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Review

Review of the Essential Characteristics of 2,4-Dinitroanisole

Jun-jiong Meng¹⁾, Lin Zhou²⁾, Fei-chao Miao^{3,*})

¹⁾ *Composite Explosive Research Department, Xi'an Modern Chemistry Research Institute, Xi'an 710065, China*

²⁾ *State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China*

³⁾ *School of Chemical Engineering, Anhui University of Science and Technology, Huainan 232001, China*

* *E-mail: miaofeichao@qq.com*

Abstract: With the development of weapons and ammunition to achieve more powerful and safer functional systems, 2,4-dinitroanisole (DNAN), used as an insensitive melt-cast matrix explosive, has received widespread attention. Various countries have conducted significant research and developed a series of DNAN-based explosive formulations in recent years. However, some inherent limitations of DNAN have enormously restricted its comprehensive application in weapons. In this paper, the progress of DNAN research in recent years is systematically reviewed from the aspects of its essential characteristics, such as physical properties (melting point, shrinkage, irreversible expansion, solubility, and mechanical properties), sensitivity and safety, stability, compatibility, and oxygen balance and energy. The advantages and disadvantages of DNAN are analyzed, and methods to solve these limitations are described. Furthermore, several important directions to be studied in future research are highlighted, including the study of DNAN binary eutectic mixtures mechanisms, control of crystal transformation, and improvements in mechanical properties.

Keywords: 2,4-dinitroanisole, DNAN, binary eutectic mixture, irreversible expansion, physical properties, crystal transformation

1 Introduction

Melt-cast explosives have the advantages of high energy, simple technology, low cost, and singular adaptability to various kinds of specially shaped charges, resulting in significant application demand in weapons and ammunition equipment [1]. At the beginning of the 20th century, 2,4,6-trinitrotoluene (TNT) based melt-cast explosives were widely recognized in the military field and began to be loaded in large numbers of explosively formed projectile (EFP) warheads, antipersonnel warheads, demolition warheads, penetrating warheads, and torpedoes [2]. However, with the increasing attention to weapons safety in modern warfare, the development of insensitive, thermally stable and high performance munitions is a key current research activity in explosives research. In an effort to increase insensitive munitions technology options, the search for alternative ingredients has driven researchers to explore new insensitive explosive formulations.

The organic compound 2,4-dinitroanisole (DNAN, 1-methoxy-2,4-dinitrobenzene) is a type of insensitive melt-cast matrix explosive currently being widely studied and applied [1]. DNAN was first synthesized in 1849 and used primarily as an insecticide and dye ingredient at that time [3]. Because of the lack of TNT in World War II, Germany was the first to use DNAN as the main charge ingredient in Amatol 40 (50% DNAN, 35% ammonium nitrate (AN), 15% hexogen (RDX)) in the warheads of V-1 flying bombs [3]. However, because the energy of DNAN is relatively low, it was rarely used after World War II. With the development of insensitive ammunition in the United States and Europe, this typically insensitive energetic material has attracted renewed attention. The advantages of DNAN are mainly [4, 5]:

- better shock sensitivity and thermal safety than TNT,
- categorization by the UN classification of dangerous goods as a Class 4.1 “Flammable Solid,” while TNT is in Class 1.1 “Explosives”, resulting in less strict transportation requirements and lower storage costs for DNAN compared to TNT,
- less harmful to the human body and the environment than TNT [6-8].

At present, substantial progress has been made in the research of DNAN-based melt-cast explosives. DNAN-based insensitive melt-cast explosives have been developed by many organizations, including US Army Armament Research and Development Engineering Center (ARDEC), Defence Science & Technology Organisation (DSTO) Australia, High Energetic Materials Research Laboratory (HEMRL) India, and General Dynamics-Ordnance and Tactical Systems (GD-OTS) Canada. Among these, IMX-101 (43% DNAN, 20% 3-nitro-1,2,4-

triazol-5-one (NTO), 37% nitroguanidine (NQ)) and IMX-104 (32% DNAN, 53% NTO, 15% RDX) have been included in artillery projectiles, tank high explosive rounds, field mortar and mortar systems by the US military [9-11]. However, because of some inherent limitations of DNAN, such as low energy, evident irreversible expansion, and poor mechanical properties, DNAN-based melt-cast explosives may still have some charge quality problems, which have seriously restricted its popularity and application in large-caliber and penetrating warheads. It is critical to have a comprehensive understanding of the essential characteristics of DNAN in order to solve these problems completely.

In the present paper, the latest research on the physical properties (melting point, shrinkage, irreversible expansion, solubility, and mechanical properties), sensitivity and safety, stability and compatibility, and oxygen balance and energy of DNAN are investigated and reviewed. Through analysis, induction, and collation, methods to overcome these deficiencies are addressed, and key directions for future research are discussed.

2 Performance Comparison

Table 1 presents a performance comparison between DNAN and TNT. From Table 1, DNAN is superior to TNT in terms of safety, viscosity, and exudation. However, DNAN has the disadvantages of lower oxygen balance, lower density, lower energy, higher melting point, higher shrinkage rate, and higher irreversible expansion, which can be improved by optimizing the formulation and molding techniques.

