures ranging between 25 °C and 40 °C.

2.4 Homogeneity of the cast charges

Cast charges of 35 mm (diameter) × 250-300 mm (length) were sliced into pieces of about 10 mm thick discs. Three discs representing top, middle and bottom portions

were analyzed for homogeneity of the ingredients along the length of the charge. The proportion of an ingredient was determined based on the selective solubility of the ingredient in a solvent. For NTO/DNAN and NTO/TNT formulations, DNAN- or TNT-saturated distilled water at about 50 °C was used as the solvent to dissolve the NTO. While, for the FOX-7, TATB, RDX and HMX and DNAN- or TNT-based formulations, FOX-7-, TATB-, RDX- or HMX-saturated benzene at about 50 °C was used as the solvent to dissolve the DNAN or TNT. The variation in the ingredients observed in the top, middle and bottom portions was 2% max.

2.5 Characterization/evaluation methods
The standard methods used for the characterization and evaluations were as follows:

2.5.1 Impact sensitivity: Sensitivity to impact stimuli was determined using the fall hammer method (2 kg drop weight) as per Bruceton's staircase method, and the results are given in terms of the statistically obtained height for 50% probability of explosion (h_{50}).

2.5.2 Friction sensitivity: Sensitivity to frictional force was determined using Julius Peters' Apparatus (36 kg) and values given are for five consecutive no explosions.

2.5.3 Shock sensitivity: Shock sensitivity was determined by the card gap test [10] using cellulose acetate sheet as the attenuator. The thickness of the sheets was varied until No-Go was observed on the witness plate. The shock sensitivity is reported in terms of the minimum pressure of a shock wave that can initiate detonation of the formulation. The shock sensitivity results were confirmed by conducting 5 tests with consistent No-Go observation.

2.5.4 Velocity of detonation: The velocity of detonation (VOD) was measured by the standard ionization probe technique. The reported VOD is an average of three trials of each formulation and rounded to the nearest 10 m/s.

3 Results and Discussion

3.1 Characterization and evaluation of DNAN

3.1.1 Detonability study of DNAN
The detonability test of DNAN was carried out to determine the diameter close to its detonation failure diameter. The charge details and results of the tests are given in Table 2. The donor charge was 136 g tetryl pellets. The acceptance

criterion set for passing the test was a puncture in a 10 mm thick steel witness plate. Specimen photographs of the test results are shown in Figures 1 and 2. The density of the cast DNAN charges for the detonability test and the determination of VOD was in the range of 1.43 g/cm^3 to 1.48 g/cm^3, *i.e.* about 92-96% TMD. The variation observed can probably be attributed to fine porosity in the charge as well as minor measurement and rounding errors of the test piece.

It can be seen that the detonation failure diameter of bare DNAN is larger than 100 mm. The results match with the observation of Samuels [28] that the critical diameter of DNAN is larger than 3.25 inches. It can also be seen that 35 mm and 47 mm DNAN charges confined in 1.5 mm Al do not initiate to detonation. The dissipation of the decomposition products due to the failure of Al confinement after a certain run distance results from a weak shock build-up leading to partial detonation. The partially reacted charge was scattered with the remains intact. It can also be seen that a 35 mm DNAN charge confined in 1.5 mm steel does not initiate to detonation due to the small charge diameter and for reasons similar to those discussed above. However, a 47 mm DNAN charge confined in 1.5 mm steel initiated to detonation, leading to a puncture in the witness plate. The shock pressure builds up in this case within a short run distance as both steel confinement and a larger charge diameter contribute concurrently to the phenomenon. Detonability of DNAN was also confirmed in a standard shock sensitivity tube (1.5 mm thick steel of ϕ 44 mm, height 150 mm). From the above it can be established that the detonation failure diameter of DNAN confined in a minimum of 1.5 mm steel would be about 44 mm.

3.1.2 Sensitivity and explosive characteristics of DNAN

The comparative sensitivity and explosive characteristics of DNAN and TNT are given in Table 3. DNAN and TNT charges cast in a 47 mm diameter seamless mild steel tube of 1.5 mm thickness were used for the determination of VOD. The achieved VOD of DNAN was 5000 m/s, compared to 6700 m/s for TNT. The VOD of DNAN in the present study is on the low side compared to 5591 m/s (5344 m/s calculated from CHEETAH-2 code) reported by Provatas *et al.* [6] and 5690 m/s (1.45 g/cm^3) for confined DNAN (ϕ 25 mm × Cu 2.5 mm wall thickness) reported by Trzciński *et al.* [22].

