

## Synthesis, Formulation, and Testing of 3.4-DNP

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## ABSTRACT

Explosive formulations are an integral component to the performance and safety of weapon systems, especially to the Army's Future Combat Systems efforts. Research focused on explosive materials and formulations that provide baseline/enhanced energetic performance while offering improved sensitivity is critical to the continued mission success and safety of the U. S. Warfighter. Historically, TNT has been the primary melt cast binder for melt pour formulations. However, due to sensitivity, stability and exudation issues, replacements for TNT have long been of interest. Recently, 2,4-dinitroanisole (DNAN) has found widespread use as a TNT replacement. Although DNAN has slightly lower explosive performance than TNT it is considerably less sensitive to external stimuli. Even though DNAN offers many advantages as a melt cast binder, relative to TNT, ideal "next generation" candidates would offer further improvements in explosive performance and sensitivity over existing melt cast binders.

As such, BAE Systems and ARDEC have partnered to further develop the chemistry and measure the explosive performance of the melt-pour explosive ingredient 3,4-dinitropyrazole (DNP). Initial performance testing of DNP has shown it to have greater energy performance than Composition B, while significantly less sensitive to impact, friction, ESD, and shock.

The objective of the current research effort was to scale-up the melt-pour ingredient DNP to the pilot-plant scale and test the performance and shock sensitivity of the material in order to demonstrate its utility as a high-energy melt-pour within IM-compliant explosive formulations. In addition, the toxicity and potential dermal sensitivity issues of DNP were further evaluated. The end state of this project will provide knowledge of the performance and shock sensitivity of DNP as a neat and formulated material. Included in this effort was the formulation of DNP with other high energy materials to meet ARMY IM and lethality goals.

# TECHNICAL RESULTS

In an effort to continue to improve in the areas of IM and explosive performance, new ingredients are always being sought. As such, BAE Systems and ARDEC have further evaluated the scaleup and performance testing of the energetic melt-pour ingredient 3,4-dinitropyrazole (DNP). The 3-step synthesis of DNP from pyrazole was initially described by Phil Pagoria from Lawerence Livermore National Labs (LLNL) (Scheme 1). Pyrazole is treated with acetyl nitrate yielding 1nitropyrazole (1-NP) in good yield. The 1-NP is then converted to 3-nitropyrazole (3-NP) by thermal rearrangement in anisole at elevated temperature. The 3-NP is then directly nitrated to the desired product 3,4-DNP in mixed acids. Under JIMTP Task 07-02-02, improvements were made to this step by BAE Systems, most importantly, a reduction in the amount of sulfuric acid used. This resulted in the precipitation of the majority of the formed 3,4-DNP product from solution, thereby avoiding a solvent extraction step. The DNP solid can then be recrystallized using common solvents yielding pure material. BAE Systems has used the improved procedure to produce DNP on the multi-kilogram scale. An initial rate stick/plate dent performance test of DNP at ARDEC has shown DNP has greater energy performance than Composition B.

# Scheme 1. Synthesis of 3,4-DNP from Pyrazole



## Lab-Scale Development

The first phase of the investigation involved preparation of 25 grams of the DNP from pyrazole for characterization and small scale safety evaluation. Following the process shown in Scheme 1 above, pyrazole is nitrated at the N-position in the first step of the reaction pathway using acetyl nitrate generated in situ. The N-nitropyrazole (1-NP) thus produced is then subjected to solution thermolysis in solvent to give the rearrangement product, 3-nitropyrazole (3-NP). Finally, the 3-nitropyrazole undergoes mixed acid nitration with nitric and sulfuric acid to give 3,4-DNP.

Determination of the yield for the first step was complicated by the ambient pressure sublimation behavior of the product. Drying 1-NP in an oven overnight resulted in complete loss of the sample. Water-wet 1-NP was subsequently used for the second step, and a solvent/water azeotrope was utilized to remove the water prior to thermolysis. The thermolysis step was also improved upon by increasing the concentration of 1-NP in the solvent and allowing the thermolysis to continue. Previous preparations were conducted at low concentrations with short reaction times. Since the exotherm onset temperature of neat 1-NP was very close to the temperature necessary to effect its thermal rearrangement, Accelerated Rate Calorimetry experiments were performed on 1-NP solutions of varying concentrations to determine the safe range. The first two steps were then scaled up to kilogram quantities.

The nitration of 3-NP was also improved. DNP is quite soluble in water, making extraction with an organic solvent necessary for product recovery. It was found that the amount of sulfuric acid in the mixed acid nitration could be reduced, which also resulted in a large portion of the product precipitating from the reaction mixture. After diluting the filtrate, the remaining product was extracted. After recrystallization to remove residual acidity, DNP was obtained in a good overall yield.