Table 1. The performance comparison between DNAN and TNT

Property	DNAN	TNT	Ref.
Chemical formula	$C_7H_6N_2O_5$	$C_7H_5N_3O_6$	[12]
Formula mass	198.133	227.131	
Oxygen balance [%]	-97	-74	
Melting point [°C]	94.6	80.9	
Crystalline density [$g \cdot cm^{-3}$]	1.544	1.654	
Liquid-phase density [$g \cdot cm^{-3}$]	1.35	1.45	[13]
Critical diameter [mm]	>82.55	13.97-26.92	[14]
Detonation velocity [$m \cdot s^{-1}$]	5974 (1.54 $g \cdot cm^{-3}$)	6970 (1.65 $g \cdot cm^{-3}$)	[15]
Detonation pressure [GPa]	9.5 (1.54 $g \cdot cm^{-3}$)	18.9 (1.65 $g \cdot cm^{-3}$)	

Total detonation energy [$\text{kJ}\cdot\text{cm}^{-3}$]	6.692	8.001	[16]
Total gas [$\text{moles}\cdot\text{kg}^{-1}$]	24.43	24.41	
Deflagration point of 5 s delay time [$^{\circ}\text{C}$]	374.1	295	[17]
Friction sensitivity [%]	4-6	0	
Impact sensitivity [cm]	117.5	157.0	
Shock sensitivity [mm]	29.76	42.50	
Vacuum thermal stability [$\text{mL}\cdot\text{g}^{-1}$]	0.05	0.04	[14]
Self-ignition temperature [$^{\circ}\text{C}$]	346.7	306	[18]
Latent heat [$\text{kJ}\cdot\text{kg}^{-1}$]	84.1	104.0	[19]
Specific heat [$\text{J}\cdot\text{g}^{-1}\cdot^{\circ}\text{C}^{-1}$]	1.208	1.278	
Thermal conductivity [$\text{W}\cdot(\text{m}\cdot^{\circ}\text{C})^{-1}$]	0.227	0.224	
Shrinkage [%]	13.2	12.7	[20]
Dissolves RDX (100 $^{\circ}\text{C}$) [g]	14 (per 100 g DNAN)	7.53 (per 100 g TNT)	[14]
Viscosity [$\text{mPa}\cdot\text{s}$]	4.5 (100 $^{\circ}\text{C}$)	9.5 (85 $^{\circ}\text{C}$)	[21, 22]
Irreversible growth (volume change) [%]	15.01	3.10	[23]
Exudation [%]	0.068	0.57	[14]

3 Physical properties

3.1 Melting point

The melting point of DNAN is 94.6 $^{\circ}\text{C}$, meaning that it can be used as a matrix explosive (generally not to exceed 120 $^{\circ}\text{C}$, with 80-100 $^{\circ}\text{C}$ considered ideal [24, 25]). The melting point of DNAN is higher than TNT, which may help alleviate issues of void formation when munitions are stored in hot climates but still melts at a workable temperature for manufacture [26, 27]. However, the higher melting point of DNAN may lead to higher manufacturing costs, and researchers expect to lower its melting point by forming binary eutectic mixtures with different substances.

DNAN can form a eutectic mixture with TNT, and its melting point decreases accordingly. When the mass content of DNAN is between 10% and 70%, the melting point of DNAN/TNT binary eutectic mixtures is lower than that of TNT. When the mass proportion of DNAN/TNT is 1:1, the lowest melting point of the DNAN/TNT binary eutectic mixtures is 66.4 $^{\circ}\text{C}$ [28]. Davies *et al.* [29] suggested that this may be due to the π - π stacking interaction. The DNAN/TNT

binary eutectic mixtures has good vacuum stability and can form a stable binary eutectic mixtures.

Davies *et al.* [29] also found that DNAN and N-methyl-4-nitroaniline (MNA) can form a eutectic mixtures. When the mass proportion is 1:1, the melting point is decreased to 78.6 °C. When the mass proportion is 82:18, the energy of the eutectic mixtures system reaches a maximum. But to prevent the explosion energy from decreasing too much, the content of MNA in the system is generally less than 1%, causing the melting temperature to decrease by only about 2 °C. Therefore, MNA has a limited effect in reducing the melting point, but it may improve the mechanical properties of DNAN. Meng *et al.* [30, 31] confirmed the conjecture of Davies *et al.* [29] and found that adding MNA to DNAN can improve the wettability of the interface between DNAN and octogen (HMX), and DNAN and RDX, thereby increasing the interfacial bonding strength and improving the grain mechanical properties.

DNAN also can form a binary eutectic mixtures with 2-nitroaniline (NA) and 1,3-dinitrobenzene (DNB) [32]. Because of the soft π -stacking interaction between adjacent molecular layers and some unutilized hydrogen bond acceptors in the eutectic mixtures structure, the eutectic mixtures melting point is decreased to 67.5 and 48.0 °C, respectively, when the mass proportion of DNAN/NA and DNAN/DNB are 1:1. Vacuum stability tests revealed that the released gases of 1:1 eutectic mixtures of DNAN/NA and DNAN/DNB were 0.26 and 0.1 mL·g⁻¹, respectively. In addition, because of the introduction of relatively strong intermolecular interactions and special molecular stacking modes, the structure of DNAN/NA is similar to the typical insensitive explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), which exhibits parallel face-to-face molecular stacking patterns. These structures can easily slip/slide past each other and are frequently less vulnerable to the shear strain caused by impact or shock. Therefore, the safety performance of the DNAN/NA eutectic mixtures is improved. The DNAN/DNB eutectic mixtures is an irregular rough dendrite, which can easily generate hot spots under impact or friction. Therefore, the spark sensitivity of DNAN/DNB eutectic mixtures is 0.85 J, indicating inferior safety performance compared to pure DNAN (spark sensitivity 1.18 J).

Liu *et al.* [33] found that when the molar proportion of DNAN/pentaerythritol tetranitrate (PETN) is 80.1:19.9, the lowest melting point of the system is 84.94 °C, which is 8.86 and 56.06 °C lower than DNAN and PETN, respectively. Therefore, PETN can reduce the temperature parameters of DNAN melt-cast explosives and improve the process conditions.

Oxley *et al.* [34] found that DNAN can also form a binary eutectic mixtures with erythritol tetranitrate (ETN) and 1,3,3-trinitroazetidine (TNAZ).

When the molar proportions of ETN/DNAN and TNAZ/DNAN are 52:48 and 49:51, respectively, the lowest melting point drops to 46-49 °C and 65-67 °C, respectively.

Kou *et al.* [35] found that when the molar proportion of DNAN to TNAZ is 56.65:43.35, the lowest eutectic mixtures melting point is 65.14 °C. As the content of DNAN is increased, the impact sensitivity, friction sensitivity, and detonation velocity of the eutectic mixtures are significantly reduced, and the detonation heat is gradually increased. When the lowest eutectic mixtures is formed (at a molar proportion of DNAN to TNAZ of 56.65:43.35), the binary eutectic mixtures's mechanical sensitivity and detonation performance both reach their optimum values.

Gao *et al.* [36] found that when the molar proportion of the binary eutectic mixtures of DNAN/3,4-dinitrofurazanyloxyfuran (DNTF) is 63.3:36.7, the lowest eutectic mixtures melting point is 67 °C, and the safety of the binary eutectic mixtures decreases with increasing DNTF content.

3.2 Shrinkage

The specific heat and latent heat of DNAN are lower than TNT, while the thermal conductivity is higher, leading to a faster solidification rate for DNAN than TNT under the same conditions. In the solidification process, the feeding channel of DNAN is easily blocked, resulting in more severe shrinkage and porosity than TNT [19, 20], as shown in Figure 1.

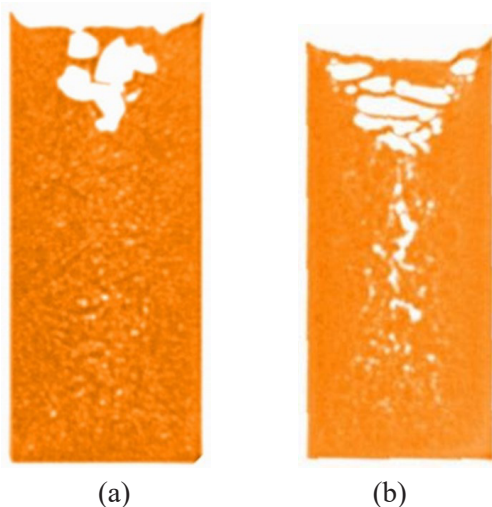


Figure 1. Computed tomography (CT) scanning photographs of (a) TNT- and (b) DNAN- grains [20]

Defects in charge quality such as shrinkage, porosity, cracking, and voids are very common in melt-cast explosives [37]. Therefore, improving the charge quality has always been a considerable challenge. The shrinkage, porosity, and cracking of DNAN explosives were improved by optimizing molding techniques. Several optimization techniques have been used, including:

- riser insulation technology to make the shrinkage position of the DNAN grain move upwards [38, 39],
- pressure forming technology to improve the feeding speed of the DNAN slurry, move up the shrinkage cavity and reduce the internal physical defects of the grain [40],
- hot mandrel technology to cause the explosive slurry on the upper part of the grain to solidify later so that it can fully feed the center of the grain, eliminating shrinkage and porosity [41], and
- shell partitioned charges with pre-inserted clapboards (see Figure 2) to reduce the thermal stress concentration and restrain the cracking of DNAN explosives [42].

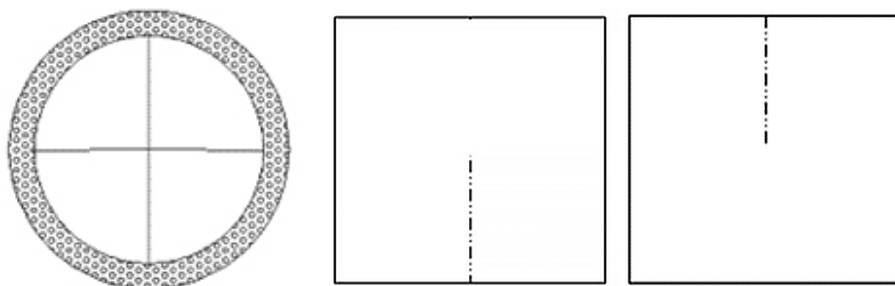


Figure 2. Shell partitioned and clapboard structure [42]

3.3 Irreversible growth

Although the irreversible growth of DNAN is more obvious than that of TNT, the physical damage to its grains is less than TNT after 30 temperature cycles between -54 and $+71$ °C [23]. Irreversible growth of DNAN of up to 15% occurs when samples are temperature cycled between -54 and $+71$ °C [23]. This growth is significantly more than the 1% maximum growth in explosive formulations specified by the Allied Ordnance Publication Volume 7 (AOP-7) [43] criteria and therefore is a major concern for DNAN formulations.

In the energetic materials industry, polymorphism is also a critical concern. Many physical properties of explosives may be affected by polymorphism, including sensitivity, stability, melting point, solubility, irreversible growth, and crystal morphology [44, 45]. Research has shown that DNAN is highly

polymorphic, with two forms present at ambient pressure and temperature. Van Alphen [46] first identified DNAN polymorphism in 1930 in discussing melting point inconsistencies reported at that time.

