Australian Melt-Cast Explosives R&D

DNAN - A Replacement for TNT in Melt-Cast Formulations

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Abstract

Researchers at Weapons Systems Division are currently investigating 2,4-dinitroanisole (DNAN), an energetic material that offers promise as a replacement for TNT in melt-cast explosive formulations. DNAN is not a new energetic material; however, its use in explosive formulations is presently undergoing a renaissance, as exemplified by the development of a range of DNAN based explosive formulations at Picatinny Arsenal (typically referred to as the "PAX explosives"). Primarily two main reasons exist for the renewed interest in DNAN. Firstly, as a less sensitive melt-cast medium than TNT, opportunities exist for the development of less sensitive melt-cast formulations than those presently incorporating TNT.[1] Secondly, it is categorised as a Class 4.1 Flammable Solid and is therefore subject to less stringent international transportation requirements than Class 1 materials.

In this paper we provide details of current DSTO work aimed at characterising DNAN and a simple formulation (ARX-4027) primarily through handling, sensitiveness, and performance (velocity of detonation). Additionally we report on a number of tests conducted to determine whether or not the shock sensitivity characteristics of reduced sensitivity RDX (RS-RDX) can be retained in a DNAN melt-cast matrix under typical casting conditions.

Introduction

The development of low vulnerability munitions, known collectively as insensitive munitions (IM), is a key driving force behind modern explosives research. In Australia additional impetus has been provided by the ratification of the ADF insensitive munitions policy [1], which is impacting upon ordnance acquisition strategies and the treatment of legacy stores within the ADF. In accord with this ADF policy and in light of the potential changes to future national manufacturing capabilities, the Commonwealth is seeking alternatives that allow it to meet its IM goals and responsibilities.

[1] The lower toxicity of this material over TNT is often quoted as another advantage, however, the toxicology of DNAN remains under review.

While a number of polymer bonded explosives (PBXs) have been shown to provide improved insensitivity the manufacture is typically more expensive than melt-cast (or pressed PBX) options, and tends to be used for large, low through-put warheads. ADI manufacturing facilities are presently geared toward melt-cast options, and logic dictates that research into the development of low sensitivity melt-cast options be continued.

Characterisation of DNAN and ARX 4027

DNAN (Figure 1) is an explosive material with slightly lower (~10%) performance than that of TNT, with a slightly higher melting point of 95°C [2]. While not entirely unsuitable for casting at this temperature, the melting point can be depressed by several degrees through the addition of small quantities of melt-soluble additives such as N-methyl-4-nitroaniline (MNA) ($T_{eutectic}$ = 79.0 °C), to provide a medium more suited to typical melt-cast processes [3]. DNAN is highly oxygen deficient (OB_{CO2} = –96.9%, OB_{CO} = –40.4%) when compared to TNT (OB_{CO2} = –74.0%, OB_{CO} = –24.7%), and exhibits much lower crystal density (1.34 gcm^{-3} versus 1.60 gcm^{-3}). These factors militate against its effective use as a stand-alone explosive, and to date DNAN has only featured as one of (usually) several ingredients in explosive formulations (eg. the PAX explosives) [4].

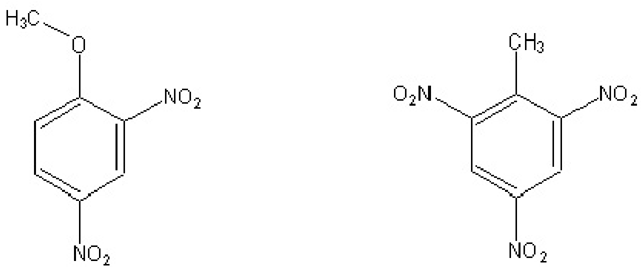

Figure 1 The structure of 2,4-dinitroanisole (DNAN) (left) and 2,4,6-trinitrotoluene (TNT) (right).

Until recently the majority of open literature studies involving DNAN have been undertaken to explore its chemistry rather than any explosive properties, and relatively little data is available with respect to its sensitiveness, chemical compatibility, thermal properties and shock sensitivity in either the pure or composite form. Studies undertaken herein address some of these deficits and identify specific areas of concern and interest with respect to future studies.

In addition to the characterisation of DNAN we have also determined the shock sensitivity properties of two very simple DNAN/RDX formulations, namely ARX-4027 (60/40 RDX/DNAN +0.25% MNA) incorporating RS-RDX (ARX-4027 M1) and non-RS-RDX (ARX-4027 M2) respectively.

Compatibility of DNAN with relevant materials

Vacuum thermal stability tests show that no specific issues arise with regard to the compatibility of DNAN with materials of immediate interest, including MNA, RDX, and TNT. TNT was of interest due to the potential for cross-contamination in DSTO melt-cast bays and because DNAN may possibly form an adduct with TNT. Table 1 lists the results of the vacuum thermal stability tests conducted at 100 °C for 40 hrs. All combinations evolved less than 2 ml/g of gas indicating suitable compatibility under the test conditions. Interestingly, reaction (complexation) of DNAN and TNT was clearly evident through a marked colour change from off-white/yellow to cabernet red upon melting of the binary mixture.[2]

Table 1 Vacuum thermal stability test results for relevant mixtures

Mixtures (50/50 w/w)	Gas evolution	Observations
DNAN/RDX	0.06 ml/g	Satisfactory
DNAN/MNA	0.07 ml/g	Satisfactory
DNAN/TNT	0.06 ml/g	Formation of red (cabernet) liquid
RDX/MNA	0.12 ml/g	Satisfactory

Sensitiveness to Impact, Friction and Electrostatic Discharge

The impact and friction sensitiveness were determined using Rotter Impact Test and BAM friction tests. The results of these tests together with ESD test results are provided in Table 2. The impact sensitivity of DNAN in both the pure form (and with grit added) is very low (F of I >220).[3] The impact sensitivity of ARX-4027 is only slightly lower than Comp B. Pure DNAN and DNAN/grit (F of I > 220) are less sensitive to impact than TNT (F of I = 170).

Similarly ARX-4027 is less sensitive to friction than Composition B. Pure DNAN is very fiction sensitive compared to TNT.

[2] Upon completion of this test the resulting red liquid did not solidify for 2 days but crystallised quickly after agitation.

[3] During the Rotter Impact Tests on pure DNAN (no grit) a single event was observed (25 tests) evolving 2 ml of gas and leaving a sticky tar in the cap. No events were observed when DNAN was mixed with grit.

Table 2 Impact sensitiveness of DNAN, ARX-4027 and related materials

Material	F of I (evolved gas [cm^3])	Friction (N)	ESD (ignition/J)
DNAN	> 220 (2.0)	160	-
DNAN (+ grit)	> 220 (0.0)	-	-
ARX 4027 (60/40 RS-RDX/DNAN)[a, c]	160 (3.2)	108	4.5
TNT – Flake[b]	170 (1.1)	216	4.5
RDX – ADI[c]	80 (12.8)	96	4.5
Comp B (60/40 RDX/TNT)[d]	140 (4.6)	80	4.5

[a] ADI Type 1 Grade A Lot 17880A + 0.25% MNA
[b] Lot MEM 0050/00
[c] Dyno-Nobel Type 2 Class 1
[d] Lot Mem 080-07/01

Temperature of Ignition

The temperature of ignition (T of I) for DNAN, MNA and a number of relevant 1:1 energetic combinations were determined (Table 3). The T of I for pure DNAN is high (347 °C) however, as expected the T of I for mixtures incorporating RDX is dominated by the lower initiation temperature of RDX. Interestingly the T of I for the DNAN/TNT adduct was lowered by 40°C when compared to the most thermally reactive of the two materials (TNT).

Table 3 T of I for DNAN and various mixtures

Material	T of I (°C)
DNAN	347
MNA	290-370
RDX - ADI	219
RDX-DYNO	212
ARX 4027 (60/40 RDX/DNAN)	220
TNT (Lot 0050/00)	306
DNAN/RDX (1:1)	211
MNA/RDX (1:1)	201
DNAN/TNT (1:1)	266

Thermal Characteristics of DNAN and Related Mixtures

DSC analysis was undertaken on DNAN and DNAN mixtures in order to determine the effects on melting point (eg. eutectic) and to confirm that no chemical incompatibilities exist beyond 100°C that may not have been detected through the vacuum thermal stability tests (Figures 2 & 3).

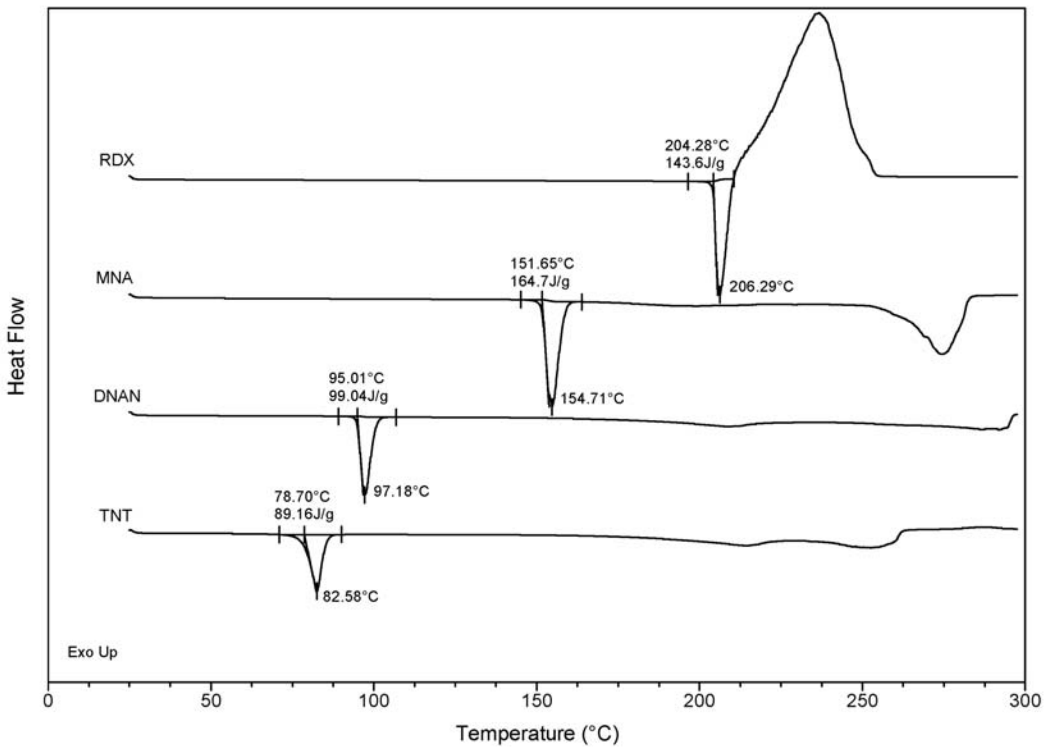

Figure 2 DSC for RDX, MNA, DNAN and TNT

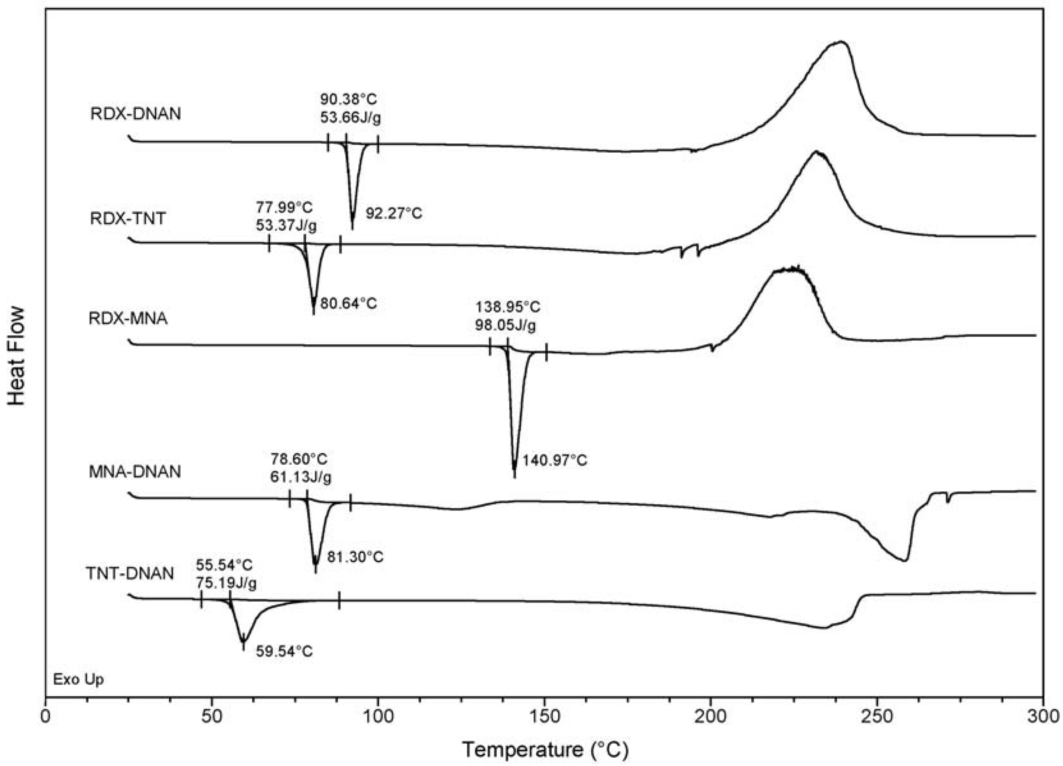

Figure 3 DSC for relevant mixtures (50/50)

The reduced melting point of DNAN in the presence of RDX is a clear indication that RDX dissolves to some degree in the DNAN melt. The eutectic composition for DNAN and MNA, determined through correlation of eutectic fusion energies (assuming a simple two-phase relationship), is approximately 80% DNAN 20% MNA. The