Characterization of DNP consisted of determination of relative purity through HPLC (>98%) and confirmation of chemical identity by comparing NMR chemical shifts and melting points onset values with those reported in the literature. Small scale safety and performance testing was then performed on the samples, and thermal data was obtained to ascertain each compound's specific

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suitability as a melt cast binder. Finally, compatibility studies were conducted with ingredients commonly used in melt pour formulations at HSAAP.

The DNP was tested for impact sensitivity (ERL), friction sensitivity (BAM), and electrostatic discharge sensitivity, with the results presented in Table 1 below. DNP is compared to RDX and the other new melt-pour ingredient DNMT (1-Methyl-3,5-dinitro-1,2,4-triazole).

	ERL Impact (cm)	BAM Friction (N)	ESD (J)
DNP	67.4	>216	>0.25
DNMT	>100	>252	>0.25
RDX	25.4	>144	>0.25

#### Table 1: DNP Sensitivity

For the small-scale performance testing effort, an attempt was made to pour a rate stick. However, the DNP (and DNMT reference) exhibited undesirable recrystallization behavior when allowed to cool at room temperature after melting. Low densities/high porosity and cracking were observed. This is not an uncommon feature in melt pour ingredients. Optimization of cooling profiles, as well as possible addition of nucleation agents, may help to mitigate this issue. In order to obtain performance data, samples of DNP and DNMT were pressed to average densities of 1.753 g/cm and 1.619 g/cm, respectively, and subjected to rate stick/plate dent testing to determine detonation velocities and pressures. Theoretical and experimental performance values are given in Table 2 below and compared to Comp. B.

#### Table 2: DNP Performance

	Pcj, Calc (GPa)	Pcj,Exp (GPa)	Energy Out, Calc. (cal/cc)	VOD, Exp (m/s)
DNP	28.8	29.4	1961	8,104
DNMT	25.4	23.3	1739	7,850
Comp. B	27.7	27.6	1837	7,960

As is shown in Table 2 above, the experimental pressure and detonation velocity of DNP is greater than Comp B, and closely matches the CHEETAH calculations for the material. As a point of reference, the experimental data from the pressed DNMT rate stick also matches the CHEETAH calculations, which show that it slightly worse than Comp. B in explosive performance. The rate stick test for the materials is shown in Figure 1 below.

#### Figure 1: DNP Rate Stick Test



Thermal experiments were conducted on DNP designed to elucidate whether it exhibits polymorphism, which would result in different melting points, as is the case for 2, 4-dinitroanisole (DNAN). The samples were heated at 5°C/min. up to 120°C, cooled at 5°C/min. to 0°C, and then heated at 5°C/min. past the exothermic decomposition temperature. When DNAN is subjected to

these experimental conditions, it shows an endotherm / melting point at 94.7°C, a recrystallization exotherm at around 48°C, and, upon reheating, an endotherm / melting point at 85.9°C. Subsequent temperature cycling always shows the melting point to be ca. 86°C, corresponding to the more stable polymorph. However, for DNP there was no recrystallization exotherm during the cooling cycle. Evidently, during the time scale of the experiment, the DNP remained in the liquid state. Visual examination of larger samples melted on the TGA instrument indicated eventual solidification, but only after unusually long time periods.

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Given interest in DNP as a melt cast binder, the impact sensitivity of the material was compared pre-melt and post-melt/solidification. If defects, inclusions or voids created hot spots in the crystalline material, the impact sensitivity should decrease post-melt. Results are given in Table 3 below. Density of the material was not determined, but DNP did indeed become less sensitive post-melt. It was also more amorphous in appearance, and resembled DNAN that had been treated in a similar fashion.

Impact Sensitivity (cm), Navy Method				
Pre-melt Post-melt				
DNP	54.1	146.9		

Table 3: DNP Impact Sensitivity

The compatibility of DNP with other energetics commonly used in explosive formulations at HSAAP was investigated, utilizing differential scanning calorimetry of 1:1, mass:mass physical mixtures of the melt pour candidates with the other materials. The binary mixtures were heated at a rate of 5°C/min., and deviations from the exotherm onsets and peaks of the neat materials were noted. A lowering of 10°C or more of either the exotherm onset or peak value of the lower of the two in the pair was considered a "fail", and additional investigation (such as VTS) would be required. The results of the compatibility study are shown below in Table 4; negative deviations in the exotherm values of  $\geq$ 10°C are shown in yellow.