The first polymorph, denoted α -DNAN, was characterized by Nyburg *et al.* [47] in 1987 and Malinovskii *et al.* [48] in 1992. It crystallizes in the monoclinic crystal system (space group $P2_1/n$) with a unit-cell volume of 1694.3 Å³ and a crystallographic density of 1.56 g·cm⁻³ at 24 °C. The second polymorph, named β -DNAN, was structurally characterized by Xue *et al.* [49] in 2007. It also crystallizes in the monoclinic crystal system (space group $P2_1/n$) but with a unit-cell volume of 845.6 Å³ and a density of 1.56 g·cm⁻³ at 20 °C. The structural information for α -DNAN and β -DNAN are summarized in Table 2. The reported melting points of α -DNAN and β -DNAN are 94.6 and 86.9 °C, respectively.

Table 2. Structural parameters of DNAN polymorphs [47-49]

Parameter	α DNAN	β DNAN
Space group	$P2_1/n$	$P2_1/n$
a [Å]	8.772 (2)	3.9793 (9)
b [Å]	12.645 (2)	13.759 (1)
c [Å]	15.429 (4)	15.445 (1)
Angle [°]	81.89 (2)	90.891 (1)
Unit-cell volume [Å ³]	1694.3	845.6
No. of formula units per unit cell, Z	8	4

Understanding and controlling polymorphism is a crucial challenge concerning materials that exhibit this phenomenon. Essential factors such as the choice of solvent system, temperature, pressure, supersaturation, and mixing can all affect the polymorph produced [50, 51].

In the 25-125 °C temperature range and 0.0001-1.5 GPa pressure range, α -DNAN can exist stably without phase transition [52]. As the pressure increases further, α -DNAN tends to be amorphous. In addition, as the pressure increases from 0.6 to 1.9 GPa, the melting point also increases from 130 to 285 °C [53].

However, although α -DNAN is more thermodynamically stable, numerous recrystallizations from a range of solvents and the melt were invariably found to produce only β -DNAN [46]. Denekamp *et al.* [54] suggested that β -DNAN is the more kinetically preferred polymorph, which is easier to form after rapid cooling in the absence of solvent. Moreover, the polymorphism and crystal shape of DNAN can be affected by changing the crystallization conditions. DNAN crystals obtained in xylene or other aromatic solvents have irregular or needle-like shapes regardless of the polymorph. When the DNAN concentration

in alcohol (methanol, ethanol, and isopropanol) was low, the crystals obtained were needle-like α - or β -DNAN. When the DNAN concentration was increased, the crystal obtained was boat-like α -DNAN. At room temperature (~ 22 °C), β -DNAN crystals were stable in solution for at least several weeks, showing no sign of a β - to α -phase transition. Furthermore, isolated dry β -DNAN is stable for at least several weeks at temperatures below 22 °C. When the dried β -DNAN crystal is exposed to a temperature above 50 °C, it completely transforms into α -DNAN while retaining the typical needle-like morphology of β -DNAN. Since the two structures are similar, the transformation barrier from β - to α -DNAN is low, but crystal defects appear, increasing the sensitivity.

Coster *et al.* [55] found that the transition from β - to α -DNAN only appears to occur in the presence of seed crystallites of α -DNAN. After introducing α -DNAN seed crystals, previously stable samples of β -DNAN were found to have converted to α -DNAN. A 50:50 mixture of α - and β -DNAN as a slurry in methanol converted entirely to α -DNAN in less than an hour. For a 50:50 dry powder mixture of α - and β -DNAN, a complete conversion to α -DNAN was found to take 1-2 days.

Shi *et al.* [56] found that when the cooling rate is below 0.1 °C·min⁻¹, molten α -DNAN would not transform to β -DNAN after solidification. For cooling rates from 0.1 to 2 °C·min⁻¹, the proportion of α -DNAN after solidification dropped sharply from 100% to 0%.

However, solidification of a melt (either derived from α -DNAN or β -DNAN) that is prevented from contacting α -DNAN often results in crystallization to produce β -DNAN or a mixture of α - and β -DNAN. This has potential significance for melt-cast munitions based on DNAN – without α -DNAN seeding; such munitions could likely contain β -DNAN. For this reason, many studies have focused on the behaviour of β -DNAN rather than α -DNAN.

Kay *et al.* [57] found that β -DNAN did not produce new materials after 30 thermal cycling tests performed at 25 to 60 °C. The existence of a low-temperature phase transition of β -DNAN was published in 2015 by Takahashi *et al.* [58]. They reported a phase transition when β -DNAN is cooled to below -8 °C and a biaxial (area) negative thermal expansion (NTE) behaviour after the phase transition. The β -DNAN volumetric thermal expansion coefficient (216 MK⁻¹) was larger than that of α -DNAN (176 MK⁻¹), indicating that the β -DNAN crystals are more “flexible” than the α -DNAN crystals. This is mainly because the thermal behaviour for the libration motion of the *o*-nitro group increases the tilt angle (θ) of π - π stacked molecules, resulting in NTE for β -DNAN. They also clarified that the disorder observed for the *o*- and *p*-nitro groups in β -DNAN is dynamic, but the disorder observed for one of the nitro groups in α -DNAN

is a static disorder. The libration motion of the β -DNAN o-nitro group would make the crystal structure unstable, which is supported by the melting point of α - and β -DNAN and the crystal transformation from β - to α -DNAN in solution.

This phase transition is in close agreement with experimental work at the University of Edinburgh, which observed a phase transition upon cooling to $-7\text{ }^{\circ}\text{C}$, or when the pressure was increased to 0.16 GPa [55]. The resulting new polymorph has been named γ -DNAN. Reducing the temperature to $-7\text{ }^{\circ}\text{C}$ or increasing the pressure to 0.16 GPa causes the unit cell to be reduced in size, decreasing the available space for the oxygen atoms around the nitrogen atom and eventually resulting in insufficient space for the nitro groups to remain disordered. The nitro groups become fixed at that point, causing an overall drop in the molecular volume and a transition from disordered β -DNAN to ordered γ -DNAN. This transition results in a sudden unit-cell volume reduction of 6.085 \AA^3 and a sudden 3.174° jump in the β -angle. The authors believed that repeated cycling across this polymorphic transition, and hence repeated growth and contraction, leads to a ratchet-type mechanism that is ultimately the cause of the irreversible growth observed in DNAN-based explosives. Therefore, if this polymorphic transition could be prevented or suppressed, then the problem of irreversible growth would be eliminated.