Photographs of the shock sensitivity test arrangement and the recovered DNAN test pieces at different shock pressures are shown as Figure 3. DNAN is quite insensitive to shock compared to TNT. Provatas *et al.* [6] reported shock sensitivity of 7.0 GPa for DNAN, which indicates that it was more insensitive to shock compared to the DNAN used in the present study (6.0 GPa). DNAN is also quite insensitive to impact and marginally insensitive to friction, compared to TNT.

Table 2.   Results of detonability test of DNAN cast charges

Sr. No.	DNAN charge dimensions [mm]		Charge density [g/cm³]	Percent TMD	Confine-ment [mm]	Result/observation of witness plate
	Diameter	Length				
1	50 and 75	240-300	1.45-1.48	93.7-95.6	No	ND #
2	100	250	1.43-1.45	92.4-93.7	No	ND-dent #
3	35	300	1.44	93.0	1.5 Al	ND #
4	35	300	1.44	93.0	1.5 MS	ND #
5	47	300	1.45	93.7	1.5 Al	ND #
6	47	300	1.45	93.7	1.5 MS	D

D – Detonation, ND – No detonation, # – DNAN recovered
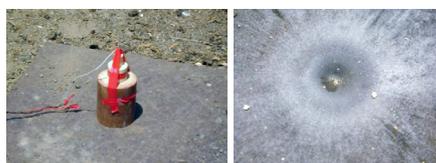
Test arrangement   Test result

Figure 1.   Detonability test Sr. No. 2 (ϕ 100 mm) DNAN charge

Test arrangement   Test result

Figure 2.   Detonability test Sr. No. 5 (ϕ 47 mm and 1.5 mm Al confined) DNAN charge

Table 3.   Sensitivity and explosive characteristics of DNAN and TNT

Explosive	Density [g/cm³]	Percent TMD	VOD [m/s]	Sensitivity		
				Shock [GPa]	Impact h_{50} [m]	Friction [kg]
DNAN	1.48	95.6	5000	6.00	>1.70	36.0
TNT	1.59	96.1	6700	4.14	1.30	32.4

The observed variation in VOD was within ±50 m/s of the average of 3 readings

3.2 Characterization and evaluation of NTO, FOX-7, HMX, TATB, and RDX formulations based on DNAN or TNT

The achieved sensitivity and explosive characteristics of Set-1 and Set-2 are given in Table 4.

a   b^1 b^2 b^3

Figure 3.   Shock sensitivity test of a DNAN charge: (a) test arrangement; (b) test results: 5.5 GPa (b^1), 5.8 GPa (b^2), 6.0 GPa (b^3)

Table 4.   Sensitivity and explosive characteristics of the various formulations

Formulation	Density [g/cm^3]	Percent TMD	VOD [m/s]	Sensitivity		
				Shock [GPa]	Impact h$_{50}$ [m]	Friction [kg]
NTO/DNAN 60/40	1.65	94.5	6750	6.80	1.38	36
FOX-7/DNAN 60/40	1.66	95.8	7000	3.20	0.64	36
HMX/DNAN 60/40	1.70	97.3	7600	1.60	0.75	36
RDX/DNAN 60/40	1.62	95.3	7400	2.10	1.08	36
NTO/TNT 60/40	1.69	94.0	7300	5.13	1.14	36
FOX-7/TNT 60/40	1.70	95.4	7600	2.45	0.53	36
HMX/TNT 60/40	1.75	97.3	8000	1.40	0.87	25.2
RDX/TNT 60/40	1.68	96.6	7640	1.87	0.99	28.8
NTO/DNAN 30/70	1.56	95.0	6200	6.50	>1.70	36
FOX-7/DNAN 30/70	1.56	95.4	6450	2.90	>1.70	36
TATB/DNAN 30/70	1.58	95.5	6250	4.40	1.68	36
RDX/DNAN 30/70	1.56	96.3	6640	2.30	1.10	36
NTO/TNT 30/70	1.64	95.0	6900	5.00	1.65	36
FOX-7/TNT 30/70	1.62	94.4	7060	2.10	1.57	36
TATB/TNT 30/70	1.65	95.5	6930	4.00	1.30	36
RDX/TNT 30/70	1.64	96.4	7230	1.75	1.04	32.4

The observed variation in VOD for these formulations was within ±50 m/s of the average of 3 readings

The average particle size of the solid ingredients NTO, FOX-7, HMX and RDX used for the preparation of the test samples in the proportion 60/40 with

DNAN and TNT was 110 µm, 261 µm, 155 µm and 155 µm respectively, while the average particle size of NTO, FOX-7, TATB and RDX used for the preparation of the test samples in the proportion 30/70 with DNAN and TNT was 14-25 µm.

3.2.1 Density

It can be seen from Table 4 that a charge density of about 94-97.3% TMD has been achieved for these formulations. The variation observed can be attributed to the normal casting method leading to fine porosity in the charge as well as minor measurement and rounding errors of the test pieces.

3.2.2 Velocity of detonation

In both sets of formulations, bare 35 mm diameter charges were used, except for the TATB/DNAN and TATB/TNT charges (of Set-2) where cased 35 mm (seamless 3 mm steel) charges were used because 35 mm bare charges detonated inconsistently.

In the first set, the VODs of the TNT-based formulations were higher than the corresponding DNAN formulations. The VOD achieved for 60/40 RDX/DNAN during the present study (7400 m/s) is in good agreement with the value (7398 m/s) reported by Provotas *et al*. [6] for the corresponding composition ARX-4027 m_2 (DNAN/RDX/MNA 39.75/60/0.25, where MNA is N-methyl-4-nitroaniline). The marginal decreases in VOD of 240 m/s and 400 m/s on substituting DNAN for TNT in the RDX/TNT 60/40 and HMX/TNT 60/40 compositions indicates an enhanced rate of reaction of DNAN in the presence of RDX and HMX. A similar trend was not observed with NTO and FOX-7. The VODs of FOX-7, NTO, RDX and HMX with TNT in the proportion 60/40 mainly depends on the VOD of the major energetic ingredient and its interaction with TNT during typical detonation reaction. The VODs of FOX-7 and RDX with TNT in the proportion 60/40 are comparable but the same does not hold well with DNAN. The trend observed is similar for the VODs of the other formulations with both DNAN and TNT.

In the second set of formulations, the VODs of TNT-based formulations are higher than those of the corresponding DNAN formulations. The decrease in VOD observed on substituting DNAN for TNT is in line with the individual explosive of the composition alone. This indicates that DNAN dominates the detonation reaction when it is in a high proportion. The VODs of formulations having FOX-7, NTO and TATB with TNT are lower than RDX/TNT. This trend can be attributed to the VOD of the major ingredient and the typical detonation reaction of the mix with TNT. The VODs of formulations having FOX-7, TATB and NTO with DNAN are lower than RDX/DNAN 30/70, indicating a slower

detonation reaction of FOX-7, TATB and NTO in combination with DNAN as compared to RDX with DNAN. The trend observed for the VODs of DNAN-based formulations is similar to that of TNT-based compositions and for similar reasons, as attributed above.

3.2.3 Sensitivity

3.2.3.1 Shock sensitivity

In the first set of formulations, the shock sensitivity of TNT-based formulations was greater than the corresponding DNAN-based formulations. The decrease in shock sensitivity on substituting DNAN for TNT shows that NTO and FOX-7 collectively form better mixtures with DNAN than with TNT for a given proportion. However, for the HMX and RDX compositions, the decrease is negligible indicating no major advantage on substituting DNAN for TNT. It is also seen that combinations of NTO with TNT and DNAN are more shock insensitive than either TNT or DNAN themselves. On substituting NTO and FOX-7 for RDX in RDX/TNT 60/40, the shock sensitivity decreases, while for HMX it increases. Similarly on substituting NTO and FOX-7 for RDX in RDX/ DNAN 60/40, the shock sensitivity decreases, while for HMX it increases. The average particle size of 110 µm of NTO could have also contributed to enhance the shock insensitivity compared to the average particle sizes of 261 µm and 155 µm of FOX-7 and RDX, respectively. The above trends also indicate that unlike for RDX and HMX compositions, where shock sensitivity depends mainly on the major energetic ingredient and to a negligible extent on binders like TNT and DNAN, in the cases of NTO and FOX-7 the shock sensitivity depends on both the major energetic ingredient and the binder.

In the second set of formulations, the shock sensitivity of TNT-based formulations formed with FOX-7, TATB and RDX are marginally more sensitive than the corresponding DNAN-based formulations, while NTO/TNT and NTO/ DNAN formulations are highly insensitive, *i.e.* NTO shows higher insensitivity with both TNT as well as DNAN unlike another explosives like FOX-7 or TATB. The decrease in shock sensitivity on substituting DNAN for TNT shows that NTO and FOX-7 improve the shock insensitivity relatively more than TATB and RDX in combination with DNAN. The improvements in shock sensitivity of TATB and RDX in combination with DNAN are comparable. On substituting NTO, FOX-7 and TATB for RDX in RDX/TNT 30/70, the shock insensitivity improves. Similarly on substituting NTO, FOX-7 and TATB for RDX in RDX/ DNAN 30/70, the shock sensitivity decreases. It can be seen that NTO- and TATB-based compositions are comparatively more insensitive to a shock

stimulus compared to FOX-7 compositions, and that the FOX-7 compositions are more insensitive than the RDX-based compositions. The loading of fine solid ingredients in the formulations was limited to 30% due to processing problems. A fine particle size of 14-25 μm adds to the shock insensitivity of these formulations. The shock insensitivity of combinations of NTO and TATB with TNT is higher and similar to, respectively, compared to the insensitivity of TNT itself. The shock insensitivity of the combinations of NTO and TATB with DNAN is higher and lower, respectively, compared to the insensitivity of DNAN itself. The shock sensitivities of the combinations of FOX-7 with TNT as well as DNAN are marginally more insensitive than corresponding RDX based formulation. As seen above, for 60% loading of NTO and FOX-7, the shock sensitivity for 30% loadings of NTO, TATB and FOX-7 also depends on both the energetic ingredient and the binder.

3.2.3.2 Impact sensitivity

In the first set of formulations, NTO-, FOX-7- and RDX-based formulations, except for HMX, formed with TNT are more sensitive than the corresponding DNAN-based formulations. The decrease in sensitivity on substituting DNAN for TNT is due to the inherent non-explosive nature of DNAN and its thicker coating over the particles. The increase in sensitivity on substituting DNAN for TNT for HMX-based formulation can be attributed to the non-homogeneity and improper preparation of the sample. The sensitivity of NTO-, FOX-7-, RDX- and HMX-based compositions is in decreasing order. The trend can be attributed to the stability of NTO due to inter- and intra-molecular hydrogen bonding and the sensitivities of the major energetic ingredients of NTO (0.56 m), FOX-7 (0.36 m), HMX (0.37 m) and RDX (0.37 m), and their average particle sizes of 110 μm, 261 μm, 155 μm and 155 μm, respectively. This trend indicates that the sensitivity to impact is also analogous to that of sensitivity to shock.

In the second set of formulations, h_{50} increases on substituting DNAN for TNT in the formulations formed with NTO, FOX-7, TATB and RDX. As discussed above, a thicker coating of DNAN helps to desensitize the energetic ingredients. An increase in insensitivity is observed on substituting NTO, FOX-7 and TATB for RDX with DNAN, as well as with TNT. These trends can be attributed to the sensitivities of the energetic ingredient as well as that of the binders DNAN and TNT.

3.2.3.3 Friction sensitivity

In the first set of formulations, NTO- and FOX-7-based compositions with both DNAN and TNT are insensitive up to 36 kg. This can be attributed to the

insensitive nature of crystals of NTO [2] and FOX-7 [29], as well as that of the binder coating of DNAN and TNT. The sensitivity of HMX- and RDX-based formulations formed with TNT are more sensitive than the corresponding DNAN-based formulations. This trend can be attributed to the relatively softer nature of DNAN compared to TNT and better wetting of RDX and HMX within the DNAN matrix, and a thicker coating of DNAN over HMX and RDX due to its low density, compared to TNT.

In the second set of formulations, the sensitivity observed for NTO-, FOX-7- and TATB-based compositions with both DNAN and TNT were insensitive up to 36 kg. As discussed above, this can be attributed to the insensitive nature of NTO, FOX-7 and TATB crystals, as well as the coating of DNAN and TNT. It is also seen that with the addition of NTO and FOX-7 up to 60% in TNT, the sensitivity of TNT decreases from 32.4 kg to 36 kg. On the other hand, with the addition of 30% and 60% of RDX in TNT, the sensitivity of TNT remains constant at 32.4 kg and increases to 28.8 kg, respectively.