utilisation of MNA to depress the melting point of DNAN appears to be somewhat superfluous given that the melting point of DNAN can be lowered by 5°C through the addition of RDX alone. This was similar to the effect seen by adding 1% MNA to DNAN.

Solubility of RDX in DNAN

As alluded to in the differential scanning calorimetry traces, some solubility of RDX was anticipated in RDX/DNAN formulations. To explore this further a rudimentary solubility study was undertaken to determine the amount of RDX soluble in DNAN at temperatures above the melting point of DNAN. These results are shown graphically in Figure 4. While further work is required it is anticipated that the solubility of RDX at the RDX/DNAN eutectic is approximately 5g / 100g of DNAN.

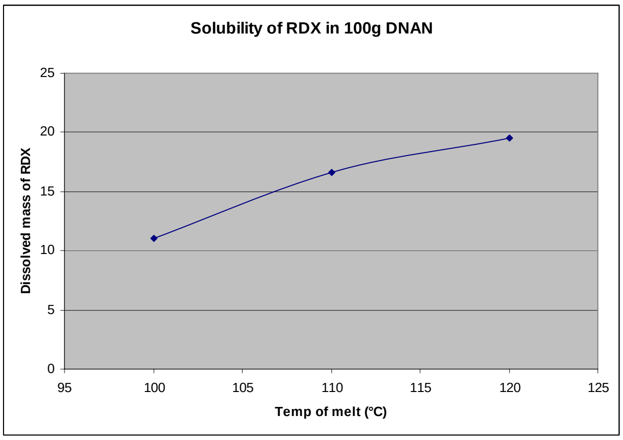

Figure 4 Solubility of RDX in DNAN

It can be seen that considerable RDX dissolves in the DNAN melt, particularly at higher temperatures (eg. 20g / 100g of DNAN at 120°C). Upon cooling plate-like crystals could be seen settling out (see Figure 5).