Doping DNAN with structurally similar molecules with smaller functional groups could provide more space within the crystal lattice for the nitro groups to be disordered, reducing the β - γ transition temperature. Ward *et al.* [59] found that by replacing molecules of DNAN with molecules of 2,4-dinitrotoluene (DNT) or 1,3-dinitrobenzene (DNB), there is more space within the lattice, and therefore the β - γ transition is suppressed to outside the temperature cycling regime. Concentrations of 5 mol% of both DNT and DNB suppressed the transition to below $-33\text{ }^{\circ}\text{C}$, broadening the transition temperature and resulting in β -DNAN persisting at high percentages at temperatures as low as $-43\text{ }^{\circ}\text{C}$. Increasing the doping level to 10 mol% further suppressed the β - γ transition to below $-63\text{ }^{\circ}\text{C}$, with β -DNAN persisting as low as $-83\text{ }^{\circ}\text{C}$. This suppression moves the β - γ transition temperature outside the -54 to $+71\text{ }^{\circ}\text{C}$ cycling range, for which irreversible growth was observed. Doping DNAN with DNT or DNB may therefore prevent the issue of irreversible growth.

A recent intriguing result from Ward *et al.* [60] shows that a new additive named 'EDX-1' at a level of 5.5 mol% completely suppresses the β - γ transition to below $-54\text{ }^{\circ}\text{C}$, outside the temperature cycling regime specified in the AOP-7. Images of the grains in Figures 3 and 4 illustrate the drastic differences between doped and undoped DNAN samples after temperature cycling. The undoped β -DNAN grain volume expands by an average of 5%, and cracking and

destabilization of the grains are observed. By contrast, the doped β -DNAN grains showed no volume increase or cracking. Unlike β -DNAN, α -DNAN does not undergo a low-temperature phase transition upon cooling. As a result, α -DNAN does not exhibit any growth when thermally cycled.

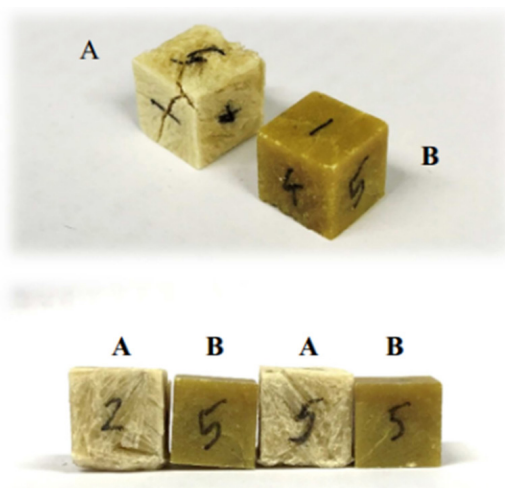


Figure 3. Images of: A – DNAN, and B – DNAN doped with 5 mol% ‘EDX-1’ after being exposed to temperature cycling for >100 cycles [60]



Figure 4. Images of pellets post temperature cycling for >100 cycles of: A – DNAN doped with 5 mol% ‘EDX-1’, B – α -DNAN, and C – β -DNAN [60]

Therefore, if DNAN products are manufactured using doped β -DNAN or exclusively from α -DNAN, the problem of irreversible growth can be eliminated. The current manufacture of DNAN-based warheads involves pouring molten DNAN into a heated shell, allowing it to cool, removing any excess, and then scaling the shell. Because the DNAN is fully molten when poured, this method will most likely result in the formation of β -DNAN inside the warhead,

which would lead to undesirable DNAN growth if the warhead is exposed to variable temperatures. However, if the DNAN is not melted sufficiently and α -DNAN particles remain present in the melt or if the shell is contaminated with α -DNAN seed particles, then the warhead may contain predominantly α -DNAN. Uncertainty about which polymorph is present is most likely why irreversible growth is not observed in every instance.

3.4 Solubility

The potential solubility of the high-energy components of the formulation in molten DNAN may also be responsible for irreversible growth. High-energy components dissolved in the DNAN during melt casting may crystallize during temperature cycling. Grau *et al.* [61] studied the solubility in DNAN of different energetic materials, showing that at 100 °C, 100 g of DNAN could dissolve 13.7 g of RDX, 3.02 g of HMX, 0.222 g of NTO, 0.45 g of NQ, and 0.088 g of AP. Provatas *et al.* [62] showed that when the temperature is 90 °C, 100 g of DNAN can dissolve 7 g of RDX, which exceeds the solubility of RDX in TNT (4.4 g at 80 °C). Luo *et al.* [63] studied the solubility of RDX in the mixture system DNAN/MNA in the 87-95 °C temperature range. The results showed that the solubility of RDX increased with increasing temperature, and the maximum value was 10.28 g of RDX dissolved per 100 g DNAN/MAN.

When molten DNAN solidifies, RDX dissolved in the DNAN recrystallization as plate-like crystals with a thickness of 0.01-0.02 mm [62]. During melt-cast explosive production, RDX repeatedly dissolve-recrystallization from DNAN, increasing the system's viscosity and adversely affecting the charge formation quality. At the same time, many RDX plate-like crystals recrystallization during solidification because of the high solubility, which filled in the interface between DNAN and RDX [64], increasing the internal stress in the grain, and causing cracks. Therefore, it is necessary to optimize molding techniques. For example, vacuum molding techniques can eliminate DNAN/RDX grain cracks [64].

3.5 Mechanical properties

The average hardness and elastic modulus for DNAN are 7.82 and 0.22 GPa, respectively, and for TNT are 12.19 and 0.48 GPa, respectively, indicating that the resistance to deformation of DNAN is weaker than for TNT and that fracture can more easily occur [65, 66]. Nano-indentation tests showed that within 50 min, the indentation depth is reduced from -270.99 to -44.28 nm for DNAN and from -415.12 to -369.21 nm for TNT, indicating that the DNAN crystal has a noticeably slower elastic resilience than the TNT crystal and that DNAN has a greater ability to absorb impact energy. This ability may be one of

the important reasons why the sensitivity of DNAN crystals is lower than that of TNT crystals [66].

The mechanical properties of DNAN can be improved using functional additives like cellulose acetate butyrate (CAB) and polyethylene glycol sorbitan monostearate-60 (Tween 60). Such additives can increase the bonding strength of DNAN/HMX and DNAN/RDX interfaces and enhance their tensile strength [30, 31, 67]. The agent pentaerythritol acrolein resin (APER) can form a high-strength interfacial bonding energy between DNAN and RDX, thereby increasing the mechanical strength and toughness of DNAN/RDX explosives [68].

4 Sensitivity and Safety

The mechanical sensitivity of DNAN is lower than that of TNT by 1.1-1.4 times [69], and its shock sensitivity and thermal safety are significantly better than TNT [70]. Rajan *et al.* [71] pointed out that the larger phonon energy gap in DNAN is a possible reason for its low impact sensitivity.

Chen *et al.* [72] used the traditional cook-off device to test DNAN explosive at a 100 g scale and found that the heating rate greatly influences the state of the explosive before ignition, which affects the intensity of the thermal reaction. When the heating rates were $0.3\text{ }^{\circ}\text{C}\cdot\text{h}^{-1}$, and 0.3 , 1.0 and $3.0\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, the temperature inside the explosive was higher than the shell temperature, and the DNAN completely melted before ignition. The ignition area was the lower portion of the grain and was a thermal ignition caused by the self-heating reaction of the explosive. The corresponding ignition temperatures were 379 , 395 , 387 , and $382\text{ }^{\circ}\text{C}$, respectively. At a relatively fast $60\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ heating rate, the shell temperature was always higher than the explosive internal temperature, and heat was transferred from the outside to the inside. The ignition area was on the edge of the explosive, and was a strong ignition under rapid shell heating. At that stage, part of the explosive near the bottom had not melted, and the explosive ignition temperature was $489\text{ }^{\circ}\text{C}$.

Wang *et al.* [18] studied the thermal safety of DNAN using a 50 g scale constant temperature cook-off test and compared it with TNT. The self-ignition temperatures of DNAN and TNT were 346.7 and $306\text{ }^{\circ}\text{C}$, respectively. DNAN had no obvious combustion reaction at $220\text{ }^{\circ}\text{C}$ ambient conditions for 48 h. Incomplete combustion occurred during 48 h in $230\text{ }^{\circ}\text{C}$ conditions, while deflagration occurred at $240\text{ }^{\circ}\text{C}$.

Liu *et al.* [73, 74] used a new thermal analysis method called dynamic pressure measurement thermal analysis (DPTA) to study the thermal

decomposition behaviours of DNAN and TNT at a 1 g scale. They found that the reaction rate constants of the two types of low melting point matrix explosives increased exponentially with increasing temperatures in the 60-140 °C range. The reaction rate constants and decomposition gas volumes of DNAN are less than those of TNT, suggesting that the reaction activity of the low melting point organic nitro compounds positively correlates with the number of the nitro group/nitrogen atoms. The gases from the decompositions of DNAN were H₂O, CO, N₂, NO, CH₂O, N₂O, and CO₂, while O₂, CH₃OH, and NO₂ were released only at high temperatures. The molten decomposition of DNAN mainly took place in the gas phase, and released NO₂ through C–NO₂ cleavage, and NO and CO through the –NO₂ rearrangement and had an equilibrium reaction of CO + NO₂ ↔ CO₂ + NO. Moreover, H₂O and CH₂O were released through α -H transfer and isomerization.

Zhang *et al.* [75] studied the thermal decomposition characteristics of DNAN and TNT at a 100 mg scale by adiabatic accelerating rate calorimetry (ARC). The results showed that the initial exotherm temperatures of DNAN and TNT under adiabatic conditions are 232.0 and 200.9 °C, respectively, indicating that DNAN has better thermal safety than TNT. When the temperature was below 280 °C, the decomposition rate of DNAN was slow (the self-heating rate increased from 0.02 °C·min⁻¹ at 232 °C to 4.1 °C·min⁻¹ at 280 °C). However, when the temperature was above 280 °C, the self-heating rate increased rapidly from 4.1 °C·min⁻¹ to the maximum value of 14.9 °C·min⁻¹ (at 300.8 °C), meaning that the DNAN decomposition reaction occurs when the temperature exceeds 300.8 °C, which could be disastrous. The maximum self-heating rates of TNT and DNAN were 811.9 and 14.9 °C·min⁻¹ under adiabatic conditions, indicating that the energy release rate from TNT is faster than from DNAN, and TNT is more likely to cause dangerous accidents when the decomposition reaction occurs. Wojtas and Szala [76] also found that the decomposition process and the increase in DNAN gas emissions are slower than those for TNT. Moreover, the temperature at the end of thermal decomposition is 400 °C.