			DNP		
			MP	Exo Onset	Exo Max
NEAT		86.5	275.8	296.9	
	RDX				
MP 203.6	Exo Onset 205.8	Exo Max 227.9	83.8	202.6	234
	HMX				
MP	Exo Onset	Exo Max	86.7	203.3	221.2
187.2	276.3	284.2			
NTO					
MP	Exo Onset	Exo Max	86.4	175.7	237.7
N/A	262.3	273.4			
TATB					
MP	Exo Onset	Exo Max	86.7	193.3	273.7
N/A	366.56	373.8			
DNAN					
MP	Exo Onset	Exo Max	57.9	203.9	302.9
94.2	326.9	342.9			
NQ					
MP	Exo Onset	Exo Max	84.2	182.5	222.7
N/A	195.2	202.8			

Table 4: DSC Compatibility of DNP

Based on the 10°C criteria, the DNP was compatible with RDX, and slightly lowered the exotherm onset for NQ, without significant change to the melting point. The more thermally stable ingredients, HMX, TATB and NTO, were negatively affected by DNP. Since the melting points were not depressed, it is possible that some degree of solubility and subsequent reactivity is taking place.

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Since DSC compatibility is only a screening tool, the vacuum thermal stability (VTS) of DNP was measured by itself and in a 1:1 mixture with HMX and RDX. The results are shown in Table 5. Per the specification, in order to pass compatibility the mixture of the two components should have a gas evolution less than 5ml/g to the component that has the maximum gas evolution individually. Based on the test results and gas evolution calculation, DNP is compatible with both RDX and HMX.

Component	Gas Evolved (mL/g)	Compatible (<5 mL/g)
RDX	0.1521	
HMX	0.0405	
DNP	0.5106	
DNP/RDX	0.4661	Yes
DNP/HMX	0.2351	Yes

## Table 5: DNP VTS Stability

## Laboratory Scale-Up

Since the DNP material and process showed good promise from the initial lab-scale effort, an additional research effort was undertaken to further scale-up the DNP in the laboratory to produce enough material for initial IM and explosive performance testing. The step of the scale-up was to synthesize DNP in the Mettler Toledo Reaction Calorimeter (RC1) to monitor for any unusual exothermic events. The results of the RC1 run are shown in Figure 2. There are no unusual thermal events and the exotherms seen during the 3-NP and nitric acid addition are easily controlled by addition rate. From this data, it was determined that no issues should be seen upon further scale-up.





The DNP synthesis process from 3-nitropyrazole was scaled-up to the 18-L scale to produce over 25 lbs of DNP from seven reactions. For the first four batches, the yields were considerably less than observed in the previous smaller lab effort to produce DNP. The lower yields were attributed to the presence of acetic acid (~0.50-1.0%) and the difficulty it presents when recovering solids in the final workup.



# Figure 3: Purified DNP



The process for the final three batches was modified slightly in an effort to avoid the laborious and time consuming acetic acid abatement. The DNP produced from the nitration are washed in a large excess of solvent and then brine to remove any residual acetic acid. The yield from this process is similar to the initial four runs although the material can be adequately dried

#### Pilot-Plant Development

For the pilot-plant campaign, DNP was synthesized in one step from 3-NP using a mixed acid nitration (Scheme 2). There were four parts to the synthesis of DNP at building D-10: 1) nitration of the 3-NP using 70% nitric acid in concentrated sulfuric acid, 2) isolation of the crude DNP and washing a solution of DNP in methyl tert-butyl ether (MTBE), 3) Concentration of the MTBE solution and swapping to toluene, and 4) crystallization and isolation of the DNP



Scheme 2: Nitration of 3-nitropyrazole (3-NP)

The objective of this program was to synthesize up to 250-lbs of DNP on the Pilot-Scale using the best available synthesis procedure for both internal future use as well as shipment of a portion of the material to ARDEC for further evaluation and testing. The effort would not focus on developing improvements or optimizations to the existing synthetic procedure, except for the final purification, if needed. Follow-on programs would look at the formulation of DNP with other high energy materials to meet performance goals as well as further optimization of DNP.

Nitration parameters were selected from both the lab scale effort and discussions within HSAAP that would most likely succeed in producing DNP of high quality. The largest concerns going into the campaign were related to the isolation of the crude DNP and purification to crystalline DNP.

Due to some in-process improvements of the isolation of DNP from the nitration and recrystallization, the actual yield from the campaign was over 300 lbs. The purity and residual acid is shown below in Table 6.



Table	e 6
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% Purity- HPLC	Nitrates (wt%)– IC	Sulfates (wt%) - IC
>99.5	<0.02	<0.02

# Critical Diameter Testing

Critical Diameter was determined by pouring conical charges of DNP in a split-mold. Two of these charges were poured with a diameter from 1.4 inches to 0.16 inches at a declining angle of 0.1 inches per 1 inch of length. The charges were set on a 16" X 6" X  $\frac{1}{2}$ " 6061 aluminum plate. The charge was then taped down and a #8 equivalent detonator was placed and taped with intimate contact to the larger diameter end of the charge/shot.

Figure 4: DNP Critical Diameter Set-Up





Propagation through the charge with no residual explosive remaining, as well as completely etching the aluminum plate is indicative of a critical diameter of less than 0.16 inches. This is similar to other RDX based explosives that show similar performance. (i.e. PBXN-5; CD < 0.1 inches) The first DNP shot deformed the plate significantly due to lack of support on the back side of the plate. This was corrected with the second shot which shows a much cleaner propagation. However, both shots showed complete propagation noted by the streaked aluminum plate across the entire length of the cone.

## Figure 5: DNP Critical Diameter Results





#### Shock Overpressure Testing

The degree of damage to surroundings during an explosion is related to shock overpressure, shock duration, and peak impulse. BAE Systems has the testing equipment set-up at HSAAP to measure these three components of a detonation. The detonation is measure by the use of Piezotronic pressure probes set-up at different distances (for the set-up at BAE Systems, the probes are oriented axially at 5, 10, and 15 feet). The test set-up is shown below in Figure 6.



Figure 6: Explosive Test Set-up

For DNP, 0.5-lb tubes were poured to a density of 1.67 g/cc and tested. The results (Table 7) confirm that DNP is an extremely powerful explosive with better performance than current melt-pour explosives. In fact, by shock overpressure, DNP has performance closer to LX-14 (95.5% HMX).

	<u>5 ft</u>	<u>10 ft</u>	<u>15 ft</u>
DNP	30.79	6.53	3.27
Comp. B	27.69	6.30	3.08
IMX-104	28.06	6.08	3.19
PBXN-7	27.46	6.44	3.15
LX-14	31.7	6.35	3.28

Table 7: Shock Overpressure Testing (Psi)

#### LSGT Testing

Large Scale Gap Testing, LSGT, was completed using standard method AOP-7 201.01.002. The LSGT is the standard test method to evaluate the shock sensitivity of energetic materials. The test is conducted where a polymethyl-methacrylate (PMMA) attenuator is placed between a donor

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explosive (pentolite: 50% PETN/50%TNT) and an acceptor explosive. The attenuator (card) gap is varied following a modified Bruceton Staircase technique until detonation is achieved in a 50% probability. The thickness of the card gap at that point can be translated into shock pressure. The lower the 50% card gap, the lower its shock sensitivity. The acceptor explosive, comprised of a poured tube with a density of approximately 1.67 g/cc (total of approximately 0.5 lbs), is placed into a mild steel seamless tube. A steel witness plate is used at the base of the acceptor to provide a clear indication of whether or not the acceptor detonates in the trial.

The testing at HSAAP utilizes a witness plate support structure that consists of a 6" long, 7" OD, 1" thick steel tube that is buried in the sand/soil floor on top of a thick steel plate in a covered test area at an outdoor range. A 9" x 9" x 5/8" witness plate is approximately centered on the steel support tube. This presents a 3" stand off from the floor to the witness plate with the witness plate supported 360 degrees.





A typical positive, GO, response is recorded as a complete split of the test plate into two separate pieces. A typical negative, NOGO, response is recorded as a failure to split the test plate into two separate pieces.

By LSGT, it was found that DNP initially had a 50% point of 243 cards (13.8 kbar). This result shows a relatively sensitive material. In comparison, Composition B usually shows a result of about 215 – 225 cards.

Some of this sensitivity could be due to how the DNP was poured and allowed to solidify (poured directly into a cold tube), which caused large crystalline domains to form, which also resulted in cracking of the material. When TNT is poured into charges, powdered TNT, or other energetics, is added to the melted TNT in order to minimize the large crystal growth. A series of tests was conducted to better understand the solidification of DNP. Improvements were made in the overall pour, which dropped the overall shock sensitivity to 193 cards (22.8 kbar). Addition of wax, or even other crystalline energetic materials may drop the card gap even lower.

# Summary and Future Work

The chemistry of DNP has been further developed and proven-out on the laboratory-scale through a joint collaboration between ARDEC and BAE Systems. DNP shows a lot of promise as a next-generation melt-cast explosive. It is insensitive to impact, friction, and ESD stimuli; it's performance exceeds Comp. B; it can be synthesized from inexpensive starting materials; and



the chemistry can readily be scaled to the pilot and production scale at the Holston Army Ammunition Plant by BAE Systems. Formulation efforts and testing of DNP are currently ongoing with model formulations predicted to have exceptional IM and performance characteristics.

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