It is discernable that the sensitivity to friction of these formulations mainly depends upon the binder or the relatively insensitive ingredient, compared to the energetic ingredients. From this observation it appears that the behaviour of sensitivity to friction differs from that of sensitivity to shock/impact.

4   Conclusions

The detonation failure diameter of a bare DNAN charge is greater than 100 mm, and under steel confinement it is about 44 mm, while for bare TATB/TNT and TATB/DNAN charges it is greater than 35 mm and under steel confinement it is about 35 mm. The rate of the detonation reaction of DNAN is enhanced in the presence of high energy ingredients such as RDX, HMX, FOX-7 and NTO to varying degrees. The VODs of TNT-based formulations formed with NTO, FOX-7, TATB, HMX and RDX are higher than the corresponding DNAN-based formulations. The VODs of FOX-7/TNT and RDX/TNT formulations are closely matched for a wide range of proportions of FOX-7 and RDX. The VODs of FOX-7/DNAN formulations decrease much faster compared to RDX/DNAN formulations, with increases in the proportion of FOX-7. The shock sensitivities of TNT-based formulations formed with NTO, FOX-7, TATB, HMX and RDX are greater than for the corresponding DNAN-based formulations. The combinations of NTO with TNT and DNAN are more shock insensitive than either TNT or DNAN themselves. The shock sensitivity of FOX-7/DNAN formulations decreases much faster, compared to RDX/DNAN formulations, with

increases in the proportions of FOX-7 or RDX. The sensitivity to mechanical stimuli of TNT-based formulations containing higher proportions of the energetic ingredients NTO, FOX-7, HMX and RDX are greater than the corresponding DNAN-based formulations, while with lower proportions of energetic ingredients they are more or less comparable for both TNT and DNAN. In general, the NTO-based melt-cast composition is comparatively more insensitive than the FOX-7-based composition.

Acknowledgements

References

[1] Akhavan, J. *The Chemistry of Explosives*. 2nd ed., The Royal Society of Chemistry, Cambridge, UK **2004**, pp. 10-11; ISBN 0-85404-640-2.

[2] Smith, M. W.; Cliff, M. D. *NTO-Based Explosive Formulations: A Technology Review*. Weapons Systems Division Aeronautical and Maritime Research Laboratory, DSTO-TR-0796, **1999**.

[3] Carleone, J. Tactical Missile Warheads. In: *Progress in Astronautics and Aeronautics*. American Institute of Aeronautics and Astronautics Inc, Washington DC **1993**, Vol. 155.

[4] 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.

[5] Van Alphen, J. Dimorphism of 2,4-Dinitroanisole. *Chem. Ber.* **1930**, *63*(B), 94-95.

[6] Davies, P. J.; Provatas, A. *Characterization of 2, 4-Dinitroanisole: An Ingredient for Use in Low Sensitivity Melt Cast Formulations*. Weapons Systems Division Defence Science and Technology Organization, DSTO-TR-1904, **2006**.

[7] Doll, D. W.; Hanks, J. M.; Allred, A. G.; Niles, J. B. *Reduced Sensitivity, Melt Pourable TNT Replacements*. Patent US 2003/005988 A1, **2003**.

[8] Wilson, A. *BAE Systems*. Holston Army Ammunition Plant Improved IM Melt Cast Explosives; imp_DNAN_MUNITIONS.pdf presentation in open literature.

[9] Samuels, P. Irreversible Growth of DNAN Based Formulations. ARDEC, *NDIA IM/EM Technology Symp.*, Las Vegas, NV, 14-17 May **2012**.

[10] Ward, D. W.; Coster, P. L.; Hope, K. S.; Pulham, C. R. Controlling a Polymorphic Transition in 2,4-Dinitroanisole Using Crystal Doping. *New Trends Res. Energ. Mater., Proc. Semin.,15th*, Pardubice, Czech Republic **2015**, 301-309.

[11] Walsh, M. R.; Walsh, M. E.; Taylor, S.; Ramsey, Ch. A.; Ringelberg, D. B.;

Zufelt, J. E.; Thiboutot, S.; Ampleman, G.; Diaz, E. Characterization of PAX-21 Insensitive Munition Detonation Residues. *Propellants Explos. Pyrotech*. **2013**, *38*: 399-409.

[12] Walsh, M. R.; Walsh, M. E.; Ramsey, Ch. A.; Thiboutot, S.; Ampleman, G.; Diaz, E.; Zufelt, J. E. Energetic Residues from the Detonation of IMX-104 Insensitive Munitions. *Propellants Explos. Pyrotech*. **2014**, *39*: 243-250.

[13] Lochert, I. J. *FOX-7 a New Insensitive Explosive*. Weapons System Division, Aeronautical and Maritime Research Laboratory, DSTO-TR-1238, **2001**.

[14] Wild, R.; Teipel, U. Characterization and Explosive Properties of FOX-7, *35th Int. Annu. Conf. ICT*, Karsruhe, Germany **2004**, 69.

[15] Mishra, V. S.; Vadali, S. R.; Garg, R. K.; Joshi, V. S.; Wasnik, R. D.; Asthana, S. N. Studies on FOX-7 Based Melt Cast High Explosive Formulations. *Cent. Eur. J. Energ. Mater.* **2013**, *10*(4): 569-580.

[16] Lee, K. Y.; Chapman, L. B.; Coburn, M. D. 3-Nitro-1,2,4-triazol-5-one, a Less Sensitive Explosive. *J. Energ. Mater.* **1987**, *5*: 27-33.

[17] Lee, K. Y.; Coburn, M. D. *3-Nitro-1,2,4-triazol-5-one, A Less Sensitive Explosive.* Patent US 4733610, **1988**.

[18] Cliff, M. D.; Smith, M. W. *Assessment of a Melt-Castable NTO/TNT Formulation*. Weapons Systems Division, Aeronautical and Maritime Research Laboratory, Australia, DSTO-TR-0998, **2000**.

[19] Spyckerelle, C.; Songy, C.; Eck, G. Eurenco, France, IM Melt Cast Compositions Based on NTO. *Insensitive Munitions & Energetic Materials Technology Symposium "International Progress in Insensitive Munitions and Energetic Materials"*, Munich, Germany, October 11-14, **2010**.

[20] Fung, V.; Alexander, B.; Balas, W. Development of Insensitive Aluminized Melt-Pour Explosive Formulation. NDIA: *Insensitive Munitions & Energetic Materials Technology Symposium*, Tucson, AZ **2009**.

[21] Radhakrishnan, S.; Vijayalakshmi, R.; Reddy, T. S.; Sikder, A. K. Micrometric Characterization Studies of Spherical NTO and its HE Formulations. *Proc. 9th International High Energy Materials Conference and Exhibits* (HEMCE), Thiruvananthapuram, India **2014**, 439-443.

[22] Trzciński, W. A.; Cudziło, S.; Dyjak, S.; Nita, S. A Comparison of the Sensitivity and Performance Characteristics of Melt-pour Explosives with TNT and DNAN Binder. *Cent. Eur. J. Energ. Mater.* **2014**, *11*(3), 443-455.

[23] Akhavan, J. *The Chemistry of Explosives*. RSC Publishing, 2nd ed. **2004**, p. 43.

[24] Kaye, S. M. *Encyclopedia of Explosives and Related Items*. PATR 2700, Picatinny Arsenal, New Jersey, USA **1980**, Vol. 9, pp. T49.

[25] Nandi, A. K.; Paramsivan, P.; Singh, S. K.; Mandal, A. K.; Pandey, R. K. Assay of the Insensitive High Explosive FOX-7 by Non-Aqueous Titration. *Cent. Eur. J. Energ. Mater.* **2012**, *9*(4): 343-352.

[26] Nandi, A. K.; Singh, S. K.; Kunjir, G.M.; Singh, J.; Mandal, A. K.; Pandey, R. K. Assay of the Insensitive High Explosive 3-Nitro-1,2,4- triazol-5-one (NTO) by Acid-Base Titration. *Cent. Eur. J. Energ. Mater.* **2013**, *10*(1): 113-122.

[27] Nandi, A. K.; Thirupathi, N.; Mandal, A. K.; Pandey, R. K. Assay of the Thermally Stable, Insensitive, High Explosive 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB). *Cent. Eur. J. Energ. Mater.* **2014**, *11*(2): 295-305.

[28] Samuels, P. Characterization of 2,4-Dinitroanisole (DNAN). NDIA: *Insensitive Munitions & Energetic Materials Technology Symposium*, Las Vegas, NV **2012**.

[29] Latypov, N. V., Bergman, J., Langlet, A.; Wellmar, U.; Bemm, U. Synthesis and Reactions of 1,1-Diamino-2,2-dinitroethylene. *Tetrahedron* **1998**, *54*(38): 11525-11536.