Eliminating Lead, RDX, and AP in a Castable, EMMS-Configured Propellant while Maintaining Performance

WP-2143

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Dr. Bradley Sleadd

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14. ABSTRACT

The objective of WP 2143 was to develop a new environmentally benign, insensitive, castable, high-performance, minimum-smoke rocket propellant formulation. The new formulation approached all of the performance requirements associated with the current minimum smoke, double-based propellant. It did not contain lead, ammonium perchlorate or cyclotrimethylenetrinitramine (RDX). It also demonstrated a reduction in toxicity compared to existing propellants and meet insensitive munition (IM) requirements. This effort met the Statement of Need in a twofold fashion: First, an innovative tactical grain configuration, Exponent Modified Minimum Smoke (EMMS), was used to eliminate the need for lead catalysts, and second, advanced energetic ingredients were incorporated into this grain design to provide performance levels meeting current minimum smoke double-base propellants, insensitivity to meet IM requirements, and a reduction in toxicity compared to existing propellant ingredients.

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RDX replacements, MBANF, DNFOA, ANAF, lead replacements, ammonium perchlorate replacements, human health evaluation, environmental evaluation, AzTA, AGDNM NT123, AGDNM NT124, AONT, DINGU, DNGU.

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Abstract

Objectives:

The objective of WP 2143 was to develop a new environmentally benign, insensitive, castable, high-performance, minimum-smoke rocket propellant formulation. The new formulation approached all of the performance requirements associated with the current minimum smoke, double-based propellant. It did not contain lead, ammonium perchlorate or cyclotrimethylenetrinitramine (RDX). It also demonstrated a reduction in toxicity compared to existing propellants and meet insensitive munition (IM) requirements. This effort met the Statement of Need in a twofold fashion: First, an innovative tactical grain configuration, Exponent Modified Minimum Smoke (EMMS), was used to eliminate the need for lead catalysts, and second, advanced energetic ingredients were incorporated into this grain design to provide performance levels meeting current minimum smoke double-base propellants, insensitivity to meet IM requirements, and a reduction in toxicity compared to existing propellant ingredients. The key objectives were:

1) Demonstrate key technologies eliminating lead and RDX in a castable, EMMS-configured rocket-motor test while providing high performance and insensitive munitions capability. Supporting objectives are:
2) Demonstrate an RDX replacement with a reduction in toxicity, acceptable performance, and insensitivity.
3) Demonstrate the use of non-lead catalyzed minimum-smoke propellants incorporating the RDX replacement which will augment insensitive munitions capability.

Technical Approach:

This effort used an innovative *castable*, *minimum-smoke* propellant grain design supported by three key components to *eliminate lead catalysts and RDX*, provide *insensitive munitions* capability, provide *high-performance*, and incorporate materials which give a *reduction in toxicity*. EMMS uses a ballistic control propellant (BCP) to control the pressure and temperature sensitivity of a rocket motor and a matrix propellant to provide total rocket motor impulse.

Results:

A variety of potential RDX replacement materials were considered initially by utilizing thermochemical calculations to rank and help down-select the candidates. These were then placed in a matrix where ease of synthesis, toxicity, density, heat of formation, sensitivity and performance were ranked. Methylene-bis-aminonitrofurazan (MBANF) was thus selected as the RDX replacement material.

The team evaluated MBANF as a potential RDX replacement in minimum-smoke rocket propellants. The sensitivity of MBANF is similar to RDX, and it provides similar performance in propellants. Propellant tailoring efforts were completed, and a propellant meeting all of the technical objectives except a hazard class 1.3 was developed. The evaluation of Naval Surface Warfare Center Indian Head Explosive Ordnance Disposal Technology Division (NSWC IHEODTD) -developed lead-free extruded propellant for the ballistic control portion of the motor was also successfully completed, and recommendations made for the final material to be used in the demonstration. A subscale motor was successfully built, but due to unforeseen issues, the motor could not be tested for safety reasons.

Benefits:

1) The rocket motor ballistics responds almost solely on the burning rate behavior of a faster-burning BCP. The BCP is only a fraction of the mass of the overall motor propellant, so it has little effect on total delivered performance.

2) The rocket motor performance is almost solely a function of the thermochemical performance of the slower burning matrix propellant (MP). Elimination of lead in the matrix propellant is thus also possible. Enhancement of the MP performance is desirable, and thus suitable RDX replacements will be evaluated.

3) Use of an end-burning grain enhances insensitive munitions response by preventing the propellant debris field and ignition on bullet and fragment impact typical of center perforated motor configurations. In addition, end-burning grains provide high-performance by allowing high volumetric loading of the propellant in the motor case. Lastly, end-burning grains can be readily manufactured by current industrial infrastructure and are typically made in a cartridge-loaded configuration.

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List of Acronyms

AGDNM NT123	Ammonium dinitro(4-nitro-2H-1,2,3-triazol-2-yl)-methanide
AGDNM NT124	Ammonium dinitro(3-nitro-1H-1,2,4-triazol-1-yl)-methanide
AN	Ammonium nitrate
ANAF	4-[2-(4-nitro-1,2,5-oxadiazol-3-yl)-2-oxidodiazenyl]-1,2,5-oxadiazol-3-amine
AONT	Ammonium 5-nitrotetrazolate-2-N-oxide
APHC	Army Public Health Center
AzTA	4,4'-azobis-1,2,4-triazole
BCP	Ballistic control propellant
BTTN	butanetriol trinitrate
CHNO	Carbon, Hydrogen, Nitrogen, Oxygen
CL-20	Hexaazahexanitroisowurtzitane
DAF	3,4-diaminofurazan
DATB	1,3-diamino-2,4,6-trinitrobenzene
DEGDN	diethyleneglycol dinitrate
DINGU	dinitroglocoluril
DNFOA	N,N'-bis(4-nitro-1,2,5-oxadiazol-3-yl)-ethanediamide
DOE	Design of Experiments
DSC	Differential scanning calorimietry
EHA	Environmental Health Assessment
EMMS	Exponent modified minimum smoke
ESD	Electrostatic discharge
ESOH	Environmental, Safety, and Occupational Health
FTIR	Fourier Transform Infrared Spectrophotometry
GAP	Glycidylazide polymer
HMDI	Hexamethylene diisocyanate
HPLC	High performance liquid chromatography
IHE	Insensitive High Explosive
IM	Insensitive Munitions
I_{sp}	Specific Impulse
I_{vol}	Volumetric Impulse
LLM-105	2,6-diamino-3,5-dinitropyrazine-1-N-oxide
LNC	Lacquer Grade Nitrocellulose

List of Acronyms (cont.)

MBANF	N,N'-bis(4-nitro-1,2,5-oxadiazol-3-yl)-methanediamine
MNA	N-methyl-p-nitroaniline
MP	Matrix propellant
NC	nitrocellulose
NG	Nitroglycerin
NSWC IHEODTD	Naval Surface Warfare Center Indian Head Explosive Ordnance Disposal Technology Division
PEP	Propellant Evaluation Program
PGA	Poly (diethyleglycol adipate)
PGN	Polyglycidyl nitrate
QSAR	Quantitative Structure Activity Relationship
RDX	Hexamethylene trinitramine
SAB	Scientific Advisory Board
TATB	1,3,5-triamino-2,4,6-trinitrobenzene
TGA	Thermogravimetric analysis

Acknowledgments

I would like to acknowledge the excellent work accomplished by the co-performers on the project, Ms. Christine Knott from Naval Surface Warfare Center Indian Head Explosive Ordnance Disposal Technology Division, Ms. Edna Grove from Aerojet/Rocketdyne Corporation and Dr. William Eck from the US Army Public Health Center. Additionally, I would like to acknowledge the Strategic Environmental Research and Development Program office for their financial and programmatic support.

Objective

The objective of this Statement of Need (SON) is to develop a new environmentally benign, insensitive, castable, high-performance, minimum-smoke rocket propellant formulation. The new formulation must meet all of the performance requirements associated with the current minimum smoke, double-based propellant. It must not contain lead, ammonium perchlorate or cyclotrimethylenetrinitramine (RDX). It must also demonstrate a reduction in toxicity compared to existing propellants and meet insensitive munition (IM) requirements. This effort will meet the Statement of Need in a twofold fashion: First, an innovative tactical grain configuration, Exponent Modified Minimum Smoke (EMMS), will be used to eliminate the need for lead catalysts, and second, advanced energetic ingredients will be incorporated into this grain design to provide performance levels meeting current minimum smoke double-base propellants, insensitivity to meet IM requirements, and a reduction in toxicity compared to existing propellant ingredients. The key objectives are:

1) Demonstrate key technologies eliminating lead and RDX in a castable, EMMS-configured rocket-motor test while providing high performance and insensitive munitions capability. Supporting objectives are:

2) Demonstrate an RDX replacement with a reduction in toxicity, acceptable performance, and insensitivity,

3) Demonstrate the use of non-lead catalyzed minimum-smoke propellants incorporating the RDX replacement which will augment insensitive munitions capability.

Technical Approach

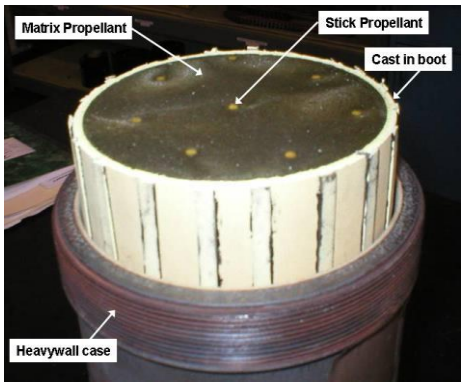
This effort uses an innovative *castable, minimum-smoke* propellant grain design supported by three key components to *eliminate lead catalysts and RDX*, provide *insensitive munitions* capability, provide *high-performance*, and incorporate materials which give a *reduction in toxicity*. EMMS uses a ballistic control propellant (BCP) to control the pressure and temperature sensitivity of a rocket motor and a matrix propellant to provide total rocket motor impulse. The advantages of this are multifold:

1) The rocket motor ballistics responds almost solely on the burning rate behavior of a faster-burning BCP. The BCP is only a fraction of the mass of the overall motor propellant, so it has little effect on total delivered performance.

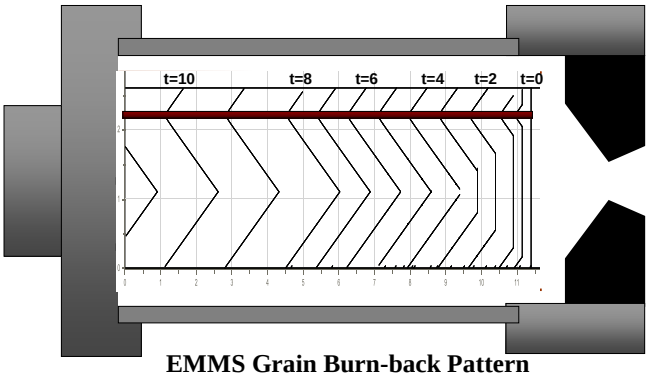
2) The rocket motor performance is almost solely a function of the thermochemical performance of the slower burning matrix propellant (MP). Elimination of lead in the matrix propellant is thus also possible. Enhancement of the MP performance is desirable, and thus suitable RDX replacements will be evaluated.

3) Use of an end-burning grain enhances insensitive munitions response by preventing the propellant debris field and ignition on bullet and fragment impact typical of center perforated motor configurations. In addition, end-burning grains provide high-performance by allowing high volumetric loading of the propellant in the motor case. Lastly, end-burning grains can be readily manufactured by current industrial infrastructure and are typically made in a cartridge-loaded configuration.

The EMMS concept was demonstrated at Aerojet using lead-catalyzed min-smoke propellants. The key concept and configuration are shown in Figure 0.1. The EMMS configuration uses a ballistic approach similar to fielded wired-endburning motors such as the standard Stinger rocket motor. For EMMS, ballistic control is achieved by incorporating sticks of faster burning propellant (the BCP) in conjunction with a slower burning matrix propellant (MP) in a castable end-burning configuration (suitable for TOW, Hellfire, and other motors).



EMMS Demo (Lead Containing)



EMMS Grain Burn-back Pattern

Figure 0.1. EMMS Motor Configuration

The burn-back pattern of the rocket motor grain is also shown in Figure 0.1. As the calculations (and the demo) show, the BCP stick burns faster, thus creating a right-circular concave conical burning surface on the face of the grain. The seven internal BCP sticks and one centerline BCP stick create eight burning conical cavities which control the regression of the entire grain. The advantages of this are considerable:

1) The rocket motor ballistics respond almost solely based on the burning rate behavior of the faster-burning BCP sticks regardless of the burning rate characteristics of the matrix propellant. The BCP sticks are only a fraction of the mass of the overall motor propellant, so these have little effect on total delivered performance. Thus, wide latitude in materials is available to eliminate lead but provide desired burning-rate response.
2) The rocket motor performance is almost solely a function of the thermochemical performance of the slower burning MP regardless of the ballistics of the matrix propellant (note: consistent with motor operating pressure and expansion ratio). Elimination of lead in the matrix propellant is thus also possible. Enhancement of the MP performance is required and thus RDX replacements will be used. Reducing the sensitivity of these replacements is highly desirable to achieve IM properties. The effects of the RDX replacements on MP burning rate are trivial since ballistic control is primarily due to the BCP sticks.
3) Use of an end-burning grain enhances insensitive munitions response by preventing the propellant debris field and ignition on bullet and fragment impact relating to configurations with center perforations. In addition, end-burning grains provide high-performance by

allowing high volumetric loading of the propellant in the motor case. Lastly, end-burning grains can be readily manufactured by current industrial infrastructure and are typical made in a cartridge-loaded configuration.

The program has been subdivided into four distinct tasks; RDX Replacement, Ballistic Control Propellant, Matrix Propellant and Motor Demonstration. The first three will be discussed in detail; the program has not yet reached the Motor Demonstration level.

RDX Replacement: A replacement material which offers equivalent performance, reduced sensitivity, and reduced environmental impact is required. This is a significant and difficult task and will be addressed with a combination of predictive performance modeling, environmental parameter management, and experimental chemical property/compatibility evaluation. RDX replacement efforts will be conducted by NSWC IHEODTD and supported by Aerojet Rocketdyne.

BCP Development: A BCP stick formulation must be developed which has the required burning-rate characteristics but without lead catalysts. The probability of success is enhanced due to the elimination of the performance constraint for this material, allowing a very wide variety of materials to be investigated. BCP development will be conducted by NSWC IHEODTD and supported by Aerojet Rocketdyne.

MP Development: A MP formulation must be developed which meets the performance criteria for the program. This effort is dependent on the RDX replacement material and on formulation efforts to minimize sensitivity and improve insensitive munitions response. MP development will be conducted by Aerojet Rocketdyne and supported by NSWC IHEODTD.

This project also involves a progressive human occupational health and environmental toxicological evaluation of chemical substances used in the development of a new energetic formulation. This evaluation will be carried out as outlined in ASTM Standard E2552-16. Initial efforts were devoted to a search of the available literature, both open source and restricted, for existing information. Data gaps identified as a result of the literature search process were addressed using Quantitative Structure Activity Relationship (QSAR) modeling. Based upon this initial evaluation, an Interim Toxicology Assessment (TA) was produced and provided to the Principal

Investigator and his designees. The Final Toxicology Assessment has also been produced and provided to the Principal Investigator and his designees, and is presented here as Appendix

Results and Discussion

1. RDX Replacement

Chemical structures based on heterocyclic groups such as furazan, furoxan, tetrazole oxides, nitrotriazoles and compounds that contain azo or azoxy bridges between these moieties, as well as other structural groups served as starting points for this project. Examples of preliminary target compounds are shown in Figure 1.1. All these compounds have been synthesized either in the U.S. or abroad and thus all were known compounds.

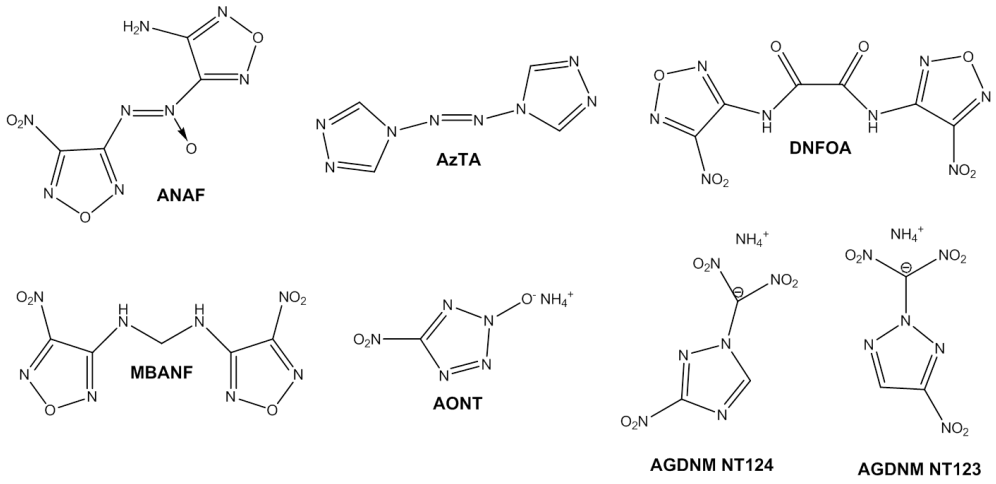


Figure 1.1. Potential RDX Replacement Molecules

In preliminary screening these compounds were assessed for material properties (Table 1.1) and for performance potential (Figures 1.1-1.3). As the data show, reported and predicted properties match closely, thus providing a level of confidence.

Table 1.1. Thermochemical calculation inputs

Compound	Formula	Mol wt	ΔH_f, kcal/mol calc/actual		Density, gm/cc calc/actual	
RDX	$C_3H_6N_6O_6$	222.11	15	18	1.816	1.799
ANAF	$C_4H_2N_8O_5$	242.11	153	---	1.87	1.856 (sol)
DNFOA	$C_6H_2N_8O_8$	314.13	73	39	1.90	1.852
MBANF	$C_5H_2N_8O_6$	270.12	119	115	1.82	1.782
AzTA	$C_4H_4N_8$	164.13	190	---	1.545	1.676
AGDNM NT123	$C_3H_5N_7O_6$	235.12	0	---	1.8	---
AGDNM NT124	$C_3H_5N_7O_6$	235.12	-35	---	1.7	---
AONT	$CH_4N_6O_3$	148.08	40	---	---	1.703

Theoretical thermochemical calculations were run on several new materials using an Aerojet Rocketdyne version of the Navy Propellant Evaluation Program (PEP) code, as summarized in Table 1.1. The materials were incorporated into a typical minimum-smoke propellant formulation, and plots of specific impulse (I_{sp}), density, and density-impulse were made. These thermochemical values were then used to calculate various performance parameters compared to RDX when the selected RDX replacements were substituted for RDX at varying solids loading levels in a baseline minimum smoke propellant formulation. Predicted I_{sp} ranges are given in Figure 1.2, predicted formulation density ranges are given in Figure 1.3, and predicted volumetric impulse (I_{vol}) ranges are given in Figure 1.4.

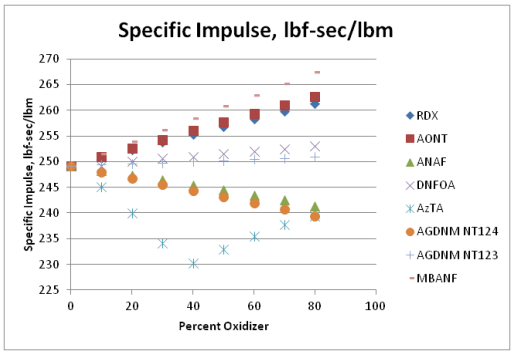


Figure 1.2. I_{sp} of Baseline Formulation

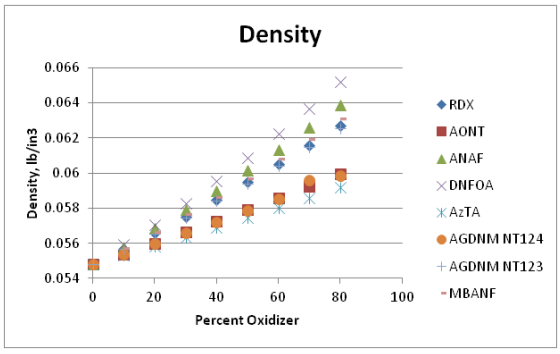


Figure 1.3. Density of Baseline Formulation

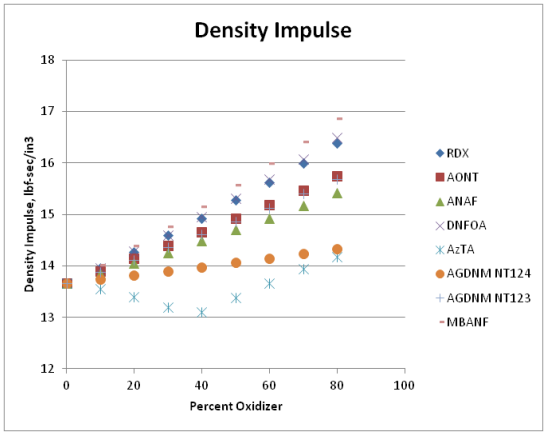


Figure 1.4. I_{vol} of Baseline Formulation

As seen in Figure 1.4, DNFOA and MBANF exhibit clear advantages in c I_{vol} over the other compounds under consideration.

Another important consideration in selecting viable RDX replacement was the relative ease of synthesis and scale-up, and the associated costs. Several of the compounds (ANAF, AGDNM NT123, AGDNM NT124) have multi-step, low yielding syntheses, and the physical properties are not well characterized. Additionally, sensitivity data for these materials have not been reported and are not well predicted using the current models. For the two materials which exhibited the highest I_{vol} in potential formulations, the syntheses are straightforward and have only two steps from a commercially available precursor. The success of the program is predicated upon the ability to produce 5 kilograms of the selected material for formulation and testing.

An evaluation of the potential environmental impact of the target RDX replacement compounds was undertaken by Dr. William Eck at the U. S. Army Public Health Center (APHC). If no experimental data were identified in the literature, toxicity values for the various parameters were predicted using Quantitative Structure Activity Relationship (QSAR) software where possible. Modeling packages include US EPA's EPI Suite™ 4.0 (USEPA, 2008a), ECOSAR™ (USEPA, 2007) and TOPKAT (BIOVIA, Inc.). (EPI Suite™ and ECOSAR™ are trademarks of the USEPA.) The banding criteria for toxicity assessment, as defined by the APHC, are shown in Figure 1.5.

Endpoint	High	Moderate	Low
LD_{50}	<150 mg/kg	150-1500 mg/kg	>1500 mg/kg
LC_{50}/EC_{50}	<0.1 mg/L	0.1-1.0 mg/L	>1.0 mg/L
Inhalation LC_{50}	<0.1 g/m^3-h	0.1-1.0 g/m^3-h	>1.0 g/m^3-h
Mutagenicity/ Carcinogenicity	Positive evidence	Mixed evidence	No evidence
Dermal/Ocular	Positive evidence	Probable evidence	No evidence

Figure 1.5. QSAR banding criteria

The target compounds were then ranked to aid in down-selection along with other criteria. Ranking is based on acute toxicity and mutagenicity/carcinogenicity projections, and is given in the general selection criteria matrix in Figure 1.6. Modeling projections should only be regarded as tentative because energetics of these types are not always well-handled by currently-available QSAR modeling tools.

Six criteria were used to down-select the final RDX replacement candidate for scale-up and evaluation; density, heat of formation, relative EcoTox ranking, insensitivity (if known), ease of synthesis and scale-up, and performance (Figure 1.6).

Molecule	Density	ΔH_f	EcoTox	Insensitivity	Ease of Synthesis/Scale-up	Performance
ANAF	H	H	7	L-M	L	H
AzTA	M	H	6	H-M	H	L
DNFOA	H	H	5	H-M	M	H
MBANF	H	H	3	H	H	H
AONT	M	H	4	H-M	L-M	M
AGDNM NT124	M	L	1	?	L	M
AGDNM NT123	M-H	L	2	?	L	H

H = High, M = Medium, L = Low

Figure 1.6. RDX Replacement Evaluation Matrix

DNFOA and MBANF were selected for further evaluation based upon the ranking in the selection criteria matrix. Laboratory-scale sensitivity data were obtained from Aerojet Rocketdyne (shown in Table 3.3), and Table 1.2 shows the preliminary *in vitro* toxicology evaluation of DNFOA and MBANF.

Table 1.2. Preliminary toxicology testing results

	DNFOA	DNFOA toxicity assessment	MBANF	MBANF toxicity assessment	RDX	RDX toxicity assesment
Ames mutagenicity	Not mutagenic; cytotoxic above 20 µg/mL	Negative	Not mutagenic; cytotoxic above 18 µg/mL	Negative	Not mutagenic	Negative
Neutral Red Uptake	243 mg/kg	Moderate	148 mg/kg	Moderate	59(mouse)	Moderate
(LD_{50} equivalent)					100(rat) 500(rabbit)	
Microtox* (LC_{50})	2.85 mg/L	Low	0.126 mg/L	Moderate	LC_{50} (fish)=3.8 mg/L	Low

*The Microtox assay is a collective estimation of toxicity to aquatic species

Both compounds exhibit lower impact and friction sensitivity compared to RDX. However, DNFOA has elevated sensitivity towards electrostatic discharge relative to both RDX and MBANF. DNFOA has also been shown to increase shock sensitivity in propellant formulations (JIMTP Task 10-2-36) relative to propellants containing CL-20 or RDX at the same solids loading. This, and some unexpected difficulties in the synthesis of DNFOA, led to the down-selection of MBANF as the RDX replacement candidate. These data were presented to the SERDP SAB in February of 2012 and satisfied the Go/No Go criteria for the identification of a suitable RDX replacement material.

MBANF had also been evaluated in propellants. In 2007, Aerojet Rocketdyne briefly studied MBANF as an oxidizer for minimum-smoke propellants in a polyglycidyl nitrate (PGN) binder system. At 16% of the formulation, an I_{sp} of 246.5 sec was calculated, and Insensitive High Explosive (IHE) card gap results showed the potential for a Class 1.3 propellant formulation, at +60/-70 cards. A subsequent mix at 30% MBANF had a theoretical specific impulse of 249.6 sec, and was positive at 90 cards in the IHE gap test, showing there is a limit to the sensitivity versus performance trade.

MBANF is synthesized in two high yielding steps from 3,4-diaminofurazan (DAF) as shown in Figure 1.7. It has been manufactured at NSWC IHEODTD at the 2 kg scale, and 4 kgs have been delivered to Aerojet/Rocketdyne.

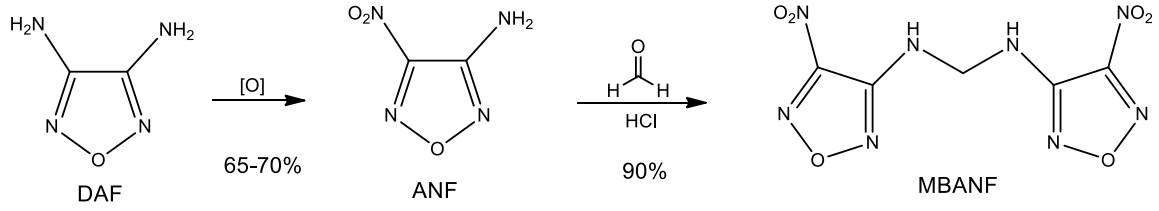


Figure 1.7. Two step synthesis of MBANF

2. Ballistic Control Propellant

The ballistic control propellant component of this program will develop a propellant formulation that will burn faster than the matrix propellant and will not contain lead, ammonium perchlorate (AP) or Cyclotrimethylenetrinitramine (RDX). M36 propellant will be used as the baseline for the ballistic control propellant. The baseline M36 propellant formulation is shown in Table 2.1 (LC-12-6 is a lead-containing ballistic modifier).

Table 2.1. M36 propellant formulation

Component	M36
Nitrocellulose (12.6%N)	49 %
Nitroglycerin	40.6 %
Di-n-propyl adipate	3.0 %
2-Nitrodiphenylamine	2.0 %
LC-12-6 (Ballistic Modifier)	5.3 %
Candelilla Wax	0.1 %

Nitroglycerin (NG), which is the plasticizer for both M36 and other double base minimum smoke rocket motor propellants, is a nitrate ester, which is a very sensitive ingredient. Alternatives for this component have been explored under the Army's Insensitive Munitions – Advanced Technical Objective (IM-ATO) gun propellant program and will be explored in this program to decrease sensitivity. Examples are butanetriol trinitrate (BTTN) and diethyleneglycol dinitrate (DEGDN).

The BCP must also have a burning rate greater than 1 in/sec at 3000 psi, exhibit plateau or mesa burning behavior and be thermally insensitive. Burn rate data for the baseline M36 propellant formulation is shown in Table 2.2. Note the plateau in the burn rate (relatively constant burn rate with increasing pressure) above 2400 psi.

Table 2.2. Burn rate data for M36 propellant

M36 Burning Rate	
Pressure (psig)	Rate @ 70°F (in/sec)
1	0.0514
2400	1.0436
2800	1.0597
3200	1.048
3600	1.0728
4000	1.0926

A matrix of mixes was evaluated using two different types of nitrocellulose (12.6% N and 13.2% N), BTTN or DEGDN substituted for NG, and two different bismuth/copper salts as ballistic modifiers instead of LC-12-6. The ratio of plasticizer (BTTN or DEGDN) to polymer (NC) was also varied. The initial mix matrix is shown in Table 2.3.

Table 2.3. Initial Mix Matrix for BCP

	1	2	3	4	5	6	7	8	9	10	11	12
NC (12.6%N)	49	49	56.67	56.67	35	35	0	0	0	0	0	0
NC (13.2%N)	0	0	0	0	0	0	49	49	56.67	56.67	35	35
BTTN	40.6	0	33.33	0	0	50	40.6	0	33.33	0	0	50
DEGDN	0	40.6	0	33.33	50	0	0	40.6	0	33.33	50	0
DI-N-PROPYL ADIPATE	3	3	3	3	3	3	3	3	3	3	3	3
2NDPA/MNA	2	2	2	2	2	2	2	2	2	2	2	2
BISMUTH COPPER RESORCYLATE	2.7	2.7	2.5	2.5	5	5	2.7	2.7	2.5	2.5	5	5
BISMUTH COPPER SALICYLATE	2.7	2.7	2.5	2.5	5	5	2.7	2.7	2.5	2.5	5	5
pl:po	0.684:1.0	0.6845:1.0	0.5:1.0	0.5:1.0	1.0:1.0	1.0:1.0	0.684:1.0	0.684:1.0	0.5:1.0	0.5:1.0	1.0:1.0	1.0:1.0

The intial mix matrix included manufacturing the BCP in two ways: solventless (12.6%N NC) and with a solvent (13.2%N NC). The goal was always to use a solventless process if that were possible to eliminate the additional environmental hazards of solvents. Since the baseline M36 formulation worked fairly well in a previous demonstration of a BCP, has significant data regarding its formulation and processability, and uses 12.6%N NC, we decided to start there. If the 13.2%N was needed to achieve the burning rate or plateau burning that was needed for the program it could be incorporated at a later date. Once these hand mixes were produced they were evaluated for sensitivity, thermal stability and processability. Eight mixes were then down-selected for production in the one pint mixer, shown in Table 2.4. After mixing they were extruded into ¼" x 4"

strands and strand burn data at various pressures was collected. The strand burn data is given in Table 2.5 and a comparative graph is shown in Figure 2.1.

Table 2.4. Pint Mix Matrix for BCP

Mix								
Ingredient	IH13DBBCP-200	IH13DBBCP-201	IH13DBBCP-202	IH13DBBCP-203	IH13DBBCP-217	IH13DBBCP-218	IH13DBBCP-219	IH13DBBCP-220
Nitrocellulose, 12.6%N	35.00%	35.00%	49.00%	49.00%	56.67%	56.67%	56.67%	56.67%
Nitroglycerin								
BTTN	49.90%	49.90%	40.50%	40.50%	33.23%	33.23%		
DEGDN							33.23%	33.23%
Di-n-propyl Adipate	2.00%	2.00%	2.00%	2.00%	2.00%	2.00%		
Triacetin	3.00%	3.00%	3.00%	3.00%	3.00%	3.00%	3.00%	3.00%
2-nitrodiphenylamine							2.00%	2.00%
Ethyl Centralite								
Candelilla wax	0.10%	0.10%	0.10%	0.10%	0.10%	0.10%	0.10%	0.10%
LC-12-6								
Bismuth subsalicylate			2.60%					
Copper salicylate			1.90%					
Monobasic copper Beta Resorcylate			0.90%					
Antimony oxide				3.60%	1.80%	1.25%	1.10%	1.40%
Tin oxide		2.25%		1.60%				
Cupric oxide				0.20%				
Bismuth stannate					3.20%	2.35%	2.80%	3.60%
Silver sulfate								
BC-12-15	10.00%					1.40%	1.10%	
Bismuth oxide		7.75%						
	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%

Table 2.5. Strand Burn Data

Lot#	Average Burning Rate at Pressures					α	β	R^2
	1500	2100	2700	3300	3900			
0200	0.544	0.642	0.722	0.788	0.853	0.01758	0.470	0.99954
0201	0.464	0.595	0.736	0.884	1.043	0.00094	0.846	0.99658
0202	0.611	0.725	0.881	0.910	0.983	0.01537	0.505	0.97321
0203	0.434	0.570	0.707	0.846	0.972	0.00087	0.849	0.99969
0217	0.463	0.585	0.680	0.780	0.821	0.00528	0.614	0.99167
0218	0.439	0.565	0.676	0.801	0.920	0.00157	0.770	0.99892
0219	0.388	0.478	0.559	0.664	0.753	0.00238	0.694	0.99524
0220	0.419	0.507	0.593	0.677	0.779	0.00381	0.641	0.99525

Burn rate (in./sec) = αP^{β} where α = burn rate coefficient, P = chamber pressure, β = pressure exponent

R^2 = measure of statistical agreement (values closer to 1 indicate less variance in the data)

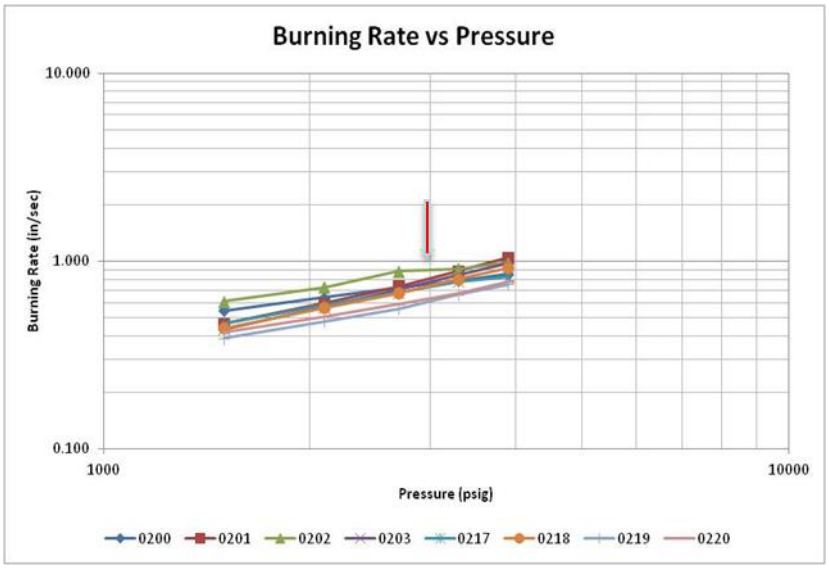


Figure 2.1. Burn Rate vs. Pressure Comparison; No NG

As can be seen from the data, the necessary burn rate and pressure exponent could not be achieved with the formulations evaluated. Only mix 202 showed a slight plateau burning region but the burn rate did not reach 1 inch/sec.

It was then determined that the use of NG rather than BTTN or DEGDN was going to be necessary to achieve the desired burn rate and plateau burning behavior. While NG is more sensitive than the other nitrate esters, its overall mass in the rocket motor will be quite small and should not contribute significantly to overall sensitivity.

At this point the BCP development experienced a thirteen month delay in schedule due to unavailability of NG paste. Mixes were finally completed in February of 2014, and extrusions were completed in March of 2014. Mix 049 is a baseline mix of the lead-containing M36 propellant. Due to differences in manufacturing (roll mills unavailable), it was decided that a baseline mix would be made to ensure that no changes in data were observed using the new process. Seven pint mixes were manufactured and evaluated for processability. After mixing they were extruded into ¼" x 6" strands and strand burn data at various pressures was collected. The strand burn data is given in Table 2.6 and a comparative graph is shown in Figure 2.2. Ongoing mechanical and utility issues delayed the collection of the strand burn data, and subsequent down-selection of the final BCP formulation.

Table 2.6. Revised Mix Matrix for BCP

Lot#	Average Burning Rate at Pressures					α	β	R^2
	1500	2100	2700	3300	3900			
046	0.526	0.656	0.875	0.988	1.247	0.00074	0.893	0.984796
047	0.644	0.835	0.900	1.133	1.401	0.00226	0.770	0.958373
048	0.717	0.849	0.998	1.128	1.243	0.00995	0.583	0.997935
049	0.897	0.964	1.061	1.190	1.274	0.05545	0.377	0.967992
322	0.717	0.853	1.010	1.147	1.241	0.00963	0.588	0.997117
323	0.704	0.906	1.086	1.298	1.467	0.00247	0.772	0.999055
324	0.606	0.737	0.881	1.037	1.194	0.00327	0.711	0.993684

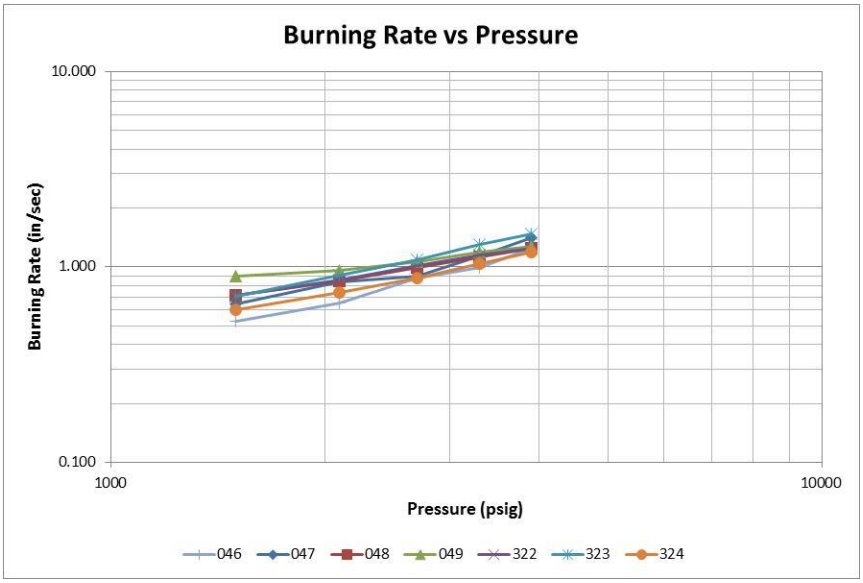


Figure 2.2. Burn Rate vs. Pressure Comparison; With NG

As can be seen from the data, the addition of NG as the plasticizer did allow us to achieve the necessary burn rate and pressure exponent for a couple of the formulations, Lots 048, 049, 322 and 324. These formulations were repeated in the next series and tested via strand burn to ensure the data is repeatable and valid. Additional strands were provided for testing in order to get data at various temperatures and pressures. Once this was completed, a DOE on the most promising of these formulations was performed in order to find the optimal ratio of plasticizer:polymer and percentage of ballistic modifier(s) to obtain the necessary burn rate and pressure exponent.

3. Matrix Propellant (MP)

NSWC IHEODTD supported Aerojet-Rocketdyne in the evaluation of potential replacements for both RDX and lead salt ballistic modifiers. Four distinct tasks were initiated: thermochemical performance calculations to determine optimal combinations of new ingredients, characterization of the novel ingredients DNFOA, DINGU, and LLM-105, initial sub-scale propellant mixes incorporating MBANF and LLM-105, and subsequent tailoring of the propellant binder system to further reduce sensitivity and enhance binder quality.

Performance Calculations

Theoretical thermochemical calculations results are given in Results and Discussion: RDX Replacement. Over 100 calculations were initially run, and the data showed that MBANF, AONT and DNFOA were all potential candidates for evaluation, as was AGDNM NT123. Iterations continued throughout the technical efforts to look at additional combinations of these materials, as well as any new materials discovered. As a goal for this effort, state-of-the-art production propellant theoretical performance properties were targeted: a specific impulse $\geq$ 244 lb_f-sec/lb_m, a cured propellant density $\geq$ 0.060 lb/in^3, and a volumetric impulse of $\geq$ 14.7 lb_f-sec/in^3.

MBANF had been identified as the least sensitive and primary candidate RDX replacement for evaluation; therefore a theoretical performance evaluation of MBANF in an initial matrix propellant was completed. Running performance calculations with Aerojet Rocketdyne's proprietary thermochemical code allowed for early formulation screening without consuming the novel energetic material.

Several formulations included the reduced sensitivity co-ingredients TATB and DATB; these could potentially be used for performance/sensitivity trades. These theoretical calculations indicated matrix propellants loaded with MBANF exhibit excellent performance characteristics. Formulation specifics and predicted performance properties are provided in Table 3.1 and Figures 3.1-3.3 below.

Table 3.1. Theoretical MBANF Formulations

MBANF, %	TATB, %	DATB, %	BTTN, %	NC, %	I_{sp} lb_f-s/lb_m	Density lb/in^3	Rho-I_{sp} lb_f-s/in^3
	10		63.75	21.25	243.4	0.0575	14
		10	63.75	21.25	244.2	0.05739	14.01
10			63.75	21.25	249.2	0.05732	14.28
10	10		56.25	18.75	243.8	0.05835	14.23
20	10		48.75	16.25	244.3	0.05923	14.47
30	10		41.25	13.75	244.7	0.06001	14.71
30			48.75	16.25	250.2	0.05903	14.77
30		10	41.25	13.75	245.4	0.06001	14.73
40	10		33.75	11.25	245	0.06106	14.96
50	10		26.25	8.75	245.4	0.06202	15.22
50		10	26.25	8.75	246.2	0.06189	15.24
50			33.75	11.25	251.2	0.06085	15.28

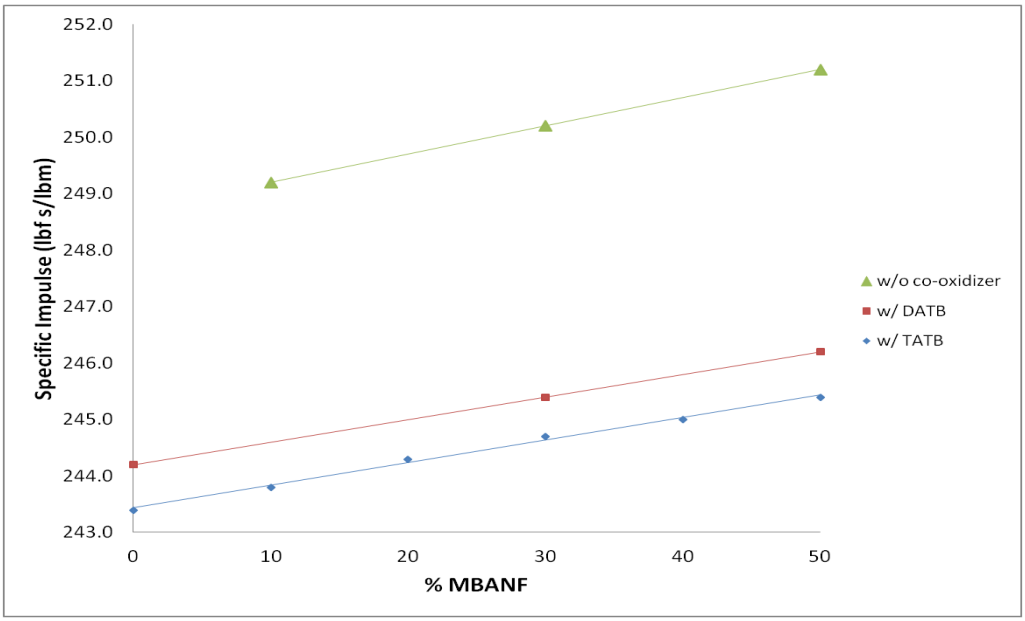


Figure 3.1. Specific Impulse of Theoretical Matrix Formulations

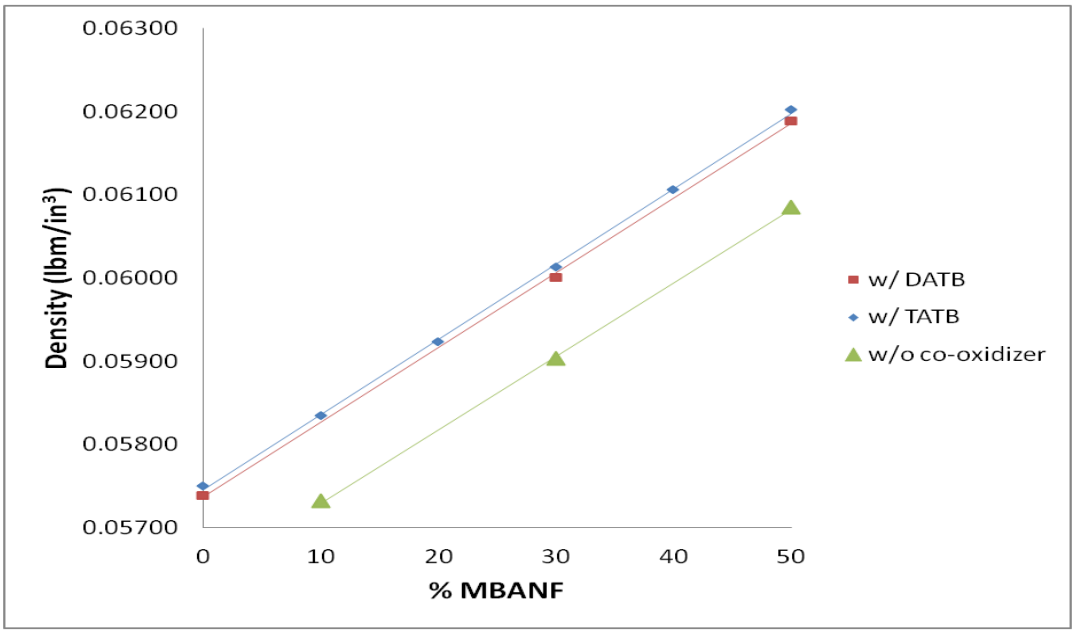


Figure 3.2. Density of Theoretical Matrix Formulations

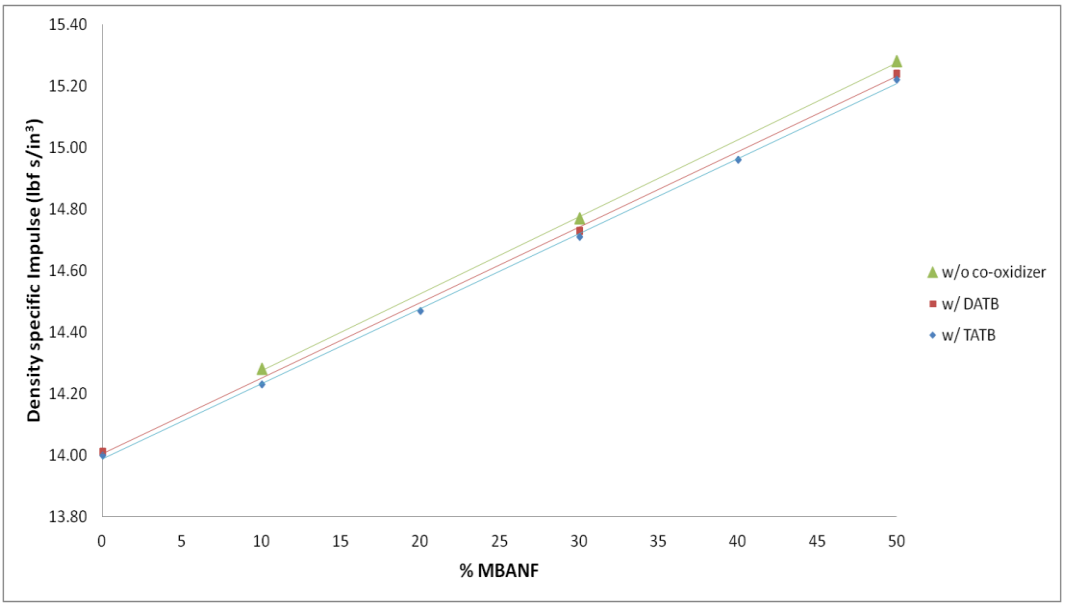
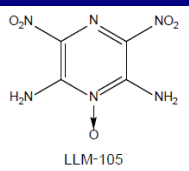
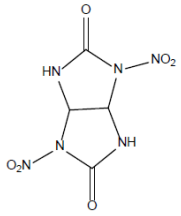


Figure 3.3. Density-Specific Impulse of Theoretical Matrix Formulation

Later in the technical effort, two additional materials were identified as potential ingredients for evaluation. LLM-105 is a proprietary material developed at LLNL, with the properties shown in

Table 3.2. Dinitroglycoluril (DINGU) is currently being made at BAE Holston. Results of performance calculations with these materials are shown in Figure 3.4.

Table 3.2. Additional Candidate Ingredients

Name	Formula	Structure	H_f Kcal/mol	Density g/cc
LLM-105	$C_4H_4N_6O_5$	 LLM-105	-3.1	1.918
DINGU	$C_4H_4N_6O_6$	 DINGU	-177	1.94

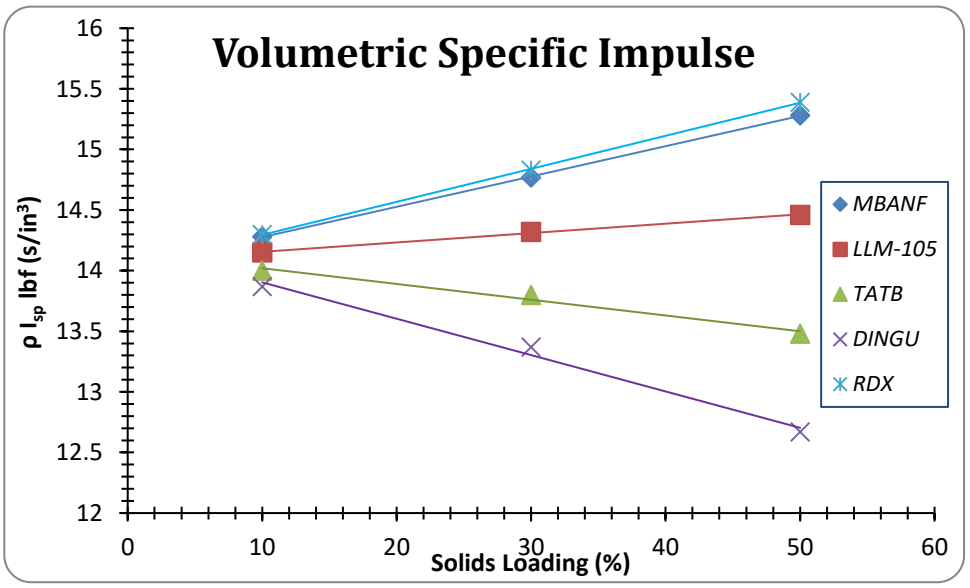


Figure 3.4. Relative Performance of RDX Replacement Candidates

Based on these results, MBANF appeared to perform most similarly to RDX. A final series of thermochemical runs was made adding DINGU at levels as low as 1% of the total solids. This

combination may be an excellent trade of performance and sensitivity. The impact of this combination of materials on density-impulse is shown in Figure 3.5.

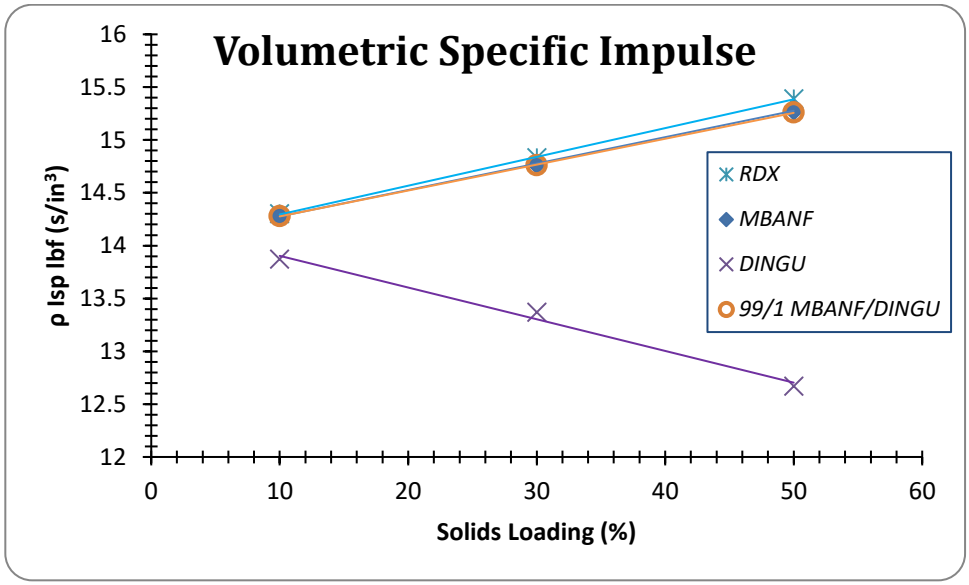


Figure 3.5. MBANF/DINGU Combination Offers RDX-like Performance

Material Characterization

Several ingredients were identified as potential performance enhancing materials, and were therefore selected for the next phase of the evaluation. Once a material was identified, samples were brought in-house for basic material characterization, including sensitivity and thermal testing, as well as compatibility with other potential propellant ingredients. Testing of each material in the analytical laboratory included the following tests:

- Isothermal TGA at 70°C
- TGA at 1°C/min for weight loss
- DSC at 4 heating rates for decomposition and kinetics data
- HPLC for purity
- FTIR
- Density
- CHN analysis

For ease in organizing the data, the testing has been grouped by material in the sections that follow.

MBANF Characterization

Initially 3 grams of MBANF was received from NSWC IHEODTD for evaluation. Testing of the MBANF was reduced somewhat, as the material had been evaluated in the past. The testing on this new lot included FTIR, HPLC, and DSC at 10°C/min (Figures A.1 – A.5 in Appendix A). The MBANF sample seemed to be quite pure, and the results obtained with this sample were very similar to results obtained in years past with different lots.

DNFOA Characterization

Five grams of DNFOA were received from NSWC IHEODTD for characterization. The sensitivity test data showed the DNFOA was slightly ESD sensitive. The data are provided in the table below.

Table 3.3. Initial Material Sensitivity Data

Material	RDX	MBANF	DNFOA	LLM-105	DINGU
Impact, kg-cm	49	220	150	90	70
Friction, psi at 90° drop angle	1200	> 1800	> 1800	> 1800	> 1800
ESD, joules	0.38	> 6	0.19	0.09	0.7
Autoignition, °C	220	213	247	324	224

The FTIR fingerprint is provided in Figure A.10. The thermal data are shown in Figures A.11-A.13.

DSC compatibilities of DNFOA with several common propellant ingredients were also completed, including: aluminum, ammonium nitrate (AN), 1,2,4-butanetriol trinitrate (BTTN), diethyl glycol dinitrate (DEGDN), glycidyl azide polymer (GAP), hexamethylene diisocyanate (HMDI), lacquer-grade nitrocellulose (LNC), *n*-methyl *p*-nitroaniline (MNA), cyclotrimethylene trinitramine (RDX), and polydiethylene glycol adipate (R18). Any shift of more than 10°C in the exotherm shows evidence of incompatibility. In this study, no dangerous interactions or incompatibilities were observed. DSC scans are displayed in Figures A.15 – A.24.

LLM-105 Characterization

In addition to DNFOA and MBANF, a sample of LLM-105 was received from NSWC IHEODTD for characterization. Laboratory sensitivity was normal for all of the tests with the exception of ESD sensitivity (as reported in Table 3.3)

Further lab characterization of LLM-105 included CHNO testing, purity by HPLC, FTIR, TGA thermal characterization (both with a temperature ramp and isothermal over time), DSC testing (including kinetics), and DSC compatibility testing with various common propellant ingredients. The CHNO analysis (Figure A.29) showed good correlation between theoretical and actual values. Purity by HPLC was attempted but was not successful; LLM-105 would not dissolve in any lab solvent available.

FTIR spectrum is shown in Figure A.25. The decomposition temperature of LLM-105 was determined to be 319.27˚C by TGA analysis (Figure A.27); isothermal TGA (Figure A.28) showed LLM-105 to be stable. Figure A.26 shows the kinetics of LLM-105 as determined by DSC. Figures 3.A.30 – A.35 show the results of 1:1 compatibility testing with common propellant ingredients using DSC; no incompatibility issues were discovered.

DINGU Characterization

Characterization of the novel energetic ingredient dinitroglycoluril (DINGU) was also completed. The sensitivity of the material was found to be normal in most categories, as shown in Table 3.3, with the exception of ESD sensitivity. Normal handling procedures will be put in place when using this material, with the addition the use of grounding wrist stats and grounding of containers. The material characterization was also completed. The kinetics as determined by DSC runs at 1, 5, 10, and 20^{o}C/min are very good for this type of material. The kinetics properties are shown in Figure A.37, and the 1^{o}C/min TGA run to 600^{o}C is provided in Figure A.38, showing good thermal stability.

Compatibility tests were completed using DINGU material from BAE/Holston, and the MBANF oxidizer from NSWC IHEODTD (Figures A.39 – A.43). No concerns were noted for compatibility of the DINGU with nitrate ester plasticizers BTTN and DEGDN, the nitrocellulose, or RDX.

There does appear to be a shift in the exotherm when the DINGU is combined with MBANF. The test was repeated, and the same results were obtained. A small 5-gram mix of the two materials, combined with an off-the-shelf lacquer, however, showed no increased sensitivity.

4. Propellant Development

Incorporation of MBANF and LLM-105

As discussed previously, early performance calculations indicated MBANF could be combined with either TATB or DATB in a propellant to achieve excellent volumetric specific impulse. However, Aerojet Rocketdyne did not have access to TATB or DATB. Thus, the initial mixes (C24793 and C24882) relied on a combination of NG, GAP, and aluminum to achieve a comparable density-specific impulse. Sensitivity data was obtained for these sub-scale mixes and is reported below in Table 4.1. The autoignition temperature is notable, as it indicates moderate sensitivity of the propellant. However, this is likely due to the incorporation of GAP in the matrix propellant. Reformulating this propellant (C24998) yielded less sensitive impact and friction characteristics, but autoignition data was not obtained due to the small mix size.

Table 4.1. Initial MBANF Formulation Sensitivity Data

Mix	C24793	C24882	C24998
Formulation			
MBANF	10%	10%	15%
Binder	27.5% NC/ GAP/HMDI	27.5% NC/ GAP/HMDI	35% NC/Polyester/HMDI
Plasticizer	62.5% NG/BTTN	62.5% NG/BTTN	50% BTTN/DEGDN
Specific Impulse, lb_f-s/lb_m	246.4	246.4	237.8
Density-Impulse, lb_f s/in^3	13.98	13.98	13.83
Cured/Uncured Sensitivity	Uncured	Cured	Cured
Impact, kg-cm	135	145	300
Friction, psi at 90°	1800	1600	1800
ESD, joules	6	6	6
Autoignition, °C	162	165	186

Propellant development work continued using ground MBANF material. Formulations were manufactured that had 20% or less MBANF which processed very well, gave fairly typical

minimum-smoke propellant burning rates, and showed normal laboratory sensitivity. However, the card gap sensitivity of these propellants was higher than desired. Table 4.2 summarizes these initial mixes. Theoretical performance calculations show all of these formulations are lower than the targeted goals for the program, but the Brookfield end-of-mix viscosities are low, allowing for additional solids to be added to the formulations to increase performance. The mix with LLM-105 did not cure well. With only up to 20% oxidizer in these formulations, there was concern that the binder was driving sensitivity, so a reformulation effort ensued.

Table 4.2. Initial Propellant Development Mixes with MBANF

Mix Number	C25171	C25287	C25371	C25372	C25418	C25473	C25474	C25475
Oxidizers, %								
MBANF	15	20	-	15	-	20	20	20
LLM-105	-	-	-	-	15	-	-	-
RDX	15	-	-	-	-	-	-	-
Other Ingredients, %								
BTTN/DEGDN	50.85	58.85	58.85	58.85	58.85	58.85	58.85	58.85
NC/R18/HMDI	16.65	17.65	17.65	17.65	17.65	17.65	17.65	17.65
Bismuth/Carbon	2.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Performance								
I_{sp}, lb_f-s/lb_m	240.4	237.8	227.7	235.7	N/A	230.8	230.4	234.9
Density, lb/in^3	0.057	0.05638	0.05443	0.05596		0.05558	0.05566	0.05651
Rho-I_{sp}, lb_f-s/in^3	13.7	13.41	12.39	13.19		12.83	12.82	13.28
EOM Viscosity, kP	1.5	0	0.5	0.5	0.5	0.5	0.5	1
Burning rate, in/s								
@ 500 psi	0.19	0.17	Not tested	Not tested	Not tested	Not tested	Not tested	Not tested
@ 1000 psi	0.38	0.33						
Exponent	0.75	0.68						
Uncured Sensitivity								
Impact, kg-cm	Not tested	300	300	45	Not tested	Not tested	Not tested	Not tested
Friction, psi		1800 @ 90°	1800 @ 90°	1200 @ 90°				
ESD, joules		6	6	6				
Cured Sensitivity								
Impact, kg-cm	295	Not tested	Not tested	Not tested	300			Not
Friction, psi	1800 @ 90°				1800 @ 90°			tested
ESD, joules	6				6			
Autoignition, C	165				165			
IHE Card gap, cards	95	95			85	85	110	

Binder Enhancement

A sub-scale binder study was undertaken in order to further refine the binder system. Energetic plasticizers, especially in high-performance propellants, can dominate propellant sensitivity by overshadowing the contribution of ingredients. Furthermore, leaching was observed in some card

gap tubes, also due to the binder system, and this can further cloud the sensitivity issue. Figure 4.1 shows the study matrix used to rapidly fine-tune the propellant binder.

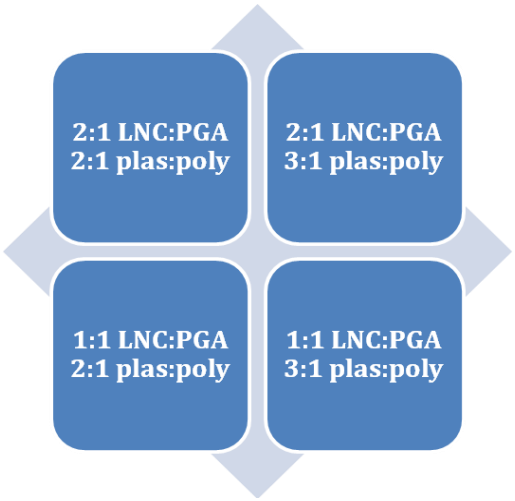


Figure 4.1. Gumstock Binder Enhancement Scheme

In the first stage of this study, a small Design of Experiments effort was conducted by varying the polymer/co-polymer ratio and the plasticizer/polymer ratio in a series of unfilled gumstocks. Each mix was closely examined at the polymer-rich surface to qualitatively assess binder integrity, and swabbed to determine the extent of plasticizer leaching. Figures 4.2 and 4.3 show the qualitative results of this gumstock study; mix III shows the poorest quality binder and the most plasticizer leaching, while mix II shows the lowest level of leaching as well as the highest quality binder (indicated by the translucent quality and uniform cure state of the gumstock sample)

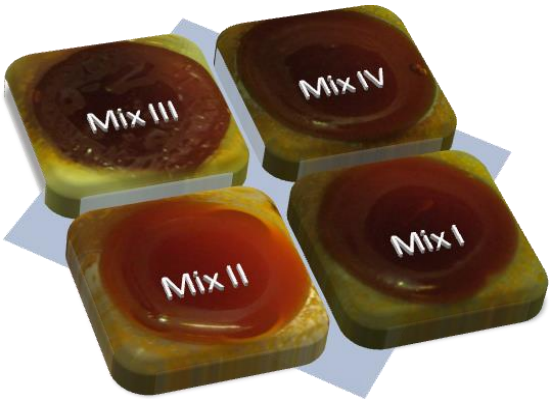


Figure 4.2. Gumstock Surfaces

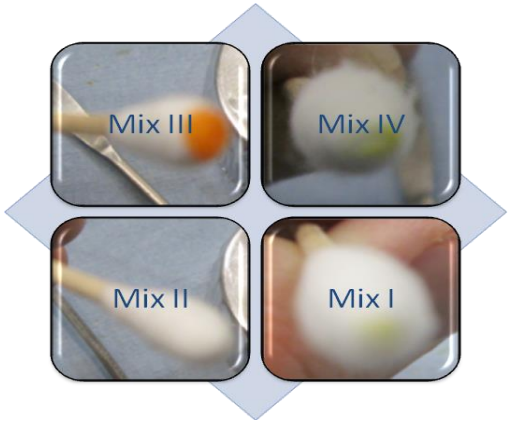


Figure 4.3. Plasticizer Leaching

Both the least effective and most effective binder system have the same level of plasticizer, indicating that the amount of secondary polymer is the critical factor in binder quality. This indicates the plasticizer/polymer ratio can be tweaked to maximize performance while retaining binder integrity (reduce plasticizer leaching). Still, as the plasticizer/polymer ratio approaches 3:1, the propellant seems to become more brittle, suggesting an effective upper limit does exist.

The next step of the binder study was to manufacture larger (pint) mixes loaded with inert solids and test IHE gap tubes with varying plasticizer/polymer ratios, as well as varying ratios of plasticizer types. Figure 4.4 is the DOE matrix for these pint mixes; each mix used ammonium sulfate to simulate the oxidizer candidates. The binder system selected for this program was a typical one used for minimum-smoke propellants, comprised of a 60/40 blend of polyester resin and nitrocellulose, which was crosslinked with hexamethylene diisocyante (HMDI).

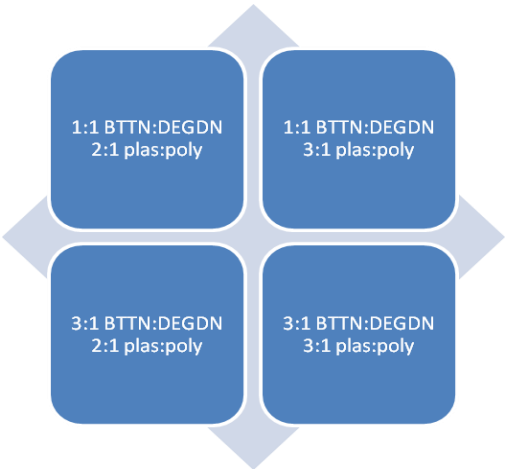


Figure 4.4: Binder Sensitivity Matrix

Table 4.3 shows the results of IHE gap tube shock sensitivity testing.

Table 4.3. Binder Shock Sensitivity Results

Mix #	C25560	C25562	C25563	C25564
BTTN/DEGDN	3/1	1/1	1/1	3/1
Plasticizer/polymer	2/1	2/1	3/1	3/1
IHE gap test (+)	44 cards	30 cards	60 cards	78 cards
IHE gap test (-)	46 cards	38 cards	62 cards	86 cards

These tests showed that the energetic plasticizers do contribute significantly to the shock sensitivity of the propellant, and indicate both the total amount of plasticizer and the types of plasticizer used are significant. Furthermore, these results show the amount of plasticizers relative to the amount of polymer exerts a larger influence over the propellant shock sensitivity than the plasticizer composition does alone. This binder study shock sensitivity information was critical to identifying the contribution of the MBANF to the propellant sensitivity later in the effort.

5. Propellant Tailoring

The goal of the next series of mixes was to determine performance gains using MBANF/DINGU, compared to RDX. The mixes have varying amounts of unground, as-received (60-micron) and ground (3-micron) material, in a nitrocellulose and polyester binder system (18.29%), plasticized with 31.71% BTTN/DEGDN. The mixes all cured well with no processing or gassing issues. Normally increasing the fine content will hurt the processing, but since these mixes are only 50% solids, processing was unaffected. The DINGU mix was not manufactured, due to not having a wide distribution of coarse and fine materials available at the time.

The card gap data show (Table 5.1), as expected, that increasing the fine content of MBANF in the formulation decreases the sensitivity. In addition, when comparing C25850 and C25810, it can be seen that the MBANF is less sensitive than a comparable RDX mix. This is encouraging data toward developing an RDX-replacement material.

Table 5.1. Sensitivity Data with MBANF and DINGU Ingredients

Mix Number	C25808	C25850	C25852	C25810	C25853
Oxidizer (50%) Coarse/fine	MBANF 67/33	MBANF 40/60	MBANF 20/80	RDX 40/60	DINGU 40/60
EOM viscosity, kP	0.9	3.0	2.0	2.6	Not made
IHE card gap, cards	+104/-112	+100/-104	+85/-92	+108/-112	
Burning rate, in/sec at 1000 psi	0.2	Not tested	Not tested	0.22	
Rho-I_{sp}, lb_f-s/in^3	13.85	13.85	13.85	13.98	11.24

A Design of Experiments (DOE) study was established for the next round of mixes that focused on maximizing the performance/sensitivity trade. MBANF, LLM-105, and DINGU were incorporated into the originally planned DOE, at levels from 20 to 60%. However, due to the availability of LLM-105 at the time, it was eliminated from the DOE. The final matrix of mixes and resulting data are shown in Table 5.2. All of the mixes were manufactured with a 1.5/1 plasticizer to polymer ratio, again using BTTN/DEGDN in a nitrocellulose/polyester binder system. Those mixes listed in the table with a "0" viscosity did not register movement on the Brookfield viscometer dial when the viscosity was measured.

Table 5.2. Revised Performance vs. Sensitivity DOE Results

Run	MBANF, %	DINGU, %	I_{sp} lb_f-s/lb_m	Density lb/in^3	Rho-I_{sp} lb_f-s/in^3	EOM Viscosity, kP	Card gap, cards
1	20	-	239.0	0.05508	13.16	0.5	+70/-80
2	-	20	218.5	0.05566	12.16	0	-70
3	60	-	250.8	0.05995	15.04	19.5	+114/-116
4	0	60	187.6	0.06205	11.64	100+	Scrapped
5	20	20	224.7	0.05804	13.04	1.0	+80/-85
6	20	10	232.0	0.05652	13.11	1.5	-80
7	10	20	221.6	0.05682	12.59	0	+70/-80
8	40	10	238.0	0.05898	14.04	1.5	108/112
9	10	40	206.0	0.05997	12.37	6.0	+94/-104

In general, the DINGU did not mix into the propellant mixes very well, and caused some problems with viscosity and casting. The DINGU arrived from BAE Holston in two sizes, 60 and 8 micron, but was very agglomerated. The material was put into a Turbula laboratory grinder for a few minutes to break up the agglomerates before adding to the mixes, but processing was still poor for many formulations. Run number 4, for example, was made several times with blends of both sizes of DINGU, different hold times, and different processing techniques, but a castable propellant was never successfully made at the 60% DINGU level. Further work needs to be done in this area to improve the wetting of the DINGU.

All of the mixes were tested for impact, friction, and ESD sensitivity, and all were insensitive. Four IHE card gap tubes were loaded from each mix, and the results are shown in Table 5.2 along with the performance calculation data. Each IHE tube contains approximately 10 grams of propellant, and the same test matrix was used for each mix. If a negative result is obtained, then the number of cards is reduced in the next test. If a positive result is obtained, the number of cards is increased. Higher numbers of cards indicate more sensitive propellant formulations. This information was then input into Minitab statistical software for analysis. A regression analysis was done, as well as plots of main effects of the variables. The data was analyzed several ways.

Figures 5.1 and 5.2 show the effect of MBANF and DINGU content on the performance (I_{vol}) of the formulations in the DOE. As expected, the graphs show that increasing MBANF content increases performance, and increasing DINGU content decreases performance. This will become an important trade in balancing sensitivity versus performance.

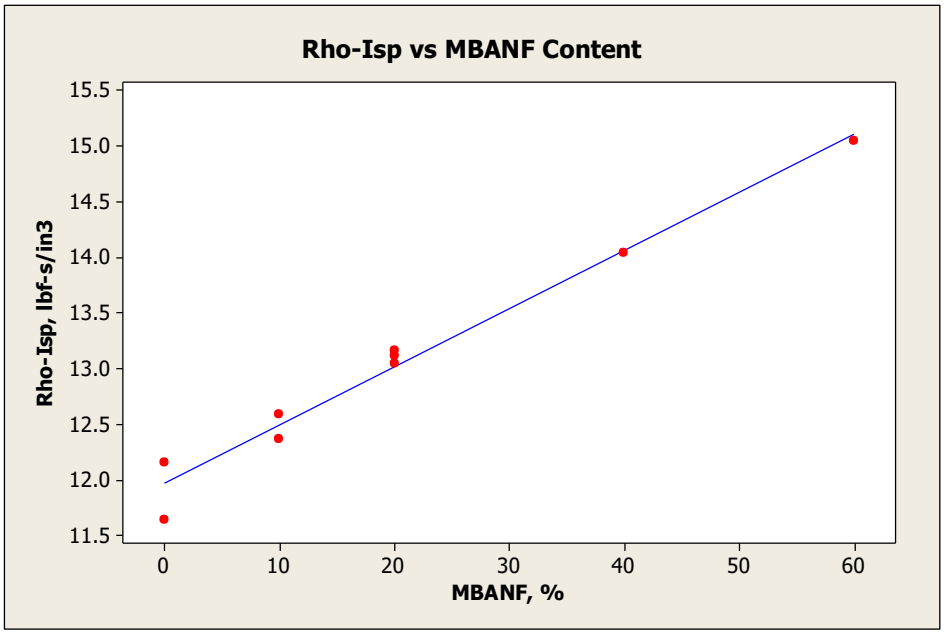


Figure 5.1. MBANF Content versus I_{vol}

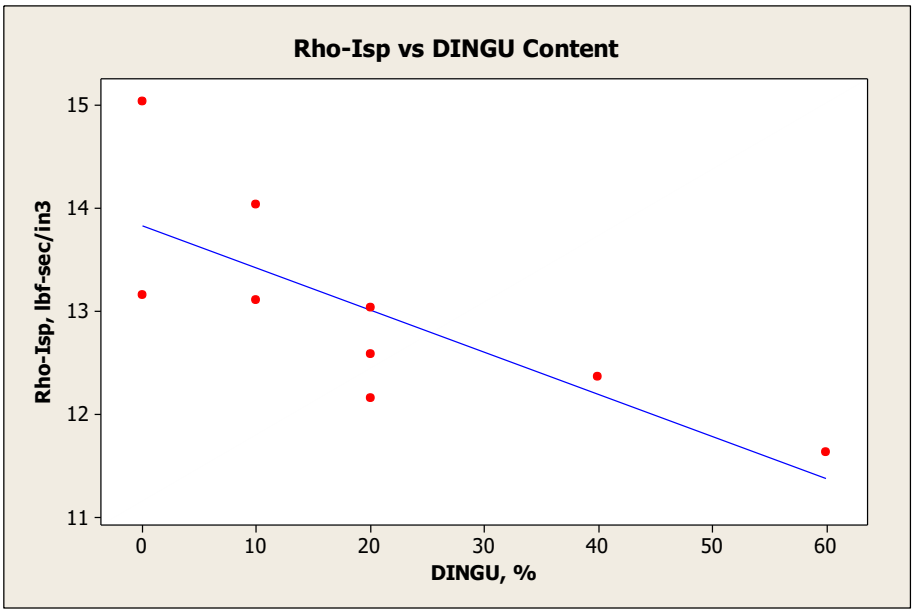


Figure 5.2. DINGU Content versus I_{vol}

The card gap data was analyzed next, and both the MBANF and DINGU contents were plotted against the lowest negative value of the four tubes tested. The results are shown in Figures 5.3 and 5.4, and show, as expected, that increasing MBANF content increases the sensitivity. There is no clear correlation with the DINGU data, possibly due to the fact that the 60% mix had no data.

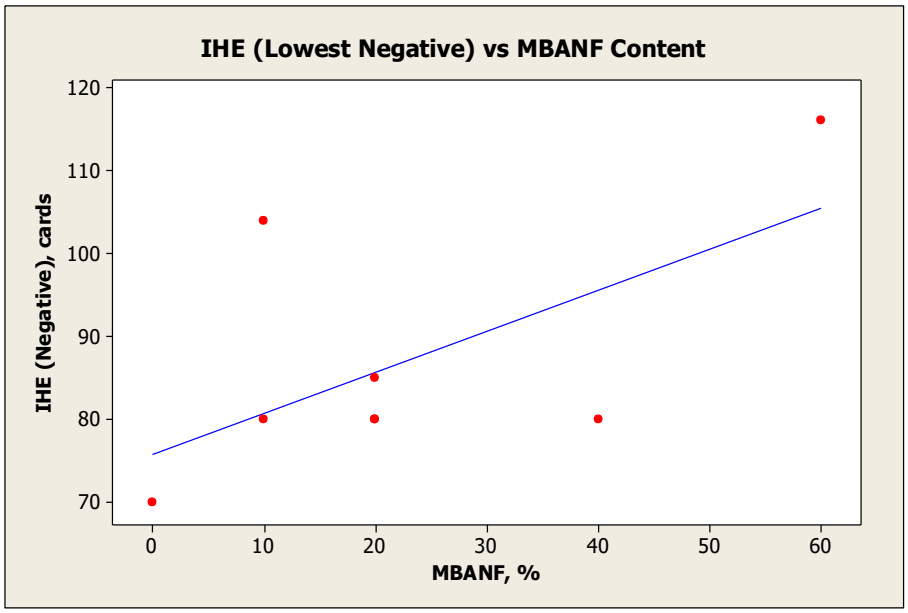


Figure 5.3. MBANF Content versus Card Gap Sensitivity

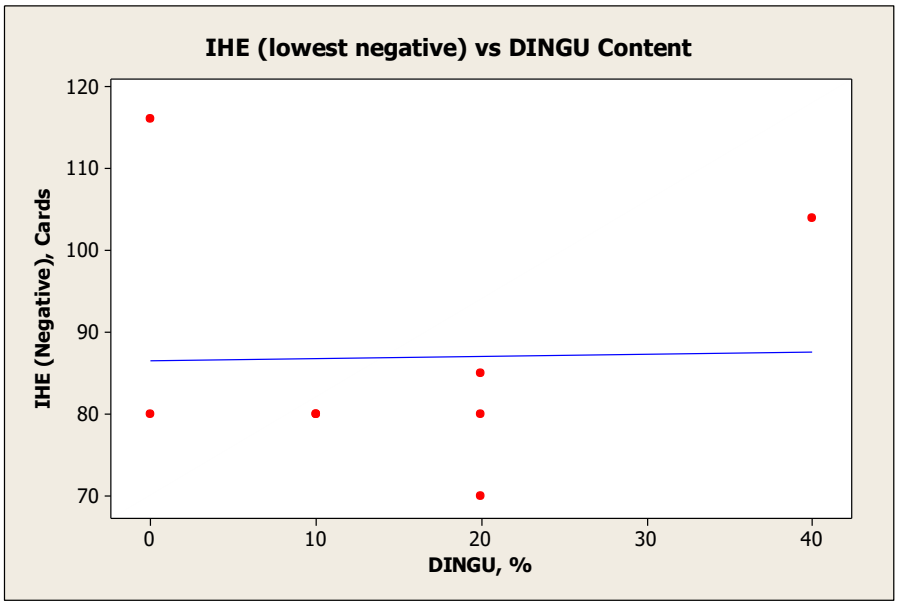


Figure 5.4. DINGU Content versus Card Gap Sensitivity

The binder content versus the card gap sensitivity was also plotted, and as expected, as the binder content goes up (total solids is lowered), the card gap sensitivity is reduced, as shown in Figure 5.5.

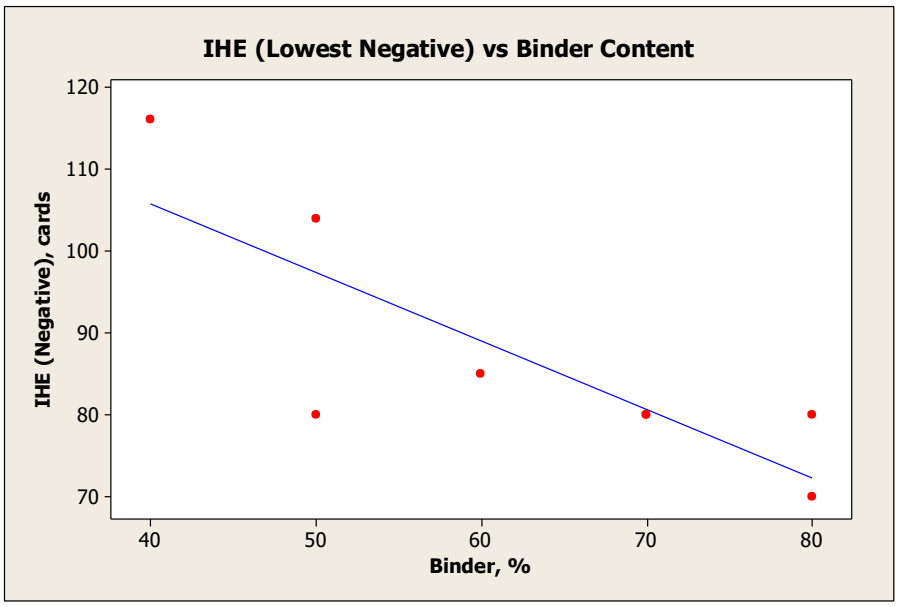


Figure 5.5. Binder Content versus Card Gap Sensitivity

The final correlation was for performance versus sensitivity. Unfortunately, there is not a clear correlation. There is a general trend that higher performance propellants give higher sensitivity, as shown in Figures 5.6-5.8, which is the typical trend.

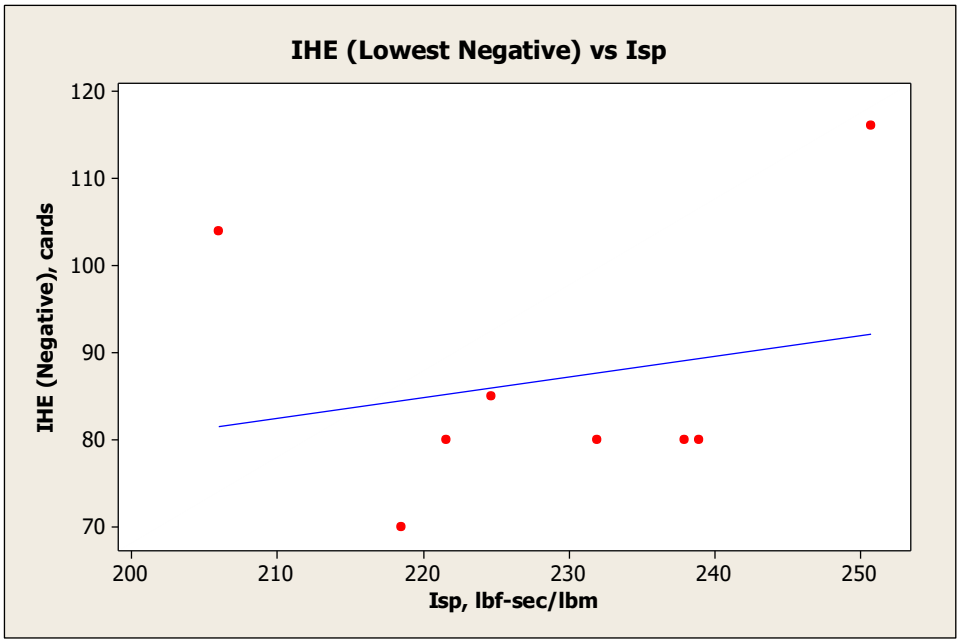


Figure 5.6. I_{sp} Performance versus Card Gap Sensitivity

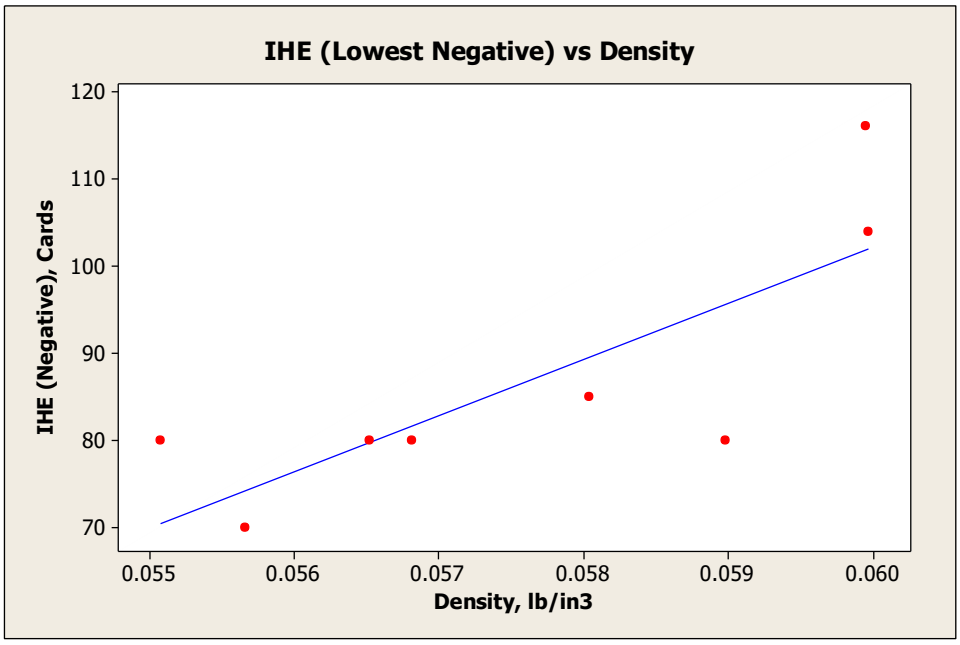


Figure 5.7. Density versus Card Gap Sensitivity

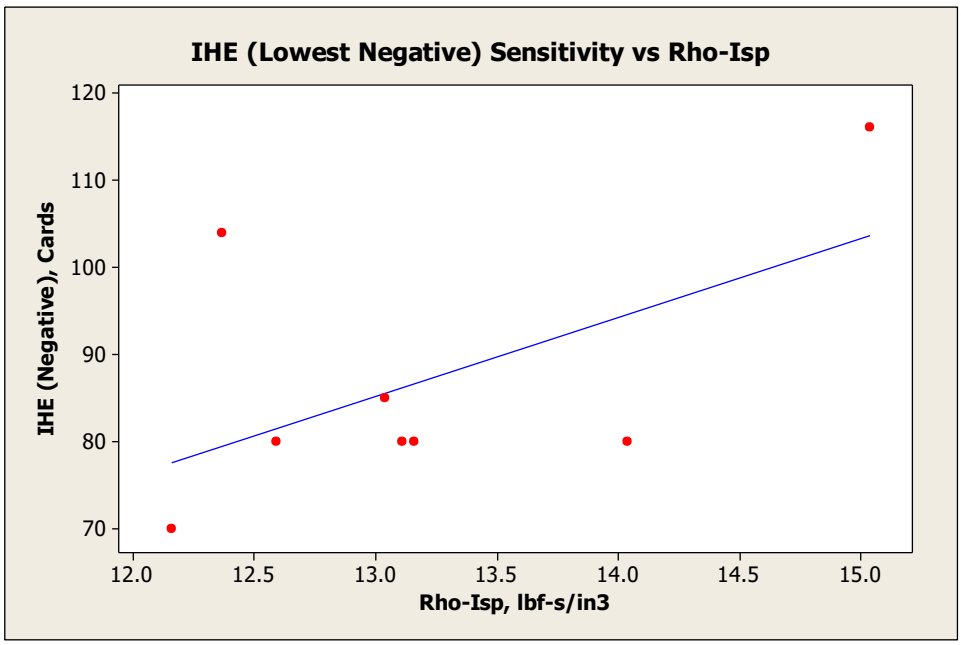


Figure 5.8. Rho-I_{sp} versus Card Gap Sensitivity

Once all of the data had been analyzed in Minitab, an optimizer routine was run to determine if specific goals could be reached within the parameters of this DOE. The optimizer routine was asked to maximize I_{vol} and minimize card gap, and returned the formulation shown in Figure 5.9, with approximately 50% MBANF and 10% DINGU. This formulation is predicted to have a I_{vol} of 14.5 lb_f-s/in^3, and a card gap sensitivity of negative at 65 cards. Ideally, the next step would be to make this formulation to confirm the results, but a concern developed over the sensitivity of the ground MBANF, as discussed in the next section. The high ESD sensitivity (<0.024 joules) of the material in a ground state makes it difficult to handle. An attempt was made to draw a correlation of MBANF particle size to sensitivity with the data available, but it was unsuccessful (Figure 5.10).

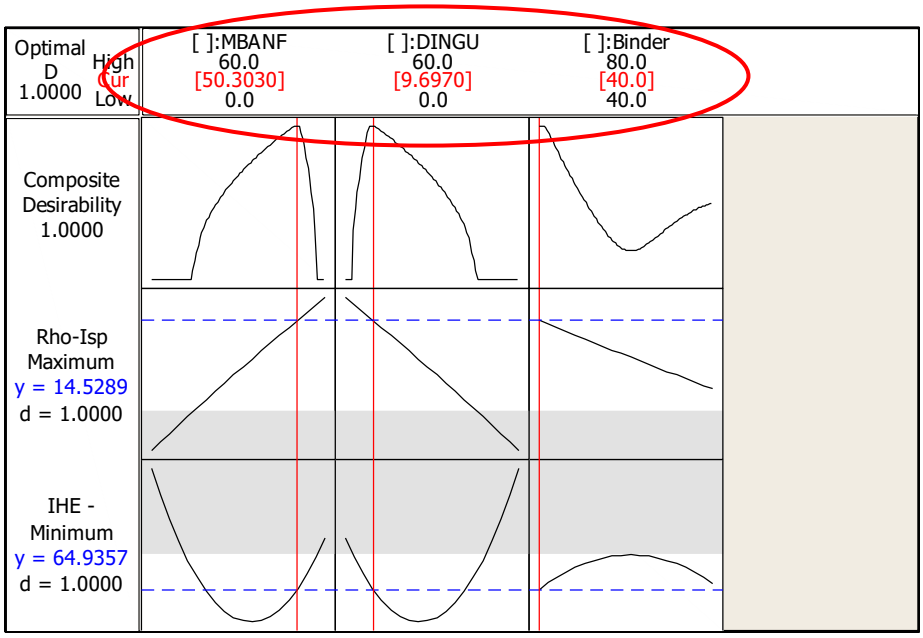


Figure 5.9. Response Optimizer Routine Output Prediction

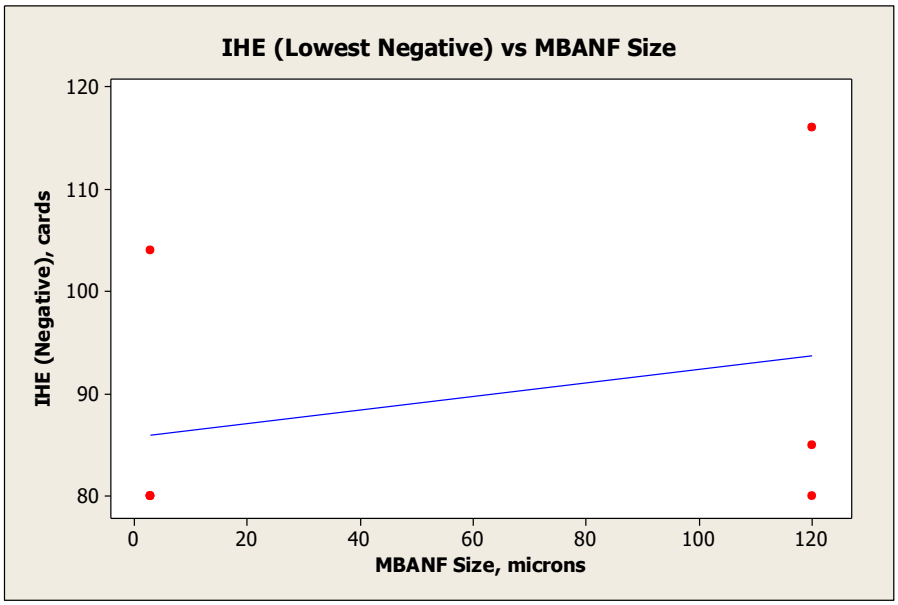


Figure 5.10. Correlation of MBANF Particle Size to Card Gap Sensitivity

6. MBANF Particle Size versus Sensitivity Study

A grinding study was initiated to determine the particle size versus sensitivity trade of MBANF ground at various times from 30 minutes to 5 hours. As-received MBANF was weighed into a laboratory-scale Turbula Shaker with one ceramic grinding ball, and the material was then covered with a non-solvent, Vertrel. The shaker was run for the specified period of time, and then the MBANF was dried to remove the Vertrel, and laboratory sensitivity tests were completed. Unfortunately, when the first sample, ground for 30 minutes, was dried, the material was highly ESD sensitive (<0.024 joules). A small sample of material from this grind was syphoned off, and 0.1% graphite added to the sample. After drying, the MBANF/graphite mixture had normal ESD sensitivity, giving 10 negative results at 1.4 joules. The grinding study has continued, adding 0.1% graphite to each run before drying.

The four grinds were completed, and the resulting particle size versus grind time is shown in Figure 6.1. Grinding for longer than 3 hours was not beneficial to reducing the particle size. In addition, as shown in Figure 6.2, the bimodal distribution began disappearing as the grinding time increased.

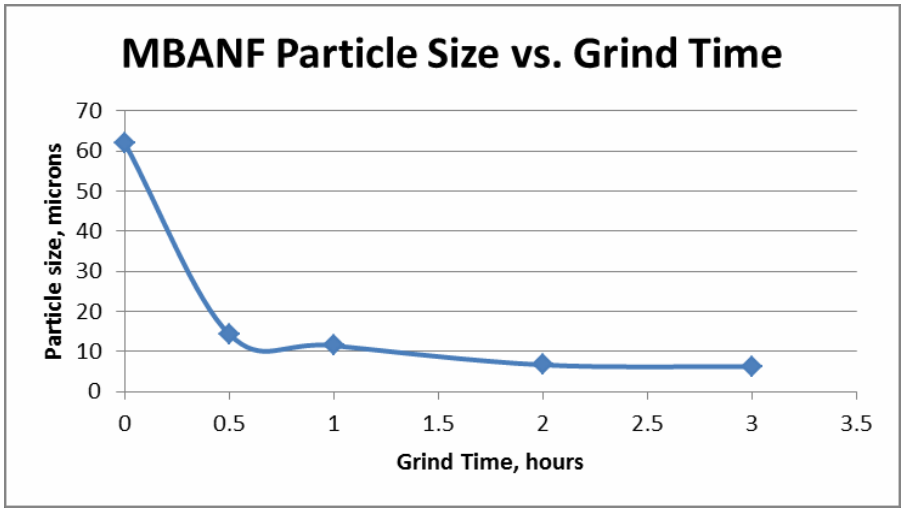


Figure 6.1. MBANF Particle Size versus Grind Time

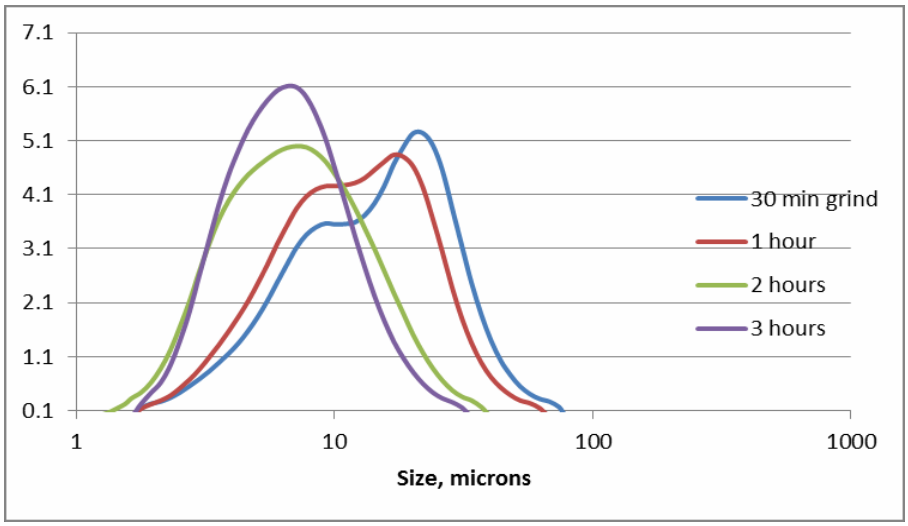


Figure 6.2. Particle Size Distribution versus Grind Time

Propellant mixes were made with 20% ground MBANF, as summarized in Table 6.1. The mixes all processed well and 4 IHE gap tubes were cast from each mix. The original test matrix started at 104 cards and was later modified to start at 70 cards after mixes C26158 and 59 were tested. It appeared that for this propellant formulation, MBANF particle size did not affect card gap sensitivity.

Table 6.1. MBANF Particle Size versus Card Gap

Mix Number	C26332	C26158	C26159	C26161
BTTN/DEGDN, % NC/Polyester/HMDI, % MBANF, %	60 20 20	60 20 20	60 20 20	60 20 20
MBANF Grind Time	--	30 minutes	1 hour	2 hours
MBANF Particle size, microns	As-received	14.34	11.46	6.65
IHE gap, cards	-70	-92 (only 2 good tubes to test)	-80 (not enough tubes to go lower)	-68/+70
Burning rate @ 1000 psi				0.21

The confirmation mix from the original performance DOE was manufactured and IHE card gap tubes loaded. This formulation contained 50.3% MBANF and 9.7% DINGU, as well as BTTN/DEGDN/nitrocellulose and polyester resin, and was predicted by Minitab statistical software to have a card gap sensitivity of -65 cards with a density-impulse of 14.5 lb-s/in^3. The end of mix viscosity was 4.5 kP, with a good propellant pot life. Laboratory sensitivity testing shows the formulation to be insensitive to impact and ESD to the maximum of our testing capability, and nearly to the max setting on friction sensitivity. Unfortunately, the IHE card gap sensitivity was positive at 100 cards with this formulation. This indicates that the particle size may be more of a factor than the original DOE predicted. This particular mix was manufactured with all as-received MBANF. Other solid oxidizer materials show a strong effect of particle size on shock sensitivity, and prior data indicated this was not the case for MBANF.

Final Formulation Effort

LLM-105 was received from NSWC IHEODTD and sensitivity tested (Table 6.2). The physical nature of the material made it difficult to handle, as shown in Figure 6.3. Ten grams of material was put into a Turbula shaker with Vertrell non-solvent, and the material was broken up for 10 minutes in the shaker. The results after this operation are shown in Figure 6.4. This material can easily be incorporated into propellant mixes.

Table 6.2. Sensitivity Data of LLM-105

Test	LLM-105 Result
Impact, kg-cm	95
Friction, psi	1800
ESD, joules	0.09
Autoigntion, C	299

Figure 6.3. Photograph of LLM-105

Figure 6.4. LLM-105 After Shaking

The DINGU and MBANF needed for the next series of mixes were ground in the Turbula Shaker. The DOE confirmation mix was repeated with ground MBANF as opposed to the unground originally used. Once again, the IHE card gap value was high at +90/-100 cards (C26470), as shown in Table 6.3. The next mix, C26480, was made to substitute the DINGU with LLM-105, but no change in card gap sensitivity was noted. There was, however, a significant increase in the theoretical performance. Mix C26487 used all ground MBANF (no as-received material), and again shows no change in card gap sensitivity. Mix C26474 was made using all three oxidizers and although this mix processed really well, no improvement in sensitivity was noted.

Table 6.3. Final Propellant Tailoring Pint Mixes

	C26470	C26480	C26487	C26474	C26488	C26493	C26494
MBANF, %							
Ground	35.21	35.21	50.03	29.1766	53.7373	41.08	44.91
Unground	15.09	15.09	-	15.09	- 6.2627	15.09	10.09
LLM-105, %	-	9.7	9.7	7.9167	-	3.83	-
DINGU, %	9.7	-	-	7.8167		-	-
EOM Visc. kP	7	10	20.1	4.6	13.6	9.4	4.4
I_{sp}, lb_f-s/lb_m	240.8	246.5	246.5	239.4	248.4	244.8	233.7
Density, lb/in^3	0.06006	0.0599	0.0599	0.0602	0.06021	0.05935	0.05890
Rho-I_{sp}, lb-s/in^3	14.46	14.77	14.77	14.41	14.96	14.53	13.76
IHE gap, cards	+90/-100	+90/-100	+90/-100	+90/-100	+90/-100	+100	+90/-100
Comments	Repeat of DOE mix with some unground	Sub LLM-105 for DINGU	All ground MBANF version of C26480	Use all 3 oxidizers	Increased perform. of C26471	Reduced LLM-105	All MBANF, lower solids level

The laboratory sensitivity (friction, impact, and ESD) were all normal with these propellants. In general, those mixes that contained DINGU were lower in performance. The final two mixes were made to trade performance versus sensitivity, and to get an indication of the propellant mechanical properties. The card gap sensitivity was unchanged. The mechanical properties (JANNAF microbones) are shown in Table 6.4, and are good for this highly-solids-loaded nitrocellulose propellant. The properties of the lower solids mix are slightly better than the 60% solids mix, but this formulation is considerably lower in performance. Future efforts will likely be at the 60% solids level.

Table 6.4. Mechanical Properties Comparison

	C26480	C26493	C26494
Total Solids, %	60	60	55
Curative/Polymer	1.2	1.05	1.05
145°F Stress, psi Strain, % Modulus, psi	Not tested	65 42 313	60 29.6 347
70°F Stress, psi Strain, % Modulus, psi	118 21 874	113 22.6 756	127 31 635
-45°F Stress, psi Strain, % Modulus, psi	Not tested	611 14.3 7960	512 18.3 55.6

At this point in the program, many of the technical objectives were met with batch C26494 and a summary of this formulation is shown in Table 6.5. A propellant with state-of-the-art performance had been developed using a new, environmentally friendly material, MBANF, to replace RDX. The card gap sensitivity was reduced 50 cards over standard production propellants, but the goal of a Class 1.3 hazard classification level was not reached.

Table 6.5 Candidate Matrix Propellant

Property	Criteria	C26494 Properties
Formulation	Environmentally friendly / eliminate RDX	32% BTTN/DEGDN 11% NC/Polyester/HMDI 10% As-received MBANF 35% Ground MBANF 9.7% LLM-105
Theoretical Performance I_{sp}, lb_f-sec/lb_m Density, lb/in^3 I_{vol}, lb_f-sec/in^3		 233.7 0.0589 13.76
Card gap, +/- cards	< 70	90/100

The burning rate in the demonstration motor will be driven by the ballistic control propellant, so

tailoring of the matrix propellant burning rate was not a useful task. The mechanical properties were acceptable for this stage of a development effort. Additional tailoring of this formulation was not conducted.

7. Ballistic Control Propellant Evaluation

The Ballistic Control Propellant (BCP) drives the ballistic properties of the motor. NSWC IHEODTD completed the lead-free formulation efforts, and provided samples of the most promising formulations to Aerojet-Rocketdyne. The list of formulation samples received is provided in Table 7.1. These formulations differ in ballistic modifier type, as well as nitrate ester/nitrocellulose concentration.

Batch number 047 was randomly chosen to run sensitivity tests, and all of the test results fell into the normal range, with the exception of autoignition, which was “yellow”. Most formulations of this type have a lower autoignition temperature, so this was not unexpected. The sensitivity data as compared to RDX are shown in Table 7.2.

Table 7.1 Ballistic Control Propellant Samples

Batch Number	06	047	048	049	050	051	052
	Baseline	047 mods			048 MODS		
Nitrocellulose, 12.2%N		56.00%	55.00%		52.40%	51.00%	
Nitrocellulose, 12.6%N	49.50%			51.90%			51.90%
Nitroglycerin	40.00%	31.00%	35.20%	35.00%	34.70%	37.90%	37.00%
Triacetin		7.00%	3.00%	4.00%	5.00%	4.00%	3.50%
Di-n-Propyl Adipate	3.00%						
2-NDPA	2.00%	2.00%	2.00%	2.00%	2.00%	2.00%	2.00%
Ethyl Centralite							
Antimony oxide		1.40%	3.00%	3.00%			
Tin oxide		1.00%	1.00%	2.00%			
Cupric oxide		1.50%	0.70%	2.00%			
Candelilla Wax	0.10%	0.10%	0.10%	0.10%	0.10%	0.10%	0.10%
LC 12 6	5.40%						
Bismuth Subsalicylate					2.70%	3.00%	1.50%
MBCBR					1.10%	1.00%	2.00%
Copper Salicylate					2.00%	1.00%	2.00%

Table 7.2. Sensitivity Data of Ballistic Control Propellant

Material	RDX Standard	BCP Batch 047
Impact, kg-cm	49	49
Friction, psi @ 90^{o}	1300	800
ESD, joules	0.38	6
Autoignition, ^{o}C	215	169

Compatibility testing was completed on six samples of Ballistic Control Propellant received from NSWC IHEODTD. The mixes listed in Table 7.1 (with the exception of the baseline mix) were tested against an isocyanate curative, hexamethylene diisocyanate, a polyester resin called R-18, the MBANF supplied by NSWC IHEODTD, and the cure catalyst triphenyl bismuth. All other ingredients contained in the matrix propellant are also contained in the Ballistic Control Propellant, and were therefore not run in 1:1 compatibility tests.

Each of these propellant samples was tested using the Differential Scanning Calorimeter, at a rise rate of 10^{o}C/min. Any shift of more than 10^{o}C in the exotherm onset temperature shows evidence of an incompatibility. None of the tests showed any evidence of incompatibility.

NSWC IHEODTD provided the strand burning rate data from the mixes listed in Table 7.1 (with the exception of the baseline mix). These data are plotted in Figure 7.1, and show the various plateau regions of each propellant.

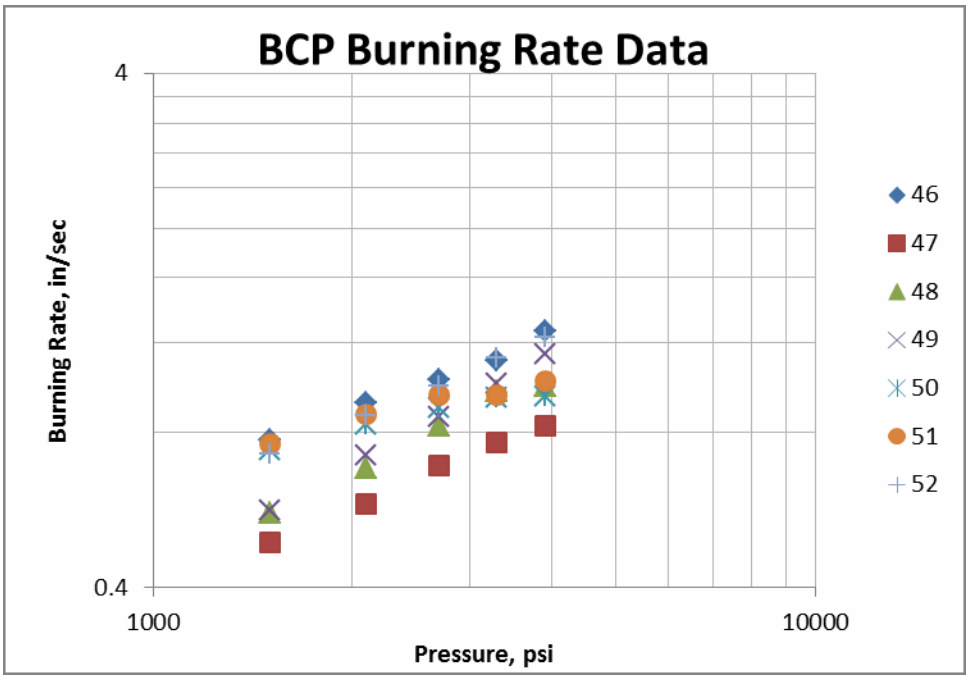


Figure 7.1. Strand Burning Rate Data

Batches 050 and 051 both show plateau regions from approximately 2800 psi to around 4000 psi, but batch 051 shows a slightly higher burning rate and potentially a wider plateau region. For this reason, batch 051 was selected as the BCP formulation for the demonstration effort going forward. NSWC IHEODTD manufactured sticks of this formulation and provided them to Aerojet-Rocketdyne for the final motor demonstration.

8. Final Motor Demonstration

The objective of this part of the program was to combine the new RDX-replacement matrix propellant developed by Aerojet Rocketdyne, with the lead-free Ballistic Control Propellant developed by NSWC IHEODTD in a demonstration motor. In preparation for that task, the MBANF was ground to a smaller size. The particle size of the starting material was over 300 microns, as shown in Figure 8.1.

Figure 8.1. SEM Image of Recrystallized MBANF

The first test grind for 30 minutes in the Turbula Shaker reduced the particle size to approximately 30 microns, but the Turbula Shaker could not support the quantities needed for grinding for the large mix. The Ball Mill was set up to grind larger quantities. The MBANF was coated with graphite in each grind, because the ESD sensitivity increased into the High Hazard category when ground in the Turbula shaker, at 0.048 joules.

The first ball-mill grind decreased the particle size of the MBANF down to 210 microns after 15 minutes of grinding, which is satisfactory for this mix. The remaining grinds were made at 30 minutes in length. The Microtrac particle size distribution curve is shown in Figure 8.2. A total of

5.5 pounds of MBANF was ground in the ball-mill for use in the motor-loading mix.

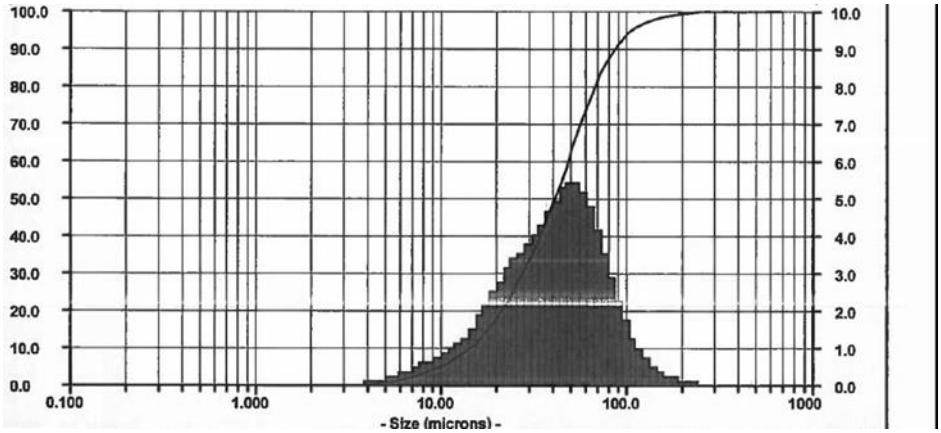


Figure 8.2. Microtrac Particle Size Curve of Ball-Milled MBANF

The configuration of the demonstