QUALIFICATION AND TESTING OF 2,3-DIMETHYL-2,3-DINITROBUTANE (DMDNB) MANUFACTURED AT HOLSTON ARMY AMMUNITION PLANT

by

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ABSTRACT

The International Convention on the Marking of Plastic Explosives for the Purpose of Detection requires an approved chemical marking agent to be added to plastic explosives. 2,3-dimethyl-2,3-dinitrobutane (DMDNB) is currently the preferred marking agent for explosives manufactured by Royal Ordnance North America, Inc. (RONA), the operating contractor for Holston Army Ammunition Plant (HSAAP). DMDNB is currently only available from one commercial source.

Last year, RONA and ANGUS Chemical Company reported a successful joint testing program, which qualified ANGUS as an alternate commercial source of DMDNB. However, subsequent acquisition of ANGUS Chemical Company by DOW Chemicals prevented the developed product from being introduced into commercial markets. In response, RONA made the decision to evaluate the feasibility of scaling up and manufacturing DMDNB at HSAAP using a synthesis technique that had been developed at Holston Army Ammunition Plant in the past. Bench-scale studies are in progress to evaluate both the synthesis process and DMDNB product generated using this manufacturing method.

This paper provides a brief description of the HSAAP DMDNB synthesis technique, characterization tests on RONA-produced DMDNB material, results obtained to date, and a technical discussion of the implications for using this DMDNB in explosive product.

INTRODUCTION

1.1. In 1991, the International Convention for the Marking of Plastic Explosives mandated that all plastic/sheet explosives be marked with a chemical taggant for the purpose of detection. The international agreement further stipulated that all plastic/sheet explosives produced after January 1, 1994 must contain a taggant and that all authorized military devices containing plastic/sheet explosives made after January 1, 1997 must contain tagged explosives.

1.2. An estimated 90% of the tagged plastic explosive produced in the world today uses 2,3-dimethyl-2,3-dinitrobutane (DMDNB) as the chemical marker. Of the four taggants currently approved for use in plastic explosives (DMDNB, p-MNT, o-MNT, and EGDN), DMDNB is widely considered the superior choice. This material is stable, is considered less toxic than the alternative taggants, and is chemically and physically compatible with most current plastic explosive compositions. DMDNB is currently the only taggant approved for use in plastic explosives produced for both the U.S. Military and the U.K. Ministry of Defense.

1.3. Hampshire Chemical Corporation is currently the only certified manufacturer of DMDNB.

1.4. Royal Ordnance North America, Inc. (RONA), the operating contractor of Holston Army Ammunition Plant (HSAAP), utilizes significant quantities of DMDNB in the manufacture of Composition C-4 and other plastic/sheet explosives. Being manufactured by just one supplier, DMDNB is relatively expensive. RONA also believes that the supply issues for DMDNB significantly increases the manufacturing risks for the production of plastic explosives.

1.5. In 1999, ANGUS Chemical Company, headquartered in Buffalo Grove, Illinois, introduced its own proprietary process for the manufacture of DMDNB. RONA worked closely with ANGUS Chemical to qualify this DMDNB as an alternate source of material. The results of this certification program were reported last year at the 1999 NDIA Insensitive Munitions and Energetic Materials Technology Symposium in Tampa, FL. However, in December 1999, public announcement was made that ANGUS Chemical Company had been acquired by Dow Chemical, which is also the parent company of Hampshire Chemical. Following this corporate acquisition, ANGUS Chemical decided not to compete in the commercial market for DMDNB.

1.6. Based upon the continued supply issues with DMDNB, Royal Ordnance North America has made a decision to evaluate the feasibility of manufacturing DMDNB at Holston Army Ammunition Plant using technology developed in previous years at HSAAP. The purpose of this paper is to report RONA's initial development efforts and evaluation of the DMDNB material produced at HSAAP.

2. RONA / HSAAP DMDNB SYNTHESIS TECHNIQUE

2.1. The general synthesis technique utilized by RONA to produce DMDNB was initially developed at Holston AAP in 1995 by the technical staff of Holston Defense Corporation, the former Operating Contractor of HSAAP. This DMDNB synthesis mechanism was further developed at HSAAP in 1997 under an U.S. Army funded study. In this program,

the "Holston" process was demonstrated on about a one-pound scale while achieving reasonably good product yields (≈80%).

2.2. The "Holston" synthesis process for DMDNB is essentially a two-step reaction mechanism. Under controlled conditions, 2-nitropropane (2-NP) is reacted with sodium hypochlorite to obtain 2-chloro-2-nitropropane. This chlorinated product is then further reacted with 2-NP and sodium hydroxide to produce the DMDNB.

3. MATERIAL TESTING PROGRAM

3.1. Representative "specification grade" DMDNB material generated at Holston AAP was evaluated versus commercial products from both Hampshire Chemical Corporation and ANGUS Chemical Company for its ability to meet the following requirements:

- Conformance to the military requirements as outlined in Commercial Item Description (CID) No. A-A-59410 for DMDNB (available from TACOM-ARDEC at Picatinny Arsenal, NJ). This CID includes specifications for appearance, purity, water content, chloride content, methanol content, melting point, and confirmation by FTIR.
- Exhibition of satisfactory processing properties when used to manufacture Composition C-4 or other plastic explosives at HSAAP. These evaluations included vacuum thermal stability, reactivity/compatibility with RDX/HMX, differential scanning calorimetry (DSC), and particle size distribution analysis of the DMDNB products.

4. RESULTS AND DISCUSSION

4.1. Supplier Certification Data

The Hampshire Chemical DMDNB product evaluated in this study was identified with Hampshire Lot No. OF1617KY01. The ANGUS Chemical DMDNB product evaluated in this study was identified with ANGUS Lot No. 9G08JG06. The data reported in the following table were taken directly from the certificate of analysis sheet provided by Hampshire Chemical for this production lot of DMDNB.

Attributes	**Hampshire Chemical DMDNB (Lot No. OF1617KY01)**	**ANGUS Chemical DMDNB (Lot No. 9G08JG06)**
Appearance	Fine crystalline solid	Fine crystalline powder
Assay (wt. %)	> 98.5	98.7
Water (wt. %)	0.08	0.2
Chlorides (ppm)	56	90
Methanol (wt. %)	< 0.5	None
Melting Point (°C)	210 – 214	210
FTIR Confirmation	Spectrum conforms to standard.	Spectrum conforms to standard

4.2. **Conformance to Commercial Item Description**

Both supplier lots of DMDNB were subjected to full specification analysis by RONA as outlined in CID A-A-59410, "DMDNB (2,3-dimethyl-2,3-dinitrobutane)," dated 18 March 1992. The product attributes outlined in the specification includes:

- FTIR Characterization
- Appearance
- Purity
- Moisture Content
- Chloride Content
- Methanol Content
- Melting Point

4.2.1. The CID specification test results, as generated by RONA for the three sources of DMDNB, are summarized in the table below:

CID A-A-59410 SPECIFICATION TEST RESULTS

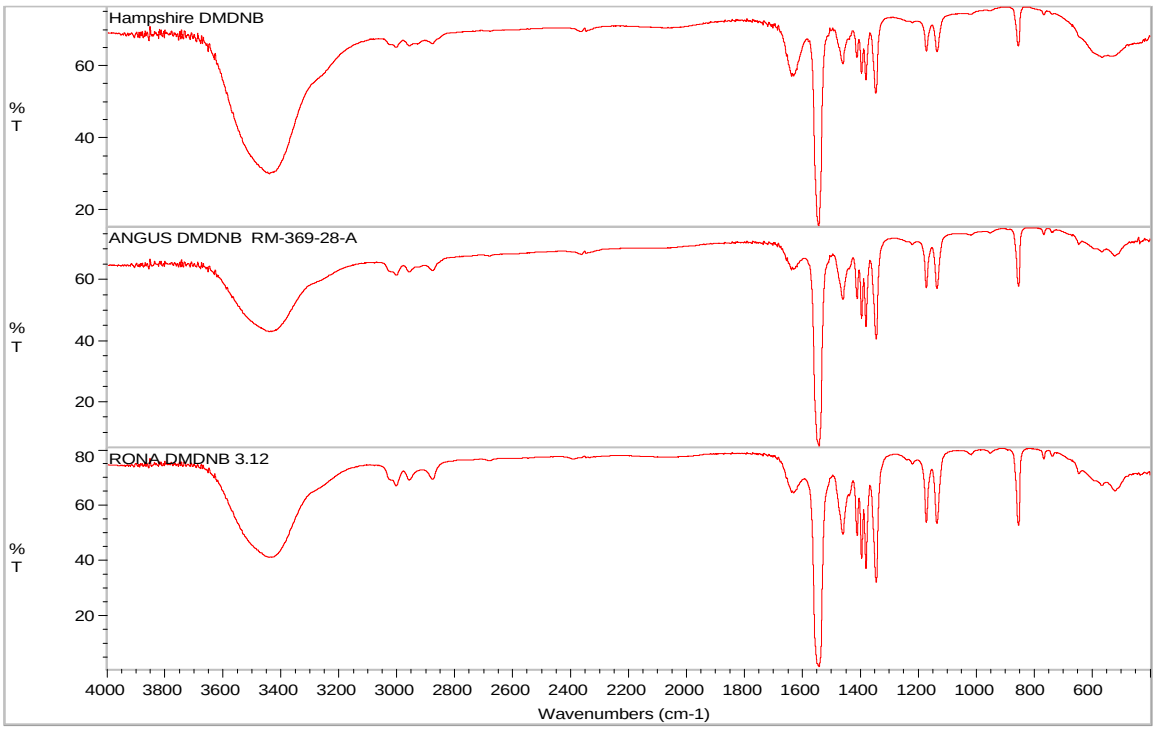
Attributes	Hampshire DMDNB	ANGUS DMDNB	RONA DMDNB	CID Specifications
Appearance	White Solid (Crystalline)	White Solid (Crystalline)	White Solid (Crystalline)	White Solid (Crystalline)
Purity (wt. %)	>98.5	>98.5	>98.5	98.5 min.
Moisture (wt. %)	0.00	0.04	0.18	0.5 max.
Chloride (ppm)	-	-	-	200 ppm max.
Methanol (wt. %)	-	-	-	0.5 max.
Melting Point (°C)	-	-	-	210 - 214
FTIR	Pass	Pass	Pass	Pass

4.2.2. Collection of analytical data is currently in progress on select attributes of the DMDNB materials. Data not reported in the previous table will be reported in a future update of this technical program.

4.2.3. Analyses of the DMDNB materials from the three sources shows all of the products to be within specification range and to be similar on most attributes. Each product appeared by microscopic examination to be a white/opaque crystalline solid with distinct oblong shaped crystals. Upon visual inspection, the DMDNB product from Hampshire Chemical did appear to have a coarser particle size distribution (i.e. less fines) than either the ANGUS or RONA material; otherwise there was no significant differences in the appearance of the three products.

4.2.4. No significant differences were observed in the product purity (assay) and moisture content (within normal experimental deviation). FTIR characterization can be used to

quantitatively identify a given substance. The FTIR spectra shown for the Hampshire, ANGUS, and RONA products are typical for high purity DMDNB.



4.3. Additional Product Attributes Required by RONA / HSAAP

In order to be used in the manufacture of Composition C-4 or other plastic/sheet explosives at Holston Army Ammunition Plant, DMDNB taggant must exhibit a number of satisfactory processing parameters. Evaluation of DMDNB made using the RONA synthesis technique, against both ANGUS DMDNB and the product historically supplied to HSAAP by Hampshire Chemical Corporation, is in progress. These evaluations include:

- Particle Size Distribution
- Differential Scanning Calorimetry
- Vacuum Thermal Stability
- Reactivity / Compatibility with RDX and HMX

4.3.1. Particle Size Distribution

4.3.1.1. The particle size distribution of the three DMDNB products has been determined using a wet sieve technique. The particle size of the materials will also be evaluated at a later date using a laser diffraction method.

4.3.1.2. In the wet sieve testing, a sample of the DMDNB is washed through a series of sieve screens with known, calibrated mesh sizes. The amount of material retained on the

various sieves is collected, dried, and weighed. The particle size data for the three DMDNB products is summarized below:

DMDNB PARTICLE SIZE DATA BY WET SIEVE TECHNIQUE

USSS Sieve No.	Mesh Size (Microns)	Hampshire DMDNB Passing Sieve (%)	ANGUS DMDNB Passing Sieve (%)	RONA DMDNB Passing Sieve (%)
50	300	91.6	99.5	99.5
100	150	13.1	56.7	58.0
120	125	9.7	38.4	45.0
200	75	6.6	13.2	12.6
325	45	6.2	12.0	2.7

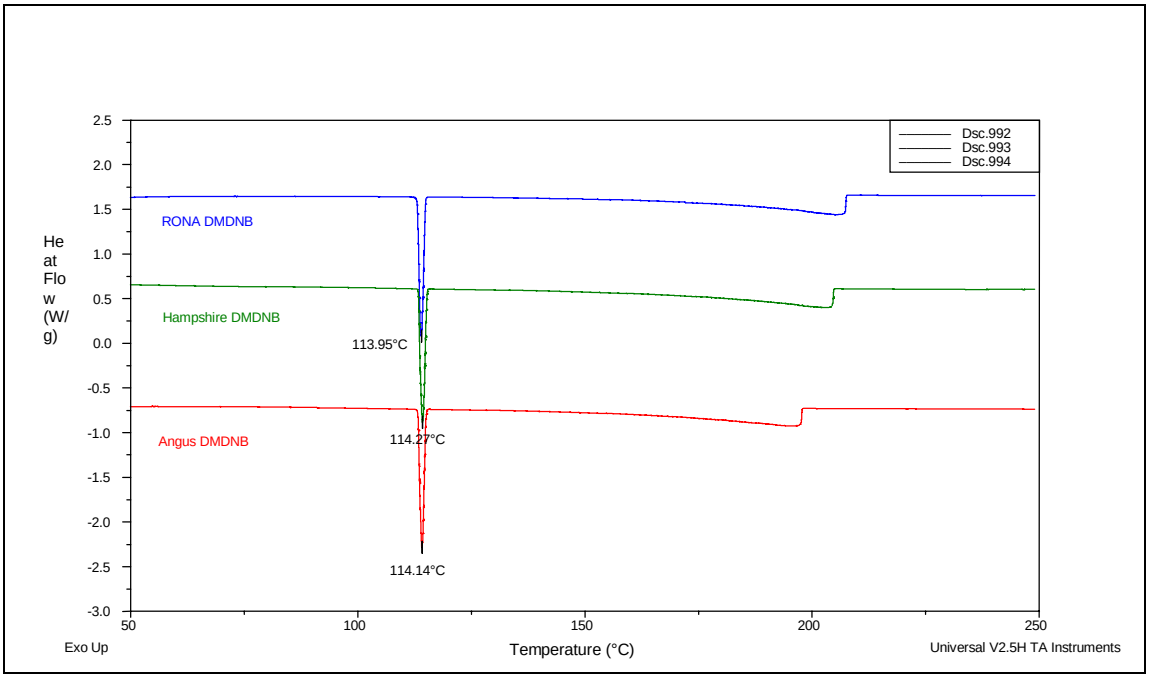
4.3.1.3. The particle size data generated using the wet sieve technique clearly shows that both the ANGUS and RONA DMDNB is significantly finer that the Hampshire product historically used as a taggant in Composition C-4. As an example of how to interpret this data , the 9.7% of the Hampshire DMDNB passing a USSS No. 120 Sieve means that 9.7% of the Hampshire material has a particle size of 125 microns or below. In contrast, approximately 38% of the ANGUS product and 45% of the RONA product has a particle size of 125 microns or below. At this time, the effect of differences in the particle size distribution of DMDNB on large scale processing of Composition C-4 and other plastic explosives is unknown but expected to be insignificant, based upon earlier work. However, the impact of the particle size distribution of the DMDNB in the processing of explosives will be studied further by RONA.

4.3.1.4. As part of the overall experimental program, the particle size distribution of all sources of the DMDNB will also be tested using a laser diffraction technique. These data will be reported in a future update on this technical program.

4.3.2. **Differential Scanning Calorimetry**

4.3.2.1. Differential Scanning Calorimetry (DSC) was used to provide a thermal “fingerprint” of the DMDNB products. DSC will show the temperatures at which a material will melt (endotherm), degrade (exotherm), and in the case of DMDNB, sublime. The DSC scans for the three DMDNB products are provided. As shown, all of the DMDNB materials exhibited similar thermal “fingerprints.”

DSC Scans for the DMDNB Products



4.3.3. Vacuum Thermal Stability

Vacuum Thermal Stability (VTS) will be used as a method to determine the stability of the DMDNB products, as pure ingredients and mixed with RDX / HMX. In this test, 5-gram samples of each test sample is held at 120°C for 48 hours in calibrated capillary tubes filled with mercury. The volume of gas liberated during the test is calculated and expressed in milliliters of gas evolved per gram of sample at a standard temperature and pressure. Although Composition C-4 does not require VTS analysis, explosives that require this parameter to be tested typically allow no more than 0.5 or 1.0 ml of gas evolved per gram of sample. The VTS test results showed that all DMDNB products pass this criterion:

VACUUM THERMAL STABILITY RESULTS ON DMDNB (ml / g)

ANGUS	HAMPSHIRE	RONA
0.09	0.30	0.24

4.3.4. Reactivity / Compatibility with RDX and HMX

Any reactivity of the DMDNB materials with RDX and HMX will be determined by testing the vacuum thermal stability of the materials separately and in combination. If the combined volume of gas evolved for a mixture of the materials (for example, a mixture of DMDNB and RDX) exceeds the sum of the volume of gases generated by the individual components, unacceptable reactivity is said to have occurred. The reactivity of all sources of DMDNB with RDX and HMX are given below. No significant reactivity was observed between the RDX/HMX and any of the DMDNB products evaluated:

REACTIVITY / COMPATIBILITY RESULTS ON DMDNB WITH RDX AND HMX (ml / g; due to reactivity)

SUBSTANCE	ANGUS	HAMPSHIRE	RONA
RDX	0.03	0.30	0.00
HMX	0.05	0.47	0.00
Note: all values below 1.0 ml/g are considered negligible			

5. CONCLUSIONS

5.1. Plastic explosives are required by international law to be tagged with a chemical marking agent.

5.2. 2,3-dimethyl-2,3-dinitrobutane (DMDNB) is the preferred tagging agent employed by the U.S. DOD.

5.3. Royal Ordnance North America, Inc. (RONA), based at Holston Army Ammunition Plant (HSAAP), is the current manufacturer of the plastic explosive Composition C-4 for the U.S. DOD.

5.4. RONA is a significant user of DMDNB.

5.5. Hampshire Chemical Co., a subsidiary of Dow Chemicals, is the only manufacturer of DMDNB.

5.6. Being manufactured by just one supplier, DMDNB is relatively expensive. RONA also believes that the supply issues for DMDNB significantly increases the manufacturing risks for the production of plastic explosives.

5.7. A synthesis technique for DMDNB had been developed in the past at Holston Army Ammunition Plant.

5.8. RONA decided to evaluate the feasibility of manufacturing DMDNB at HSAAP. Having a stable, alternate source of DMDNB will alleviate the risks, associated with limited supply of a very critical raw material in explosive processing, to RONA and the U.S. DOD.

5.9. In recent months, RONA has conducted bench-scale development studies on this DMDNB synthesis that has demonstrated excellent product yields, better than obtained in the past.

5.10. In testing conducted to date, DMDNB produced from the RONA / HSAAP process has met or exceeded all of the specification requirements of Commercial Item Description (CID) No. A-A-59410, dated 18 March 1992. Additional testing is in progress to determine if the RONA produced DMDNB demonstrates process attributes that are suitable for the manufacture of Composition C-4 and other plastic/sheet explosives.