Maharrey *et al.* [77, 78] studied the thermal decomposition characteristics and decomposition mechanism of DNAN at a 10 mg scale using a simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) instrument (shown in Figure 5) invented by the Sandia National Laboratory in the United States. The results showed that DNAN starts to evaporate significantly at about 130 °C, about 40 °C above the melting point, indicating that liquid-phase DNAN has a low vapour pressure [79]. When the molten DNAN was 120 °C above the melting point, the decomposition product 2,4-dinitrophenol (DNP) appeared, and decomposition occurred over a wide temperature range (210-300 °C).

The thermal decomposition process of DNAN includes four steps (see Figure 6):

- (1) melting of DNAN,
- (2) evaporation of liquid-phase DNAN,
- (3) production of condensed-phase DNP and CH_2 by liquid-phase DNAN decomposition through a simple bond-rearrangement reaction involving a hydrogen atom transfer from the methyl group to the oxygen atom on the methoxy group, followed by the formation of a liquid-phase mixture of DNAN and DNP, and
- (4) achievement of an equilibrium state between the gas-phase DNAN and DNP and the liquid mixture.

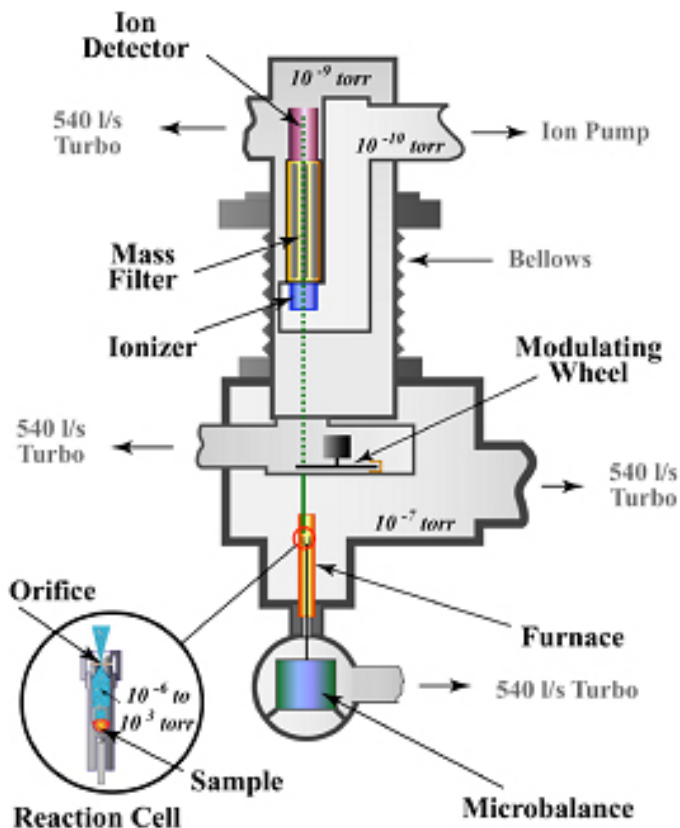


Figure 5. Schematic diagram of the simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) instrument [77]

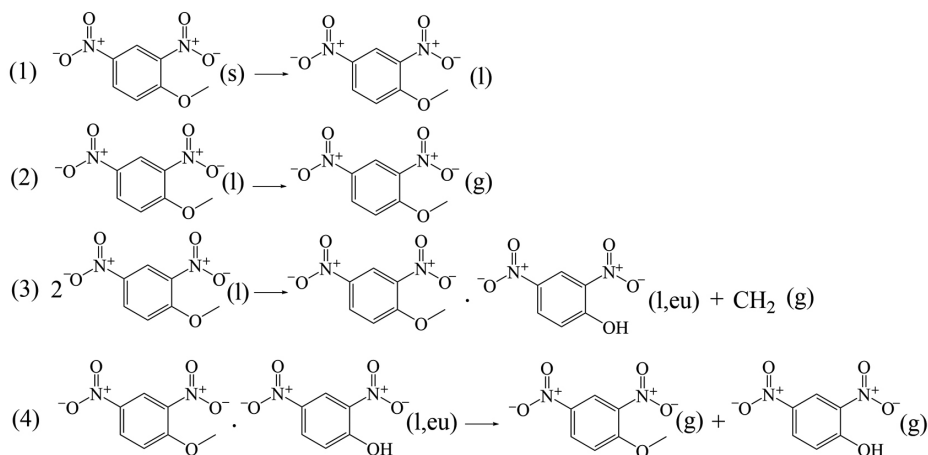


Figure 6. DNAN thermal decomposition mechanism [78]

Trzciński *et al.* [80] found that DNAN is very stable in a 5 mg level TG/DTA experiment. When the temperature is below 160 °C during the heating process, the DNAN quality remains unchanged, but when it exceeds 160 °C, DNAN volatilizes quickly.

Oxley *et al.* [81] found that about 50% of DNAN decomposed when heated in a sealed capillary tube at 200 °C for five days in a 0.5 mg thermal decomposition experiment. However, when DNAN was mixed with NTO or NQ, noticeable thermal decomposition was observed within 1 h at 200 °C, and the decomposition rate was noticeably accelerated, mainly because the ammonia generated during the decomposition of NTO or NQ accelerates the decomposition rate of DNAN. DNAN can be decomposed by about 50% when heated at 200 °C for 5 min in the presence of ammonium carbonate. When DNAN containing ammonium carbonate was heated at 200 °C for 3 h, it was completely decomposed, and the main product was dinitroaniline and a small amount of dinitrophenol.

5 Stability and Compatibility

The amount of gas generated in a DNAN vacuum thermal stability test is slightly more than in the case of TNT. However, because of the acidity of TNT, it promotes thermal decomposition at higher temperatures [32], which makes the vacuum stability test results of TNT-based explosives worse than DNAN-based explosives. For example, the amount of gas for IMX-101 and IMX-104 is less than for Composition B [11].

DNAN is compatible with common explosives such as TNT, RDX, HMX, and DNTF. It also has good compatibility with additives such as ammonium perchlorate (AP), aluminum powder, and MNA [62, 82]. Therefore, in the formulation design of DNAN-based explosives, common explosive components are applicable, and the energy adjustment range is large.

6 Oxygen Balance and Energy

The oxygen content can be increased by adding an oxidizer such as AP. Wang *et al.* [82] found that adding AP to DNAN improves its oxygen balance and increases the oxidation of aluminum powder in DNAN formulations. Therefore, DNAN's density and explosion heat are greatly improved, while its detonation speed is not reduced.

John *et al.* [16] have shown that the addition of AP increases the predicted density, detonation velocity and detonation pressure, and ultimately the explosive energy relative to TNT. In addition, CO₂ and the total moles of gas produced are also enhanced by adding AP. As the AP concentration is increased, the predicted total energy of detonation is increased up to a certain point; AP concentrations above 70 wt.% result in oxygen as a detonation product, which lowers the predicted detonation energy. A DNAN/AP ratio of 55:45 exhibits nearly the same total detonation energy as TNT.

Trzciński *et al.* [80] compared the acceleration capability of DNAN and TNT explosives in cylinder expansion tests. The results showed that tube velocities for TNT are higher than those for DNAN (by approximately 250 m/s at the final stage of expansion), and the Gurney energies of DNAN and TNT were 2060 J/g ($\rho = 1.52 \text{ g}\cdot\text{cm}^{-3}$) and 2795 J/g ($\rho = 1.59 \text{ g}\cdot\text{cm}^{-3}$) respectively, indicating that the acceleration capability of DNAN is lower by about 25% compared to TNT. Mishra *et al.* [83] also compared the explosion performance of DNAN and TNT. However, the test result of detonation velocity was lower than that measured by Trzciński *et al.* [80]. This difference can be explained because Trzciński *et al.* [80] placed the DNAN grain in a 250 mm long copper tube with a 25 mm inner diameter and 2.5 mm wall thickness, which reduced the weakening effect of the lateral rarefaction wave on the reaction zone.

Although the total detonation energy of DNAN is 83% that of TNT, its viscosity is only 47% of TNT [21] at their respective process temperatures (generally 85 °C for TNT and 100 °C for DNAN). Therefore, the total detonation energy of DNAN-based melt-cast explosives can be increased by increasing the high-energy solid explosive content. Zhu *et al.* [84] found that under the same

charging conditions, the maximum solid content of the TNT/HMX system is about 75%, while the DNAN/HMX system can reach 80%. When adding up to 80% HMX to DNAN, the detonation performance of the formulation is better than Octol (TNT/HMX 25/75) [85, 86]. However, higher solid content inevitably leads to higher viscosity, and particle gradation technology must be used to reduce the system's viscosity. Zhu *et al.* [87] showed that when the grade ratio of HMX particles with d_{50} particle sizes of 785.3 and 100.7 μm is 2:1, the HMX content can reach 80%. Its viscosity is also significantly reduced and is essentially the same as TNT/HMX (25/75) explosive with the same grade ratio.

7 Conclusions and Prospects

- ◆ Given the challenges in applying DNAN-based melt-cast explosives, this paper has considered the essential characteristics of DNAN. It summarizes the latest progress in DNAN applications in terms of physical properties (melting point, shrinkage, irreversible expansion, solubility, and mechanical properties), sensitivity and safety, stability and compatibility, and oxygen balance and energy. This paper also puts forth methods to address the deficiencies of DNAN, such as low energy, irreversible expansion, and poor mechanical properties.
- ◆ However, current research still has certain shortcomings, and urgent research directions include the following three aspects:
 - (1) *Studies on DNAN binary eutectic mixtures mechanisms:* Binary eutectic mixtures are a fast and effective way to lower the melting point of DNAN. Presently, some research work has been conducted in certain countries, a variety of DNAN mixture systems and related properties have been reported, and some have been applied in formulations. However, most existing research has focused on the melting point of binary eutectic mixtures compounds and less on the structure, formation mechanism, and their influences on formulation performance. Therefore, intensive research is needed on the influence of DNAN mixture compounds on safety, energy characteristics, mechanical properties, and environmental adaptability.
 - (2) *Control of crystal transformation:* Researchers have demonstrated that in the absence of any seeds of α -DNAN, crystallization from the melt results in the formation of the metastable β -DNAN, leading to the irreversible growth of DNAN explosive. By controlling the cooling rate or by doping, α -DNAN alone can be produced after solidification, which

can fundamentally solve the problem of irreversible growth. However, reports on these subjects are rare at present.

- (3) *Improvement of the mechanical properties*: DNAN is a brittle material with poor elasticity and toughness, which increases the probability of a “hot spot” being formed during storage, transportation, or launch of the warhead, resulting in accidental explosions. There are presently few studies on the toughening and elasticity of DNAN. Therefore, further research is needed on DNAN’s mechanical modification, toughness, and elasticity and to find additives with a similar molecular structure to improve toughness and elasticity by intermolecular hydrogen bonding compound modification. The toughening techniques used for other composites could guide melt-cast explosives research, especially the toughness and elasticity enhancement techniques involving nanoparticles and polymeric materials. In addition, research on the dynamic mechanical properties of DNAN and its modified materials under complex stress states and extreme conditions should be expanded to reveal the ignition mechanism of DNAN melt-cast explosives during penetration.

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