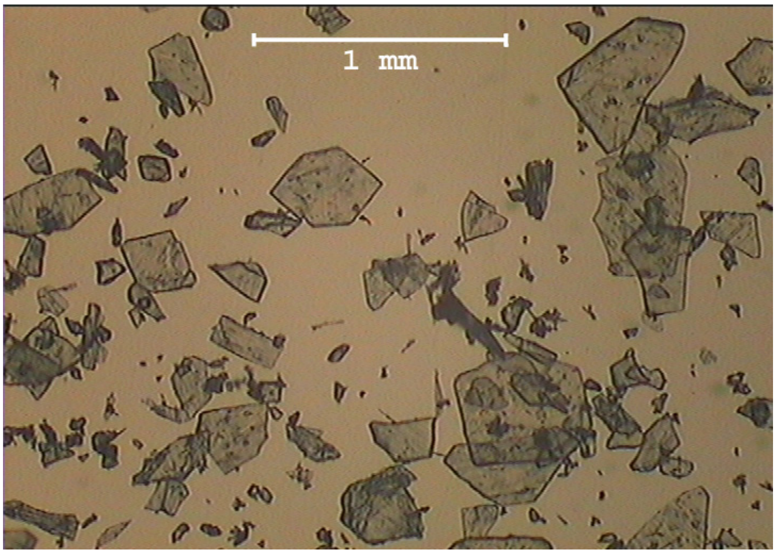

Figure 5 Micrograph of RDX plates recrystallised from DNAN. Typical crystals were 0.01 - 0.02 mm thick.

Sublimation/evaporation of DNAN

Due to concerns arising over the sublimation/evaporation of DNAN during melt-cast operations the rate of mass loss was monitored using TGA over several temperatures (Figure 6). The rate of evaporation is linear and ranges from -0.002 to -0.034 %/minute. Based on these rates and accounting for available surface area it is anticipated that DNAN at 95°C in a typical mixer (with surface area of approx. 1000 cm^2) would evaporate at a rate of ~2mg/min. This mass loss is manageable when considering typical melt-cast filling processes.

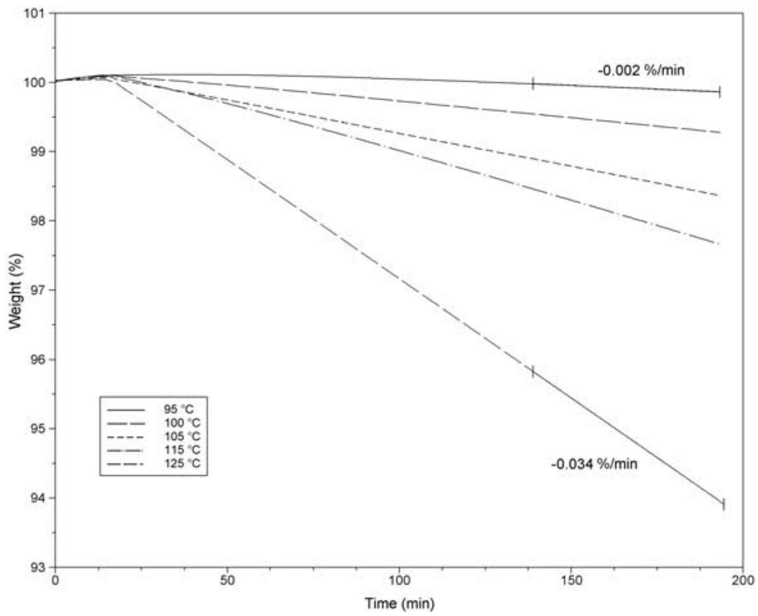

Figure 6 Sublimation/evaporation of DNAN at elevated temperature via Isothermal TGA.

Formulation of ARX-4027

A simple test formulation, namely ARX-4027, comprising 40% DNAN and 60% RDX (0.25% MNA) was developed in order to conduct an assessment of the efficacy of utilising DNAN in melt-cast formulations.

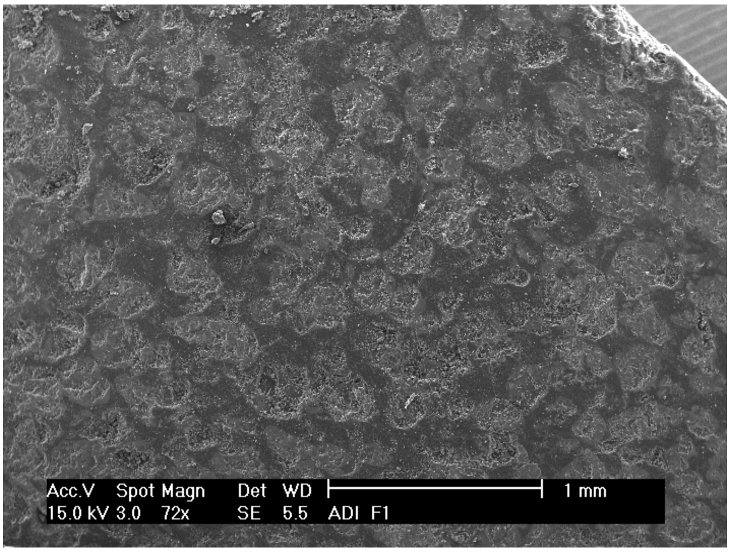

Figure 7 SEM image of ARX-4027

The SEM image (Figure 7) of a typical cross-section of a cylinder of ARX-4027 shows good incorporation of RDX within the DNAN matrix. RDX crystals tend to break rather than pull out of the melt-cast material. This was anticipated given the solubility of RDX in DNAN, which is likely to result in a higher degree of inter-molecular interaction during the cooling process.

Figure 8 shows that the viscosity of ARX-4027 is lower than Composition B, which is not surprising considering the lower DNAN density compared to TNT (1.35 *c.f.* 1.60 gcm^{-3}).

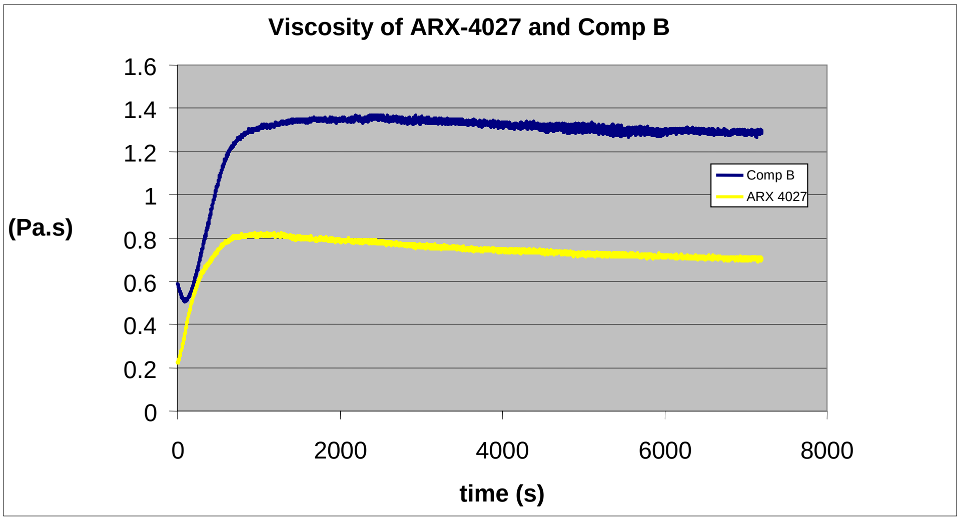

Figure 8 Viscosity Profile for ARX-4027 & Composition B

Clearly there is scope for the introduction of much higher levels of RDX than explored here. Indeed this has already be seen in PAX 41 which contains slightly higher levels of RDX than ARX-4027 (65% bimodal RDX, ultra-fine material produced via a fluid energy mill) [4].

Performance Studies of DNAN and ARX-4027M1/M2

ARX-4027 M1 & M2 and DNAN formulations have been tested for warhead performance (velocity of detonation). Charge dimensions were 25.4 mm diameter, 220 mm length, unconfined and cast-cured to required density.

Velocity of detonation of DNAN and associated formulations were measured in triplicate using a flexible printed circuit board design that has accurately spaced 20 mm intervals and aligned alongside the charge. Shots were boosted with 50:50 pentolite cylinders (25.4 mm x 25.4 mm diameter) and initiated with Resi 501 EBW detonators. Simple calculation of the VoD over each of the nine intervals via CRO provides evidence of accelerating, decelerating or steady-state detonation of the charge. A low standard deviation in the VoD implies steady-state detonation.

Additionally, calculated VoD were obtained using the CHEETAH V2.0 program. CHEETAH V2.0 utilises traditional Chapman-Jouget thermodynamic detonation theory to accurately model and predict performance of new explosive compositions as well as ideal explosives and serves as a useful tool for comparison of experimental data to one-dimensional theory [5],[6].

Good performance in velocity of detonation values were achieved between actual and predicted VoD for all shots fired with low standard deviations obtained (Table 4).

Table 4 Experimental and Calculated Performance Parameters (Averaged Values)

Formulation	Experimental VoD, (m/s)	Calculated VoD, (m/s)
DNAN	5591 (2.0%)*	5344
ARX-4027 M1 (RS-RDX)	7356 (1.0%)	7296
ARX-4027 M2 (Dyno RDX)	7398 (1.1%)	7296
Comp B	7860 (2.4%)	7630

* standard deviation values in brackets.

Shock Sensitivity of DNAN and ARX-4027M1/M2

In order to determine if the shock sensitivity of RS-RDX can be retained in a DNAN based melt-cast explosive, we compared two simple DNAN/RDX formulations (analogous to Composition B); one incorporating reduced sensitivity RDX (Type 1 RS-RDX ADI Grade A) and the other incorporating standard RDX (Dyno Nobel Type 2 Class 1).

While DNAN is presently classified as a Class 4.1 Flammable Solid, initial shock sensitivity testing via the UN Series 2 Gap Tests on pure DNAN was conducted resulting in detonation of DNAN when the shock attenuator (50 mm PMMA spacer) was removed (Figure 9). This led us to conduct LSGT tests on pure DNAN to elucidate its shock sensitivity. The results of the LSGT are shown in Table 5; PBXN-109 is included for comparison to a polymer bonded explosive, PBX.

Table 5 LSGT results

Material	Gap cards (mm)	GPa
DNAN	71 (18)	7.02
ARX-4027 (DYNO)	184 (47)	2.62
ARX-4027 (ADI)	202 (51)	2.24
Comp B	181 (46)	2.69
PBXN-109	196 (50)	2.35

The low shock sensitivity of RS-RDX in a DNAN melt-cast support matrix is not retained (see LSGT results in Table 5). Non RS-RDX gives slightly higher initiation pressure results than the RS-RDX.

Figure 9 (a) UN Series 2 Gap Test Set-up prior to firing, (b) witness plate no reaction and (c) holed witness plate after booster removed from pure DNAN charge.

Summary and Future Work

DNAN shows promise as an insensitive replacement for TNT in melt-cast formulations. By use of thermal analysis techniques, typical thermal properties of DNAN and its admixtures have been determined along with the sublimation/evaporation rate at various temperatures. Furthermore, an initial indication of the solubility of RDX in molten DNAN has been determined. From such observations it appears that RDX can be loaded to high levels in a DNAN matrix.

ARX-4027, a Composition B analog, was formulated using DNAN (40%) and RDX (60%). The viscosity profile shows promise over Composition B and reasonable settling properties were exhibited.

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