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Characterisation of 2,4-Dinitroanisole: An Ingredient for use in Low Sensitivity Melt Cast Formulations

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ABSTRACT

In recent years TNT has fallen out of favour as an ingredient in melt-castable explosive formulations due to its demonstrated failure to meet sensitivity requirements, and alternatives with suitable chemical and physical properties have been sought. 2,4-Dinitroanisole (DNAN) is a promising alternative that prima facie appears to possess adequate properties and, by virtue of reduced sensitivity, may enable the development of a new class of low sensitivity melt-cast formulations for use in Insensitive Munitions (IM). This paper provides a baseline characterisation of DNAN and includes the determination of the sensitivity and explosive properties of a simple DNAN-based formulation (ARX-4027) analogous to Composition B. Key properties that impact upon the use of DNAN in melt-cast formulations are identified.

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Executive Summary

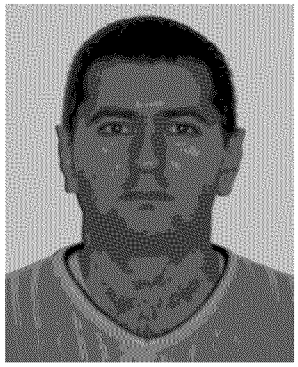
Due to perceived toxicity and sensitivity problems associated with some TNT-based melt-cast formulations, TNT has fallen out of favour with western militaries and alternative materials for use in melt-cast formulations have been sought. 2,4-Dinitroanisole (DNAN) has been proposed as a suitable alternative to TNT and has been employed previously by Picatinny Arsenal in range of melt-castable formulations (typically termed "melt-castable PAX explosives") that show improved sensitivity properties over equivalent or similar TNT formulations. As part of the redevelopment of Australian explosives manufacturing facilities, and in line with a recently ratified Australian Insensitive Munitions (IM) Policy [DI(G) LOG 07-10], 2,4-dinitroanisole is being considered by the Commonwealth as a viable alternative for replacement of TNT, in low sensitivity melt-cast formulations.

While some information on the properties of DNAN and DNAN-based explosives has been made available, or can be sourced in the open literature, the efficacy of its employment in melt-cast formulations had been questioned. Accordingly, DSTO embarked on a program of work to establish the bounds of employment for this contemporary ingredient.

In this work a limited review of available literature has been undertaken, together with experimental work to determine relevant sensitiveness, chemical compatibility and thermal properties of DNAN. The sensitivity, mechanical and performance properties of a simple Composition B analogue, namely ARX-4027 (60/40 RDX/DNAN), were also determined.

In conclusion, it was found that DNAN is a potentially suitable replacement for TNT in melt-cast explosive formulations. While its thermal properties are (arguably) not as ideal as those of TNT for processing in current melt-cast facilities (e.g. higher melting point), no insurmountable barriers to implementation were found to exist. Chemical compatibility with typical ingredients was found to be suitable. A potential incompatibility with TNT was observed but this is unlikely to pose a risk in single melt-medium facilities. The shock sensitivity for two variations of ARX-4027, one incorporating reduced sensitivity RDX (RS-RDX) and another incorporating normal (non-RS) RDX, was measured. The results showed that the insensitiveness of RS-RDX is not retained in these formulations.

Authors



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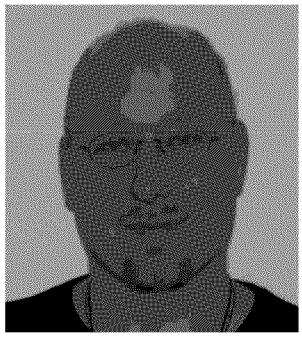
Arthur Provatas graduated with a PhD (Chem. Tech.) from the University of South Australia in 1997 in polymer chemistry and commenced work for the Explosives Group, Weapons Systems Division of DSTO investigating energetic polymers as binders in polymer bonded explosives. Dr Provatas is the Chemical Safety Officer for WSD and the Australian POC for environmental issues with TTCP (The Technical Cooperation Program). His current research interests reside with melt-castable Insensitive Munition fills, IM testing, investigations into the characteisation of RS-RDX and he is also working in the area of counter terrorism.



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Phil Davies obtained a PhD in Physical and Inorganic Chemistry from Flinders University of South Australia in 1998. He joined DSTO in 1999 and has been involved in Operations Analysis in support of future land warfare, soldier modernisation, urban operations and counter-terrorism. In 2003 he moved "back into chemistry" and joined Explosives and Pyrotechnics Group (Weapon Systems Division) to undertake research aimed at the development of Insensitive Munitions technologies, including novel formulations and physical mitigation techniques. He is also currently undertaking research aimed at the synthesis and characterisation of improvised explosive materials.

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Abbreviations

ADF	Australian defence force
Amatol 40	DNAN/AN/RDX 50/35/15
BAM	Bundenssanstalt für materialprüfung (friction testing)
Composition B	RDX/TNT 60/40
DG	Dangerous Goods class
DNAN	2,4-Dinitroanisole
DNCB	Dinitrochlorobenzene
DSC	Differential scanning calorimetry
EBW	Exploding bridge wire (detonator)
ESD	Electrostatic discharge
F of I	Figure of insensitiveness
GPa	Gigapascal
HEFC	High explosive firing chamber
HMX	Cyclotetramethylenetetranitramine
IM	Insensitive munitions
LD_{50}	Lethal dose (50% mortality)
LOAEL	Lowest observed adverse effect level
LSGT	Large scale gap test
MNA	N-methyl-4-nitroaniline
MPa	Megapascal
NOAEL	No observed adverse effect level
OB	Oxygen balance
Octol	HMX/TNT 65/35
PAX	Picatinny arsenal explosives
PBX	Polymer (or plastic) bonded explosive
P_{CJ}	Chapman-Jouguet (detonation) pressure
PETN	Pentaerythritol tetranitrate
Pentolite	PETN/TNT 50/50
PMMA	Polymethyl methacrylate
RDX	Cyclotrimethylenetrinitramine
RS-RDX	Reduced Sensitivity RDX
SEM	Scanning electron microscope
TGA	Thermogravimetric Analysis
TMD	Theoretical maximum density
TNT	2,4,6-Trinitrotoluene
T of I	Temperature of ignition
VoD	Velocity of detonation
VTS	Vacuum thermal stability

1. Introduction

The development of low vulnerability munitions, known collectively as insensitive munitions (IM), is a key driving force behind modern explosives research. Additional impetus within the ADF has been provided by the ratification of Australia's Insensitive Munitions Policy DI(G) LOG 07-10 [1], which impacts upon the acquisition of future ordnance 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.

A number of successful strategies have been employed to reduce the response of ordnance to planned and unplanned aggressive stimuli.[1] A range of physical mitigation technologies can be employed to militate against the risk of a higher than acceptable response to specific stimuli, however, it is generally accepted that IM will not be achieved without the use of intrinsically insensitive explosive formulations to contribute to lower order responses across the spectrum of ammunition types and designated threats. While a number of polymer bonded explosives (PBXs) have been shown to provide improved insensitivity, their manufacture is typically more expensive than melt-cast (or pressed PBX) options, and tends to be used for large, low through-put warheads. Australian manufacturing facilities are presently geared toward melt-cast operations and research into the development of more insensitive melt-cast formulations is warranted.

In this paper we provide details of recent DSTO work aimed at characterising DNAN and a simple formulation (ARX-4027) primarily through handling, sensitiveness and thermal studies. 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.

1.1 Background

DNAN is not a new energetic material (see [2]). One of its first recorded uses in an explosive military device was as a main charge ingredient in Amatol 40 (50% DNAN, 35% ammonium nitrate, 15% RDX) in the warhead of some V-1 flying bombs during World War II [3]. Its use was not necessarily due to any performance gains, but more likely to its availability when higher performance materials such as TNT were becoming increasingly scarce.[2] Indeed DNAN exhibits slightly lower (~10%) performance than TNT. Despite the performance shortcomings, the use of DNAN in explosive formulations is presently undergoing a renaissance. This is exemplified by the development of a range of DNAN based explosive

[1] In accord with Australian Defence Instruction DI(G) LOG 07-10, threat stimuli include; Fast Heating, Slow Heating, Bullet Impact, Fragment Impact, Sympathetic Reaction, Shaped Charge Jet Impact and Behind Armour Debris.

[2] Germany developed numerous "Eratzpsrengstoffe" or substitute explosives to address shortages in TNT and NH_4NO_3. In the most desperate times (e.g. September 1944) the German High Command ordered the use of 40:60 TNT/NaCl, with much reduced performance [3].

formulations at Picatinny Arsenal (typically referred to as the "melt-castable PAX explosives").

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. An example of this class of explosives is PAX-21[3], which has been shown to have lower shock sensitivity than Composition B (60% RDX and 40% TNT) [18], and contributes to improved responses to threat stimuli when employed in appropriate munitions (for example US Army 60 mm Mortar M720A1). Secondly, it is categorised as a Dangerous Goods Class (DG) 4.1 "Flammable Solid" and is therefore subject to less stringent transportation requirements than DG 1.1 materials, such as TNT.

DNAN is used industrially as an ingredient in the syntheses of dyes [4]. It has also found use as an insecticide by US Armed Forces [2, 5]. However, a review of more recent literature shows that current interest in DNAN is predominantly as an ingredient in explosive formulations.[4] The majority of studies conducted on DNAN as an explosive ingredient are either dated (pre 1950) or provide minimal information. Relatively few studies have been made available that demonstrate its explosive properties, sensitiveness and chemical compatibility and shock sensitivity in either the pure or composite form. Studies undertaken herein address some of these deficiencies and identify specific areas of concern and interest with respect to future studies.

2. Characterisation of DNAN for Melt-Cast Explosive Formulations

Reports indicate that DNAN (Figure 1) is an explosive material with about 90% of the explosive power of TNT [2, 6]. The melting point of DNAN is high (94-95 °C) compared to that of TNT (78-81 °C). While not entirely unsuitable for casting at this temperature, the melting point can be depressed readily by several degrees through the addition of small quantities of melt-soluble additives such as N-methyl-4-nitroaniline (MNA), which is addressed in this study, to a provide a medium more suited to typical melt-cast processes [7]. DNAN is highly oxygen deficient (OB_{CO_2} = –96.9%, OB_{CO} = –40.4%)[5], even when compared to TNT (OB_{CO_2} = –74.0 and 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) [7-13]. Table 1 provides some fundamental properties of DNAN and TNT (for reference).

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[3] A formulation developed at Picatinny Arsenal containing RDX 36%, DNAN 34%, ammonium perchlorate 30%, and N-methyl nitroaniline ≤ 1%.

[4] DNAN is manufactured by Holston Army Ammunition Plant (US), Kangda Chemicals Co. Ltd. (China), and Apros Corporation (South Korea).

[5] OB = Oxygen Balance

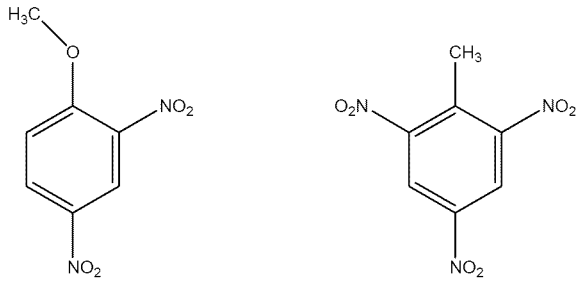


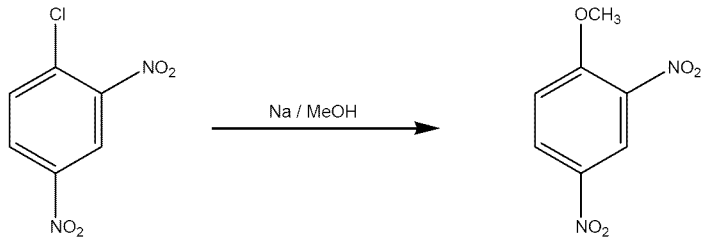
Figure 1. The structure of 2,4-dinitroanisole (DNAN) (left) and 2,4,6-trinitrotoluene (TNT) (right).

Table 1. Fundamental properties of DNAN and TNT (from CRC Handbook [14]).

	DNAN	**TNT**
CAS Number	119-27-7	118-96-7
Molecular Formula	$C_7H_6N_2O_5$	$C_7H_5N_3O_6$
Formula weight	198.133	227.131
Composition (%)	C (42.43) H (3.05) N (14.14) O (40.38)	C (37.02) H (2.22) N (18.50) O (42.26)
Density (gcm^{-3})	1.336	1.654
Melting Point (°C)	94.5	80.5
Physical Form	Needles (ethanol or H_2O), monoclinic	Orthorhombic (ethanol)
Solubility	*sl* (H_2O), *s* (ethanol, ether, acetone, benzene), *vs* (pyridine)	*i* (H_2O), *sl* (ethanol), *s* (ether), *vs* (acetone, benzene)

2.1 Synthesis of DNAN

DNAN can be prepared through further nitration of *p*-nitro- and *o*-nitroanisole, but can be more readily synthesised in high yield by the methoxylation (etherification) of 1-chloro-2,4,-dinitrobenzene (DNCB). 1-chloro-2,4,-dinitrobenzene is an important chemical intermediate used in the production of Sulphur Black and many other dyes. Typical synthesis of DNAN involves simple nucleophilic aromatic substitution of the highly labile chloro substituent with a methoxide anion, as shown in Scheme 1 below.



Scheme 1. Synthesis of DNAN from 1-chloro-2,4-dinitro benzene (DNCB).

The use of sodium metal[6] to produce methoxide, a process involving the liberation of heat and hydrogen gas, is generally unnecessary, as the methoxylation proceeds well in aqueous methanol in the presence of potassium or sodium hydroxide. A recent example is given by Cao and co-workers, who have reported a method for synthesis of DNAN (in up to 97% yield) through the methoxylation of 1-chloro-2,4-dinitrobenzene using methanol in the presence of sodium hydroxide [15]. It is likely that current industrial processes employ a similar method. This is supported by observation of the impurities in manufactured DNAN, which include up to 0.25% 1-chloro-2,4,-dinitrobenzene (see for example [16]).

2.2 Toxicity of DNAN

Prior to 2002 only limited toxicological data was available on DNAN. It had been proposed that due to the increased solubility of DNAN over TNT in aqueous solution at biologically relevant pHs, the propensity of DNAN to form harmful (solubilised) metabolites would be reduced. This is at least partly abrogated by the fact that as early as 1980 it was known that DNAN is metabolised in the body to 2,4-dinitrophenol, a chemical with high acute and chronic (non-carcinogenic) toxicity [17].

In 2002 a *preliminary* study was conducted to determine the toxicity of PAX-21 in comparison with Composition B. As part of this study the toxicity of DNAN, a major ingredient of PAX-21, was also determined under a range of conditions. The mutagenic effects of DNAN, Composition B and PAX-21 were also studied. The study found that while DNAN, PAX-21 and Composition B were mutagens in bacteria (with toxicity DNAN > Composition B > PAX-21), no mutagenic effects in mammals were observed [18]. The acute and subchronic (repeated dose) toxicity resulting from exposure to DNAN via oral intake, skin absorption and inhalation were determined – a summary of these findings is presented below. Note that this study did not deal with chronic (long term) effects of either DNAN or PAX-21.

The single dose acute LD_{50} (rat) for PAX-21 (455 mg/kg) was higher than that of Composition B (197 mg/kg). Pure DNAN gave a single dose acute LD_{50} (rat) of 199 mg/kg which classifies it as Toxicity Category II (where I = most hazardous, IV = least hazard). For single dose exposure, DNAN is more acutely toxic than TNT, which possesses a LD_{50} (rat) of 794-1320 mg/kg [18]. Repeated dose (sub-chronic) oral testing was conducted on PAX-21 (but not pure DNAN) over a 90 day period. The LOAEL (lowest observed adverse effect level) and NOAEL (no observed adverse effect level) for PAX-21 were found to be 30 and 15 mg/kg-day respectively [18].

Tests for skin irritation (in rabbits) showed that DNAN, PAX-21 and Composition B were slight irritants but the effects were not long-lived, clearing after 24-48 hours. Eye irritation tests (in rabbits) found that PAX-21 and Composition B were moderate irritants whereas DNAN was only mildly irritating with effects clearing after 7-10 days in all cases. No dermal sensitisation was observed with DNAN, PAX-21 or Composition B. Dermal penetration tests

[6] Sodium metal is highly reactive with protic solvents - if used in quantities greater than a few hundred milligrams it will spontaneously ignite in water at (initially) neutral pH. Even smaller quantities will ignite spontaneously in acid. This poses ignition risks.

revealed the absorbance of DNAN and TNT through skin was much smaller (steady state flux of 0.74 and 1.14 $\mu g/cm^2$-hr, respectively) than nitroglycerin (30 $\mu g/cm^2$-hr) [18].

Acute inhalation toxicity of DNAN was found to be minimal (category IV, least hazardous). Acute inhalation tests using DNAN vapour yielded no sign of toxic effects in rats at a concentration of 3mg/m^3 (highest concentration observed) over 4 hours. Tests using a DNAN aerosol (i.e. an atomised solution of DNAN in acetone 1:3 [w/w]) at a concentration of 2900 mg/m^3 over 4 hours showed signs of toxicity in rats (decreased activity, breathing abnormalities, salivation) but no deaths occurred during the 14 day recovery period and no obvious toxic effects were observed at necropsy (post mortem). An LC_{50} (rat) for DNAN aerosol over a 4 hr exposure period was estimated to be greater than 2000 mg/m^3 [18]. For subchronic inhalation of DNAN aerosol (i.e. repeated doses of various concentrations for 6 hrs/day for 2 weeks) it was found that concentrations of 1313 mg/m^3 resulted in excessive mortality and doses of 545 mg/m^3 resulted in 80% mortality and numerous clinical signs of toxicity. However, doses of 165 mg/m^3 showed only mild signs of toxicity after two weeks of exposure.[7] The inhalation toxicity of DNAN was attributed to irritation of mucosal surfaces [18].

To put this data into perspective, a typical melt-cast operation lasting 3 hours showed breathing zone DNAN concentrations of 0.017 to 0.14 mg/m^3 [18]. The reference concentration (RfC)[8] for DNAN was determined to be 0.14 mg/m^3, giving a safety margin of *ca.* x 1-10 [18].

The proposed OEL (operational exposure level) for PAX-21 was determined to be 0.35 mg/m^3, which is almost identical to that already established for Composition B (0.34 mg/m^3) [18]. Based on this study, the claimed lower toxicity of DNAN with respect to TNT is not supported by the acute oral exposure tests. No information is readily available on the chronic (long term exposure) effects of DNAN.

2.3 Thermal characteristics of DNAN and relevant DNAN mixtures

Differential Scanning Calorimetry (DSC) analysis was undertaken on DNAN and a range of DNAN mixtures, with particular emphasis on DNAN/MNA in order to determine its melting point behaviour, and to confirm that no chemical incompatibilities exist beyond 100°C with typical explosive ingredients that may not have been detected through the vacuum thermal stability tests (discussed in Section 2.4).

The DSC trace for RDX, MNA, DNAN, and TNT is shown in Figure 2. The melting point of dry DNAN[9] was found to be 95°C which is consistent with the published melting point [19],

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[7] Note that in all of the DNAN/acetone aerosol tests the role of acetone vapour in the observed results was not established.

[8] The reference concentration is the concentration (mg/m^3) to which the human population (including sensitive subgroups) can be exposed, on a daily basis, without appreciable risk of deleterious non-cancer health effects.

[9] Note that the DNAN used to determine the thermal properties in this study was dried through azeotropic distillation from benzene (Dean-Stark). It was found that DNAN (45 kg drum) supplied by

and considerably higher than TNT (79 °C). It should be noted that an early report [20] on DNAN concluded that it exists in two different crystal forms, one with a melting point of 86.9°C and a second with a melting point of 94.6°C. Dimorphism of this type has not been observed during this study.

DSC traces for a range of relevant 50:50 mixtures is shown in Figure 3, and augments the vacuum stability tests conducted in Section 2.4. The reduced melting point of DNAN in the presence of RDX (from 95 to 90 °C) indicates that RDX dissolves to some degree in the DNAN melt. This depression is more pronounced than with TNT (5°C *vs ca.* 1°C). The solubility of RDX in DNAN is explored briefly in Section 2.6. The temperature of the eutectic for DNAN/MNA was found to be 78.6°C. The eutectic temperature for DNAN/TNT was found to be 55.5°C.

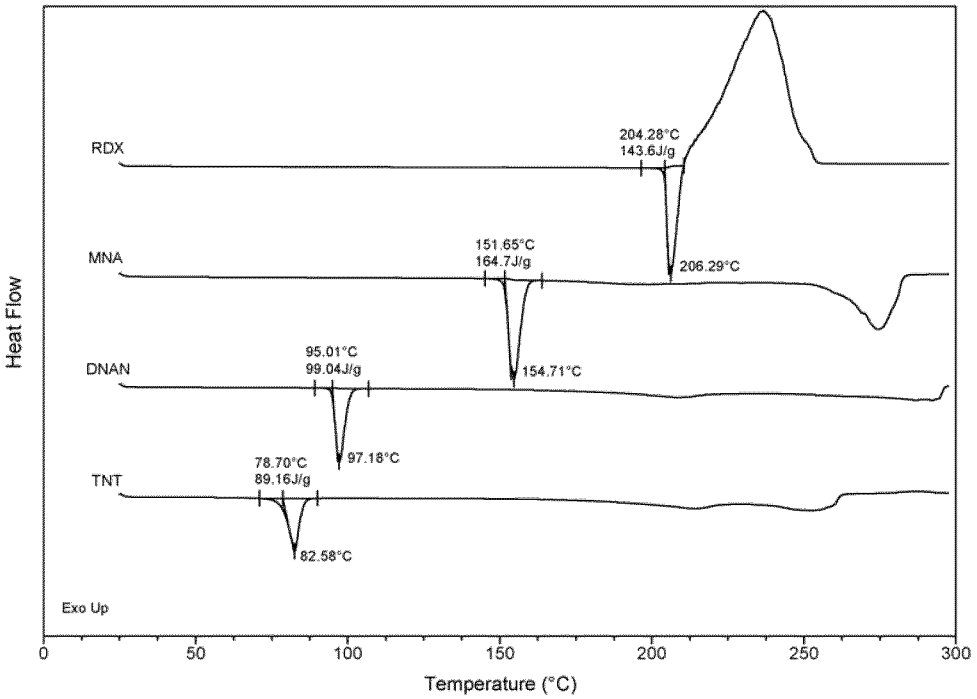

Figure 2. DSC for RDX, MNA, DNAN and TNT

BAe Systems Holsten (HAAP) contained 10-11 wt% water. For formulation work, DNAN was dried in an oven at 60°C for up to 2 weeks until (near) constant mass was reached, noting that DNAN also evaporates/sublimes slowly under these conditions.

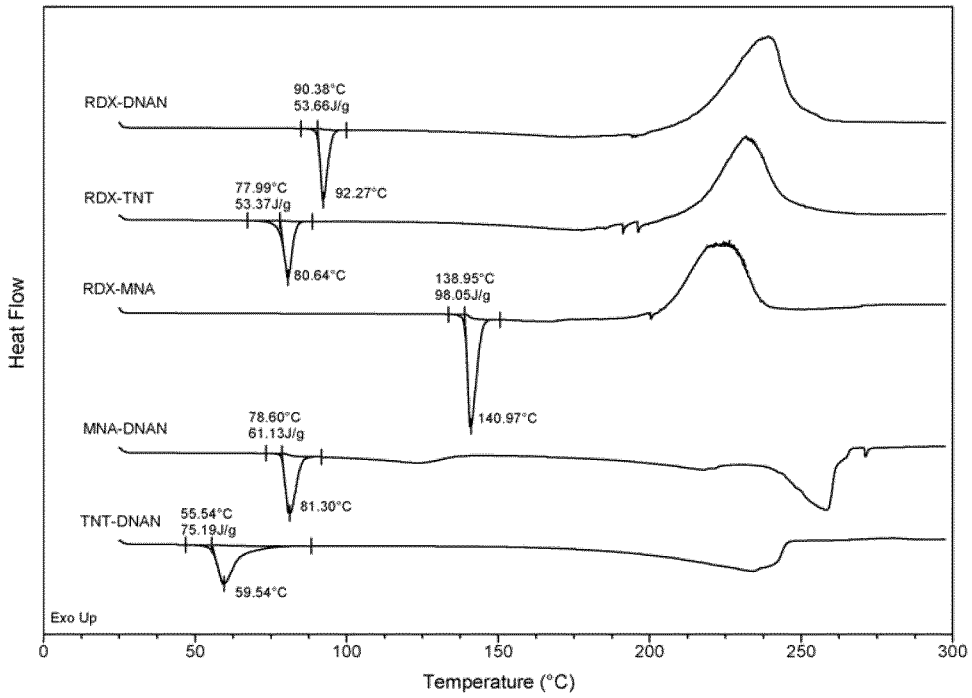

Figure 3. DSC for relevant 50:50 (wt/wt) mixtures

The impact on melt profiles when mixing MNA with DNAN over a range of concentrations is demonstrated in Figure 4. The eutectic composition assuming a simple two-phase relationship was determined through the correlation of eutectic fusion energies (Figure 5) and was found to be 82% DNAN: 18% MNA (by weight).

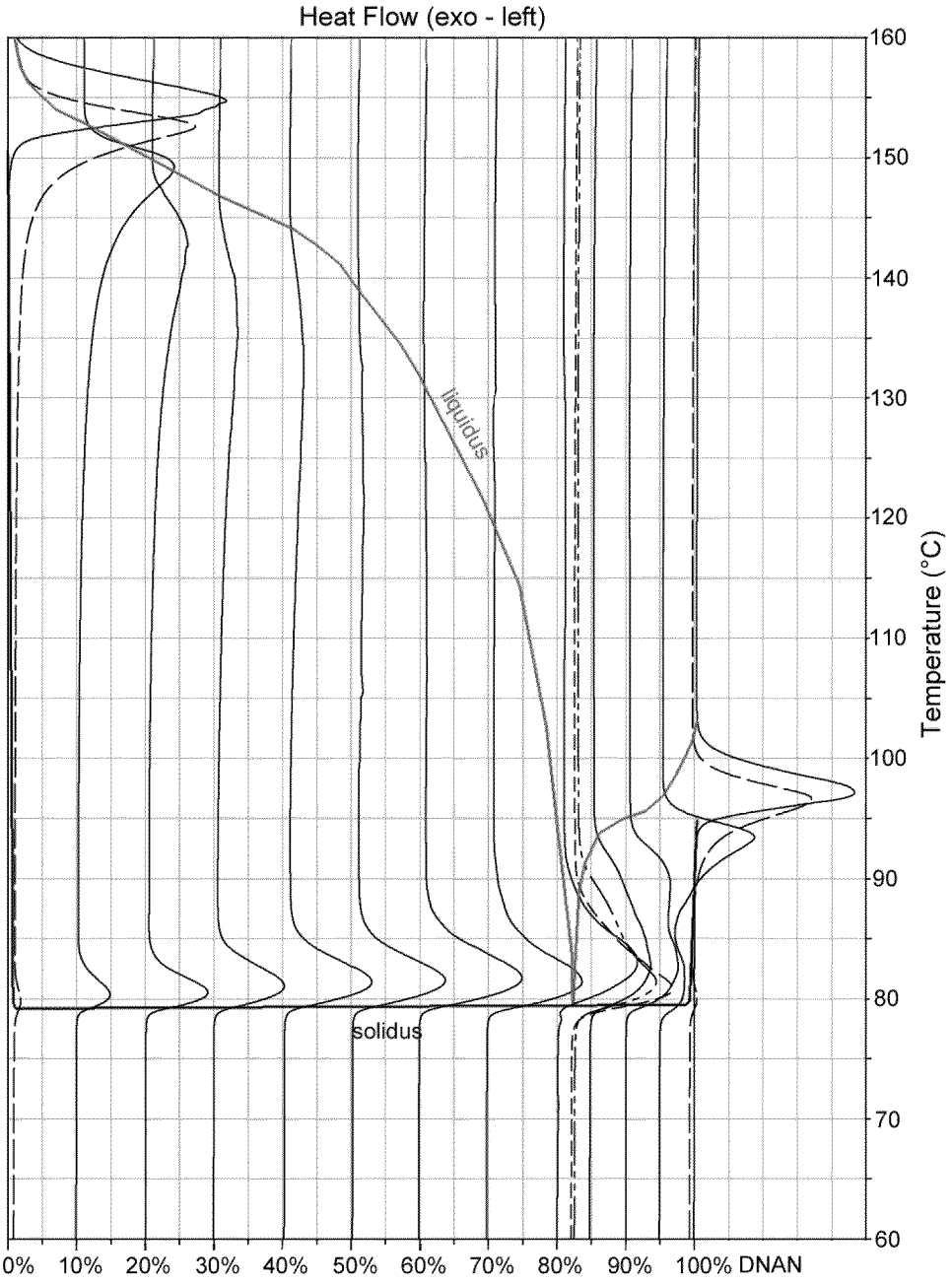

Figure 4. DSC traces for various mixtures of DNAN (by wt%) in DNAN/ MNA. Indicative phase diagram is shown by the liquidus (green) and solidus (red) lines.

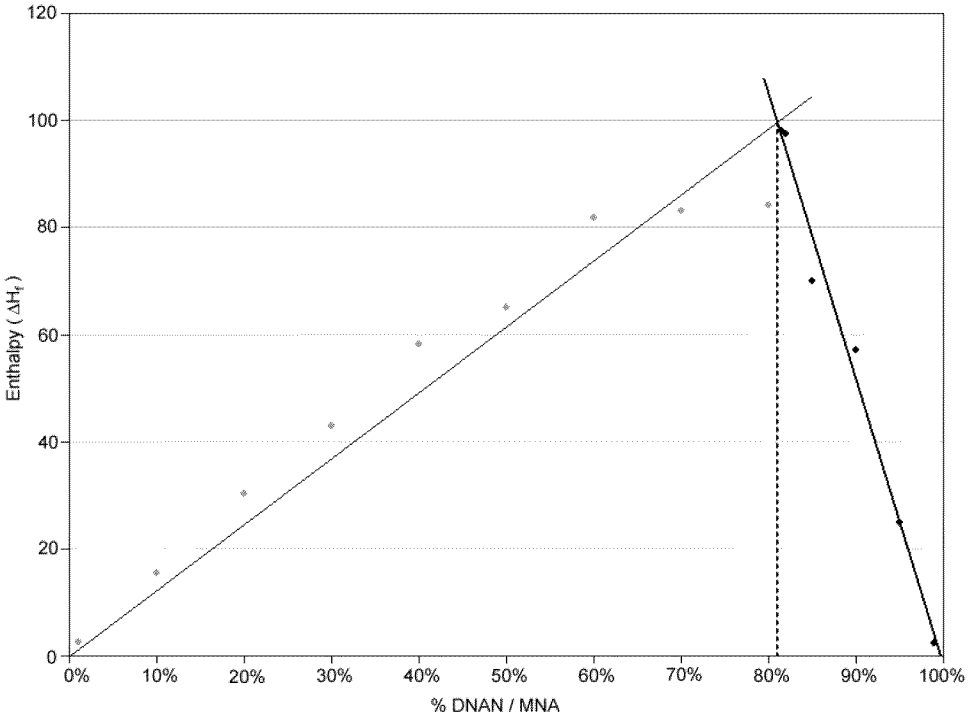

Figure 5. Plot of Enthalpy of Fusion (ΔH_f) vs %DNAN (by wt) in a mixture of DNAN/MNA showing the ΔH_f (eutectic) maxima at 82 (±1)% DNAN.[10]

The utilisation of MNA to depress the melting point of DNAN appears to be of limited use. In all DNAN/MNA mixtures a eutectic mass exists, however, in the proposed MNA concentrations of between 0.25 – 1% this mass is evidently small. Additionally the melting point of (non-eutectic) DNAN in a mixture containing 1% MNA was found to be reduced to only *ca.* 93 °C, and is therefore somewhat superfluous given that the melting point of DNAN can be lowered by 5°C through the addition of RDX alone. Other benefits may be derived from incorporating MNA into the melt-cast matrix (e.g. improved mechanical properties) but at present, and in lieu of further studies, there appears to be no clear advantage to its inclusion.

2.3.1 Sublimation/evaporation of DNAN

While the toxicological study [18], concluded that the vapour pressure of DNAN was not sufficient to cause concerns over inhalation of DNAN during melt-cast activities, we conducted confirmatory tests to determine the rate of evaporation of DNAN over a range of temperatures. The sublimation/evaporation was monitored via mass loss using isothermal TGA (Thermogravimetric Analysis) over several temperatures (Figure 6). The rate of evaporation at a given temperature is linear, ranging from -0.002 to -0.034 %/minute. Based

[10] Trendlines were fitted using the least squares method (in Microsoft Excel™).

on these rates and accounting for available surface area it is anticipated that DNAN at 95°C in a small mixer (with surface area of 1000 cm^2) would evaporate at a rate of ~ 2 mg/min. At 125°C, well over that anticipated for melt-cast operations, this rate would increase to 34 mg /min (approx. 17X). Assuming sufficient ventilation or exhaust systems are in place this quantity does not appear to pose any significant additional risk. The evaporation rate (reduction in vapour pressure) and the quantity of evaporated DNAN would be reduced even further through formulation.

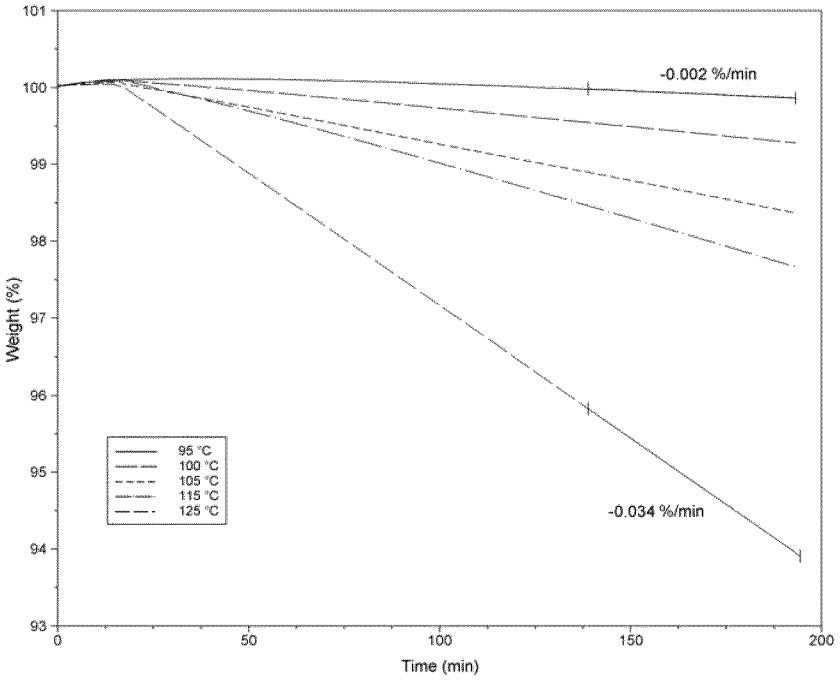

Figure 6. Sublimation/evaporation of DNAN at elevated temperature via Isothermal TGA.

2.3.2 Temperature of Ignition

The temperature of ignition (T of I) for DNAN, MNA and a number of relevant 1:1 energetic combinations were determined and results shown in Table 2. 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 even when compared to the most thermally reactive of the two materials (TNT). This is consistent with the formation of a DNAN/ TNT adduct (see Section 2.4).

Table 2. Temperature of Ignition (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 +0.25% MNA)	220
TNT (Lot 0050/00)	306
DNAN/RDX (1:1)	211
MNA/RDX (1:1)	201
DNAN/TNT (1:1)	266

To confirm the T of I for ARX 4027 the TGA at 10°C/min indicates mass loss occurs rapidly beyond 220°C, reaching a peak mass-loss rate at 235°C (Figure 7). This is broadly consistent with the T of I results.

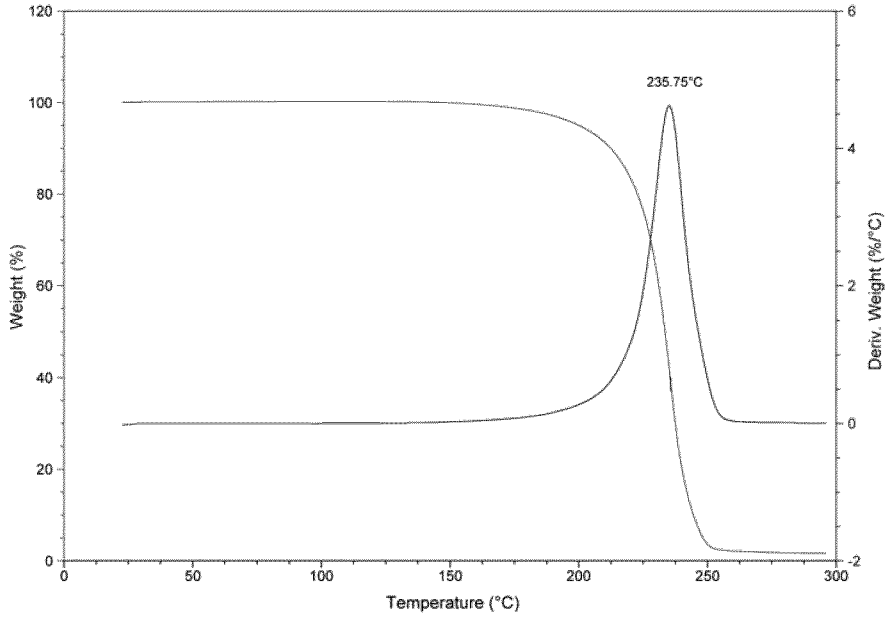

Figure 7. TGA of ARX 4027 (m1)

2.4 Compatibility of DNAN with relevant materials

DNAN has been shown to react with amines and other nucleophiles under a range of conditions via both aromatic nucleophilic substitution, leading to cleavage of the aryl-oxygen bond, and aliphatic nucleophilic substitution (S_N2) leading to cleavage of the alkyl-oxygen bond [19].

DNAN readily forms Meisenheimer complexes as both stable compounds (see, for example, Figure 8) and as intermediates during aromatic nucleophilic substitution reactions. Complexes form when reacted with nucleophilic (basic) materials including amines, alkoxide anions, $NaBH_4$ and $NaNH_2$ [21-28]. The explosiveness of some Meisenheimer complexes has been explored previously [29], however, no information has yet been found detailing the explosive properties, especially sensitiveness, of similar DNAN derived Meisenheimer complexes. It is therefore better to eliminate contact between DNAN and nucleophilic media during formulation and clean-up activities.

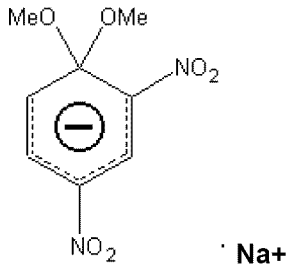

Figure 8. Example Meisenheimer complex, 6,6-dimethoxy-1,3-dinitro-1,3-cyclohexadiene anion, formed by reaction with methoxide under anhydrous conditions (see for example [25]).

2.4.1 Vacuum Thermal Stability

Vacuum thermal stability tests were conducted to determine the compatibility of DNAN with materials used in the formulation of ARX-4027[11], specifically MNA and RDX. TNT was of interest due to the potential for cross-contamination in DSTO melt-cast bays. DNAN has been shown to form stable complexes (adducts) with TNT during solidification of the melt in both 1:1 and 1:8 DNAN/TNT molar ratios [30]. These complex adducts are sufficiently long lived (stable) to enable grinding, processing and powder diffraction studies. The nature of these adducts has not been determined but $\pi - \pi$ stacking interactions are likely.

Table 3 shows 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.[12]

[11] 60% RDX, 39.75% DNAN, 0.25% MNA.

[12] Upon completion of this test the resulting red liquid did not solidify for 2 days but crystallised quickly after agitation showing evidence of supercooling. The resulting solid was a brown/red colour. The melting point of the 50:50 (wt/wt) mix was found to be 55.5°C.

Table 3. Vacuum thermal stability test results for relevant mixtures

Mixtures (50/50 wt/wt)	Gas evolution	Observation
DNAN/RDX	0.06 ml/g	Satisfactory
DNAN/MNA	0.07 ml/g	Satisfactory
DNAN/TNT	0.06 ml/g	Formation of deep red liquid
RDX/MNA	0.12 ml/g	Satisfactory

2.5 Sensitiveness to Impact, Friction and Electrostatic Discharge

The impact and friction sensitiveness were determined using Rotter Impact Test and the Julius Peters BAM friction test. The results of these tests together with the Electrostatic Discharge (ESD) test results are provided in Table 4. The impact sensitivity of DNAN in both the pure form (and with grit added) is very low (Figure of Insensitiveness >220).[13] The impact sensitivity of ARX-4027 is slightly lower than Composition 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 was found to be more fiction sensitive than TNT.

Table 4. 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	4.5
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
Composition 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

2.6 Solubility of RDX in DNAN

As evident 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 9. While further work is required it is anticipated that the solubility of RDX at the RDX/DNAN eutectic (~ 90°C) is approximately 7 g per 100 g of DNAN. This degree of solubility is greater than RDX in TNT (4.4 g at 80°C [2]) but is not expected to be a problem in formulations incorporating large quantities of RDX.

[13] 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.

Cooling of a solution of RDX in DNAN (liquid) yields plate-like RDX crystals[14] (see Figure 10). The impact of this on shock sensitivity is not yet known. While this is readily avoided by the use of large RDX quantities, where recrystallisation on available RDX surfaces is thermodynamically favoured, in formulations that use a small quantity of RDX, to increase the shock sensitivity, care should be taken. RDX should be added at a point that minimises dissolution (i.e. not added first to the DNAN melt).

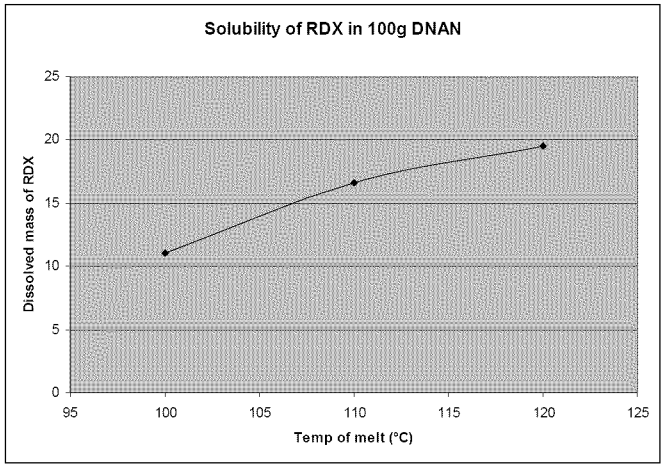

Figure 9. Solubility of RDX in DNAN

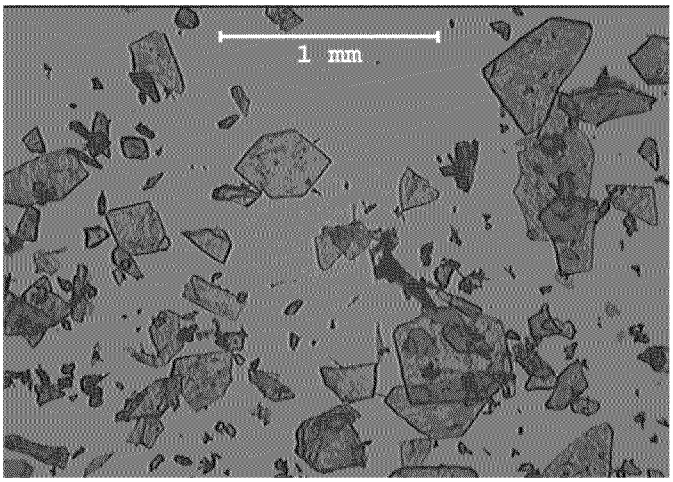

Figure 10. Micrograph of RDX plates recrystallised from DNAN. Typical crystals were 0.01 - 0.02 mm thick.

[14] A solid melt-cast material formed from a DNAN/RDX melt in which the RDX was fully dissolved, was triturated with cold benzene to dissolve away the DNAN matrix, leaving the relatively insoluble RDX crystals, which were filtered and washed with cold benzene.

3. Formulation of ARX-4027

As discussed in previous sections, a simple test formulation, namely ARX-4027 (comprising 39.75% DNAN, 60% RDX and 0.25% MNA) was developed in order to conduct an assessment of the efficacy of utilising DNAN in melt-cast formulations. Two modifications were prepared, specifically ARX 4027m1 utilising 60% Type 1 Class 1 (Grade A) RS-RDX (ADI)[15] and ARX 4027m2 incorporating 60% Type 2 Class 1 RDX. The two modifications were prepared in order to determine the impact of including reduced sensitivity (RS) and non-RS RDX in a DNAN melt-cast formulation. Both formulations are characteristically bright yellow as shown in Figure 11. This bright yellow colour is due to MNA, a very highly coloured material rather than DNAN, which is pale yellow in comparison.

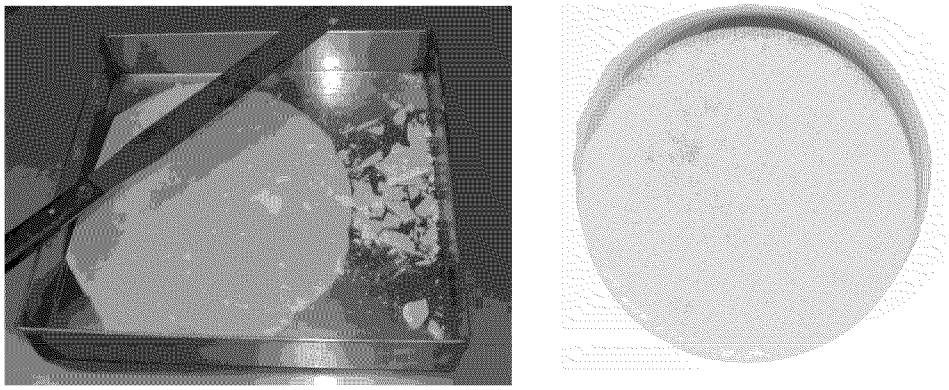

Figure 11. ARX-4027 poured into and cooled in a steel pan (left), and a 1-inch disc cut from a stick of ARX 4027 (right).

3.1 SEM imagery

The SEM images (Figure 12 and Figure 13) of cross-sectioned ARX-4027m1 and m2 show good incorporation of RDX within the DNAN matrix. No significant observable differences were seen between the two modifications. 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 high degree of inter-molecular interaction during the cooling process. The DNAN matrix (seen as the darker patches in the SEM) was found to be homogenous and microcrystalline.

[15] Reduced Sensitivity RDX (RS-RDX), also known as Insensitive RDX (I-RDX™) is a new RDX variant that imparts reduced sensitivity to shock stimulus.

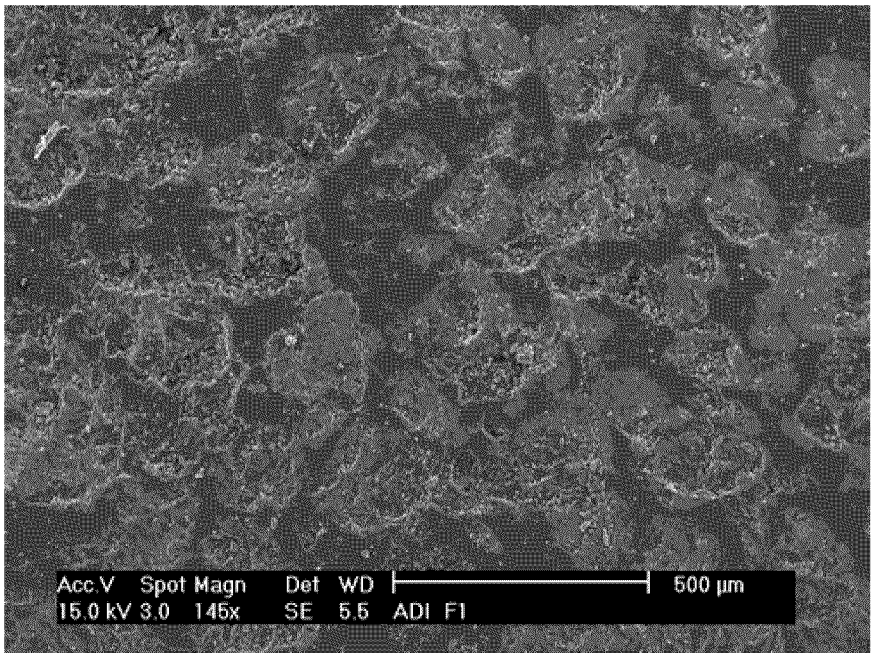

Figure 12. SEM image of ARX-4027m1

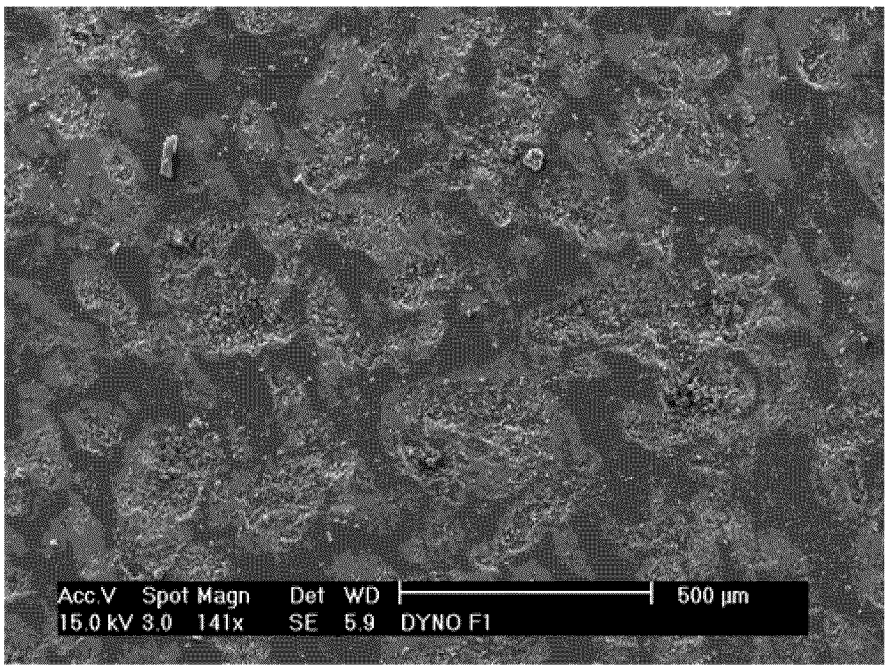

Figure 13. SEM image of ARX-4027m2

3.2 ARX 4027 Viscosity and Sedimentation of RDX

Figure 14 shows that the viscosity of ARX-4027 is lower than Composition B, which is not surprising considering the lower density of DNAN compared to TNT (1.35 *c.f.* 1.63 gcm^{-3}).[16] While there was scope to introduce higher levels of RDX than explored here, this formulation was deemed appropriate for comparison with Composition B.

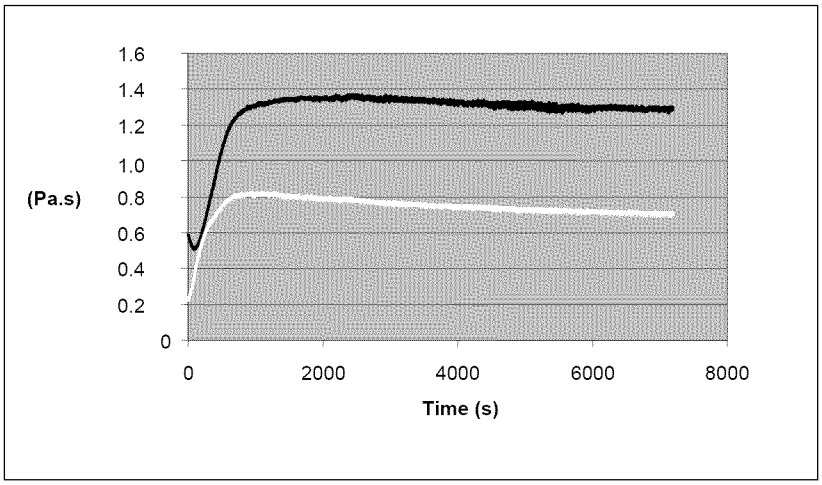

Figure 14. Viscosity profile for ARX-4027 (yellow) and Composition B (blue)

The non-optimisation of the ARX-4027 formulation led to a small amount of RDX sedimentation in the DNAN matrix, which was evident upon cooling (see Figure 15). No discernible difference between the RDX types was observed. In future, higher loadings of RDX will reduce the propensity for RDX settling. Higher loadings of RDX have already been demonstrated in PAX 41, which contains 65% RDX in bimodal distribution, and incorporates ultra-fine RDX material produced via a fluid energy mill [31].

[16] DNAN has a lower density than TNT. Assuming a small density change between the solid and liquid states, it follows that the same mass of material will take up a larger volume leading to a greater fluid to solid ratio than in TNT (for an equivalent mass %).

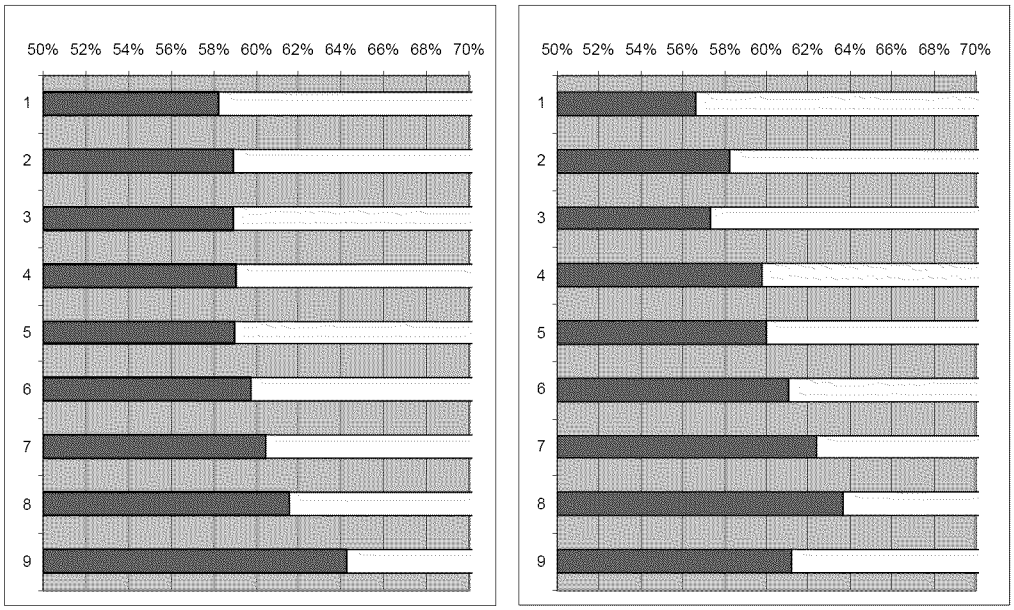

Figure 15. Percent composition (RDX = blue; DNAN = cream) of ARX-4027m1 (left) and m2 (right) along a 25.4 x 200 mm cylinder- using 20 mm long samples. The y axis represents 9 sectioned charges (20 mm length), with 9 at the bottom.

3.3 Mechanical strength of ARX-4027

The mechanical strengths of ARX 4027m1 and m2, relative to Composition B were determined on an Instron 5500 (R1185) Universal Testing Machine. Testing was undertaken at 23°C (room T) using an established method [32]. The test involved the compressive loading of 20 mm long cylinders of ARX-4027, cut from a 200 mm long 1-inch diameter stick. Samples from the bottom, middle and top sections were tested. No significant difference in mechanical strength was found between the various sections, despite the slight variation in DNAN/RDX composition due to sedimentation.

Table 5. Mechanical testing results for ARX 4027 relative to Composition B

	ARX-4027m1	**ARX-4027m2**	**Composition B**[a]
Compressive load at yield [zero slope] (kN)	11.60 (0.53)[b]	10.47 (0.45)	7.23 (0.11)
Compressive stress at yield (MPa)	22.89 (1.05)	20.67 (0.88)	-
Modulus (MPa)	1878.2 (31.9)	1462.6 (214.8)	1607.1 (23.8)
Compression at yield [t_0 = 500 N] (mm)	0.28 (0.009)	0.34 (0.015)	0.23 (0.010)

[a] Taken from Smith and Lu [32].

[b] Standard deviation shown in brackets.

ARX-4027m1 and m2 have (statistically) comparable strengths. In both cases ARX-4027 shows significantly higher compressive strength than Composition B. Compression (mm) at yield

and modulus, which provide an indication of brittleness, appears to be similar to Composition B.

4. Shock Sensitivity and Performance of ARX-4027m1/m2

4.1 Shock sensitivity of ARX-4027

In order to determine if the shock sensitivity of RS-RDX is retained in a DNAN based melt-cast explosive, the shock sensitivity of ARX 4027m1 and m2 was measured using the large scale gap test (LSGT) [33]. While DNAN is presently classified as a Class 4.1 Flammable Solid, initial shock sensitivity testing on cast DNAN utilising the UN Series 2 Gap Test revealed that DNAN could be detonated when the shock attenuator (50 mm PMMA spacer) was removed [34]. This led us to conduct LSGT tests on pure DNAN in addition to ARX-4027. The results of the LSGT are shown in Table 6.

Table 6 LSGT results for ARX-4027m1/m2 and DNAN

Material	Gap cards (mm)	GPa
DNAN	71 (18)	7.02
TNT (poured clear)	150 (38)	3.51
ARX-4027m2	184 (47)	2.62
ARX-4027m1 (RS-RDX)	202 (51)	2.24
Composition B	181 (46)	2.69

As in Composition B, the reduced shock sensitivity of RS-RDX is *not* retained in the DNAN matrix. Non-RS-RDX gives slightly higher initiation pressure results than the RS-RDX. Not unexpectedly, pure DNAN was found to have an extremely low shock sensitivity (7.02 GPa) even when compared to TNT (3.51 GPa) [33].

4.2 Performance of ARX-4027m1/m2

The velocity of detonation (VoD) and Chapman Jouget pressure (P_{CJ}, detonation pressure) for ARX-4027m1 and m2 were determined using a DSTO designed VoD circuit-board[17] in the High Explosive Firing Chamber (HEFC). Unconfined charges of dimensions 220 mm long x 25.4 mm diameter were cast for ARX-4027m1, ARX-4027m2, and pure DNAN. VoD for each formulation was measured in triplicate. Each shot was boosted with a 25.4 mm x 25.4 mm diameter (21.6 g) Pentolite booster (50:50 PETN:TNT) and initiated using an RP 501 EBW detonator.

[17] DSTO's VoD circuit-board provides a ten point (10 points each at 20 mm spacing) mechanism to determine the rate of passage of the detonation front. The system is attached parallel to, and on the outer surface of, the charge. 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. Errors are less than 1% standard deviation of the mean (between each of the nine timing points), which are typical of the technique, and provide some confirmation that steady state velocity has been achieved.

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 [35, 36]. The experimental and modelled VoD results are shown in Table 7. Good agreement was found between experimental and modelled VoD results. No detonation of unconfined DNAN occurred in the experimental tests indicating that the critical diameter of DNAN is larger than 25.4 mm. The VoD for ARX-4027 is lower than that found for Composition B. This is not unexpected as the loading (by volume) of RDX is lower in ARX-4027 than Composition B, and DNAN has lower performance than TNT. Altogether these results are promising. Higher loading of RDX will bridge this gap to some degree.

P_{CJ} was estimated via dent depth tests (concurrently with VoD measurements). Shots were fired onto a mild steel witness plate (50mm thick) and referenced to Composition B charges of identical dimensions [35, 36]. Witness plates were sourced from a single batch of 1018 cold rolled mild steel, Rockwell hardness B-74 to B-76 [37]. Dent depths were measured on a Sheffield Endeavor coordinate measuring machine (Model 9.12.7). For calibration standards, a series of Composition B charges (identical dimensions to ARX-4027 charges) were fired to give an average depth dent of 4.55 mm. The experimentally derived detonation pressures were compared to calculated detonation pressures via CHEETAH V2.0 and all show good correlation (see Table 7).

Table 7 Experimental and calculated performance parameters (averaged values from 3 runs)

Formulation	Experimental VoD, (m/s)	Calculated VoD, (m/s)	Experimental P_{CJ},[a] GPa	Calculated P_{CJ},[b] GPa
DNAN	-	5344	-	9.51
ARX-4027m1 (RS-RDX)	7356 (1.0%)[c]	7296	21.64	20.94
ARX-4027m2 (Dyno RDX)	7398 (1.1%)	7296	22.47	20.94
Composition B	7843 (1.2%)	7630	24.55	24.77

[a] based on dent depth measurements and referenced to Composition B

[b] CHEETAH V2.0

[c] % standard deviation in brackets ().

5. Summary and Conclusions

The thermal properties of DNAN and the binary phase data for DNAN/MNA have been determined. No obvious and significant benefit was observed for the use of small quantities of MNA (as a processing agent) in simple DNAN formulations. The thermal properties of DNAN in the presence of other ingredients were determined by DSC in support of the vacuum thermal stability data; no chemical compatibility issues were evident with typical ingredients. A potential incompatibility with TNT was observed, however, this only poses a risk if contamination by TNT is a possibility during processing activities. It is anticipated that

further studies will enable mitigation of this risk. Isothermal TGA studies show that the evaporation rate at typical melt-cast temperatures is low, which supports the conclusions of a previous external toxicological study. An initial indication of the solubility of RDX in molten DNAN has been determined and was found to be slightly higher than RDX in TNT.

A simple Composition B analogue, namely ARX-4027 (comprising 60% RDX, 39.75% DNAN and 0.25% MNA) was developed in order to determine typical mechanical, viscoelastic and explosive properties. The mechanical strength was found to be greater than Composition B. The viscosity profile at 100°C was lower in comparison to Composition B and reasonable sedimentation properties were observed. More formulation work needs to be undertaken to address optimisation of RDX loading in DNAN through the use of multimodal RDX blends. Performance of ARX-4027 was *ca.* 5% lower than that of Composition B, however, increased loading (a further 5-10%) of RDX will bridge this gap.

The shock sensitivities for two variations of ARX-4027, one incorporating reduced sensitivity-RDX (RS-RDX) and another incorporating normal (non-RS) RDX, were measured. Results showed that the insensitiveness of RS-RDX is not retained under typical casting conditions. Further research into the effect of the solubilisation of RDX in molten DNAN may contribute to the characterisation and better understanding of RS-RDX. While the shock sensitivity of RS-RDX does not appear to be retained, the general insensitiveness of the formulations to accidental stimuli (impact, friction, thermal initiation and electrostatic discharge) is excellent.

In conclusion, DNAN was found to be a potentially suitable replacement for TNT in melt-cast explosive formulations. While thermal properties are (arguably) not as ideal as those of TNT for processing in current melt-cast facilities (e.g. higher melting point), no insurmountable barriers to technology transfer were observed.

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7. References

1. Australian Defence Force (2005) *Defence Instruction (General) Logistics 07-10, Insensitive Munitions (DI(G)-LOG 07-10)*, Canberra, Australia.

2. Fedoroff, B. T. (1960) *Encyclopedia of Exposives and Related Items*, Picatinny Arsenal, Dover, New Jersey, Vol. 3, C616.

3. Fedoroff, B. T. (1958) *Dictionary of Explosives, Ammunition and Weapons (German Section)*, Picatinny Arsenal Technical Report 2510.

4. Chudgar, R. J. and Oakes, J. (2003) *Kirk-Othmer Encyclopedia of Chemical Technology - Section on Azo Dyes*, John Wiley & Sons, Inc.

5. Nelson, A. A. (1948) *Toxicological investigations of compounds proposed for use as insect repellents. C. Pathological examination*, J. Pharmacology and Experimental Therapeutics, **93** 26-39.

6. Wöhler, L. and Wenzelberg, I. O. (1933) *Neues zur Schlagempfindlichkeit der Explosivstoffe (New test for impact sensitivity of explosives)*, Angewandte Chemie, **46** p.175.

7. Nicolich, S., Niles, J., Ferlazzo, P., Doll, D., Braithwaite, P., Rausmussen, N., Ray, M., Gunger, M., and Spencer, A. (2003) *Recent developments in reduced sensitivity melt pour explosives*, 34th Int. Ann. Conf. of ICT, Karlsruhe, Germany, 24-27th June, 135(1)-135(21).

8. Doll, D. W., Hanks, J. M., Allred, A. G., and Niles, J. B. (2003) *Reduced-sensitivity, melt-pourable explosives based on non-TNT nitroaromatic compounds as replacements for Tritonal*, US Patent No. 2003140993.

9. Doll, D. W., Hanks, J. M., Allred, A. G., and Niles, J. B. (2003) *Melt-pourable explosive compositions, with reduced sensitivity and decreased toxicity, for TNT substitutes*, US Patent No. 2003005988.

10. Doll, D. W., Hanks, J. M., Highsmith, T. K., and Lund, G. K. (2001) *Reduced sensitivity melt-cast explosives*, US Patent No. 2001046092.

11. Niles, J. (2003) *PAX-21, PAX-25 and PAX-28: A Family of New Low Cost Insensitive Melt Pour Explosives*, 6th Australian Explosive Ordnance Symposium, 29th– 31st October, Canberra, Australia.

12. Niles, J. and Doll, D. (2001) *Development of a practical reduced sensitivity composition B replacement*, 32nd Int. Ann. Conf. of ICT, Karlsruhe, Germany, 3-6th July, 28(1)-28(8).

13. Niles, J., Nicolich, S., Doll, D., and Rasmussen, N. (2004) *Mitigating Shaped Charge Jet Impact on Munitions, Insensitive Munitions & Energetic Materials Technology Symposium (IMEMTS 2004)*, 15-17th November, San Francisco, CA.

14. CRC Press, (2005) *Handbook of Chemistry and Physics.*

15. Cao, R. and Mei, D. (1994) *Study of nucleophilic aromatic substitution reaction - study of the etherification of 2,4-dinitrochlorobenzene,* Xi'an Jiaotong Daxue Xuebao **28**(8) 7-11.

16. Kangda Chemical Co. Ltd. (2006) http://www.kangdachem.com/.

17. U.S. Department of Health and Human Services (1995) *Toxicological Profile for Dinitrophenols.*

18. Dodd, D. E. and McDougal, J. N. (2002) *Recommendation of an Occupational Exposure Level for PAX-21,* AFRL-HE-WP-TR-2001-0103.

19. Nudelman, N. S. and Palleros, D. R. (1981) *Reactions of Nitroanisoles. Part 2. Reactions of 2,4- and 2,6-Dinitro-anisole with piperidines in Benzene,* J. Chem. Soc. Perkin Trans. **2** 995-999.

20. van Alphen, J. (1930) *Dimorphism of 2,4-dinitroanisole,* Chem. Ber. **63B** 94-95.

21. Ohsawa, S. and Takeda, M. (1980) *Effect of solvation on Meisenheimer complex,* Ibaraki Daigaku Kogakubu Kenkyu Shuho **28** 101-112.

22. Gold, V., Miri, A. Y. and Robinson, S. R. (1980) *Sodium borohydride as a reagent for nucleophilic aromatic substitution by hydrogen: the role of hydride Meisenheimer adducts as reaction intermediates,* J. Chem. Soc. Perk. Trans. 2: Phys. Org. Chem. **2** 243-249.

23. Terrier, F. and Millot, F. (1980) *Trifluoromethylsulfonyl Meisenheimer complexes. II. Interaction of methoxide ion with nitro(trifluoromethylsulfonyl)anisoles and 2,4-bis(trifluoromethylsulfonyl)anisole,* Nouveau Journal de Chimie **4**(4) 255-259.

24. Bernasconi, C. F. and Gandler, J. R. (1977) *Intermediates in nucleophilic aromatic substitution. 17. Kinetics of spiro Meisenheimer complexes. Effect of ring size,* J. Org. Chem. **42**(21) 3387-3393.

25. Olah, G. A. and Mayr, H. (1976) *Carbanions. II. Carbon-13 nuclear magnetic resonance study of Meisenheimer complexes and their charge distribution pattern,* J. Org. Chem. **41**(21) 3448-3451.

26. Bowden, K. and Cook, R. S. (1971) *Reactions in strongly basic solutions. III. Correlation of the rate of alkaline hydrolysis of 1-substituted 2,4-dinitrobenzenes in aqueous methyl sulfoxide with an acidity function. Mechanistic path,* J. Chem. Soc. Section B: Phys. Org. **9** 1771-1778.

27. Bernasconi, C. F. (1968) *Intermediates in nucleophilic aromatic substitution. I. Temperature jump study of the decomposition of 1,1-dimethoxy- 2,4-dinitrocyclohexadienate in methanol,* J. Am. Chem. Soc. **90**(18) 4982-4988.

28. Byrne, W. E., Fendler, E. J., Fendler, J. H., and Griffin, C. E. (1967) *Intermediates in nucleophilic aromatic substitutions. I. Meisenheimer complexes of dinitro-substituted aromatic ethers,* J. Org. Chem. **32**(8) 2506-2511.

29. Norris, W. P., Spear, R. J., and Read, R. W. (1983) *Explosive Meisenheimer complexes formed by addition of nucleophilic reagents to 4,6-dinitrobenzofurazan 1-oxide,* Aust. J. Chem. **36**(2) 297-309.

30. Burkardt, L. A. (1956) *X-ray powder diffraction data of some molecular complexes of TNT,* Anal. Chem. **28** 1271-1273.

31. Nicolich, S., Niles, J., Doll, D., Ray, M., Gunger, M., and Spencer, A (2003) *Development of a Novel High Fragmentation/High Blast Melt Pour Explosive, Insensitive Munitions and Energetic Materials Technology Symposium, (IMEMTS 2003),* 10-13th March, Orlando, Florida, USA.

32. Smith, M. and Lu, J. P. (2004) *Aging of the Insensitive Explosive, ARX 4024,* DSTO-TN-0586.

33. Wolfson, M. G. (1994) *A Large Scale Gap Test at MRL for Measuring Shock Sensitivity of Explosives Fillings for Insensitive Munitions,* MRL-TR-93-43.

34. Provatas, A., Davies, P. J., and Franson, M. D. (2006) *Implementation of the UN Series 2(a) Gap Test for Use with Explosives,* DSTO-TN-0703.

35. Lu, J. P. (2001) *Evaluation of the Thermochemical Code - CHEETAH 2.0 for Modelling Explosives Performance,* DSTO-TR-1199.

36. Fried, L. E., Howard, W. M., and Souers, P. C. (1998) *CHEETAH 2.0 User's Manual,* UCRL-MA-117541 Rev. 5.

37 Smith, L.C. (1967) *On Brisance, and a Plate-Denting Test for the Estimation of Detonation Pressure,* Explosivstoffe, **5/6** 106-110/130-134.

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Characterisation of 2,4-Dinitroanisole: An Ingredient for use in Low Sensitivity Melt-cast Formulations

Phil J. Davies and Arthur Provatas

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Insensitive munitions, Casting, Formulations, Characterisation

19. ABSTRACT

In recent years TNT has fallen out of favour as an ingredient in melt-castable explosive formulations due to its demonstrated failure to meet sensitivity requirements, and alternatives with suitable chemical and physical properties have been sought. 2,4-Dinitroanisole (DNAN) is a promising alternative that prima facie appears to possess adequate properties and, by virtue of reduced sensitivity, may enable the development of a new class of low sensitivity melt-cast formulations for use in Insensitive Munitions (IM). This paper provides a baseline characterisation of DNAN and includes the determination of the sensitivity and explosive properties of a simple DNAN-based formulation (ARX-4027) analogous to Composition B. Key properties that impact upon the use of DNAN in melt-cast formulations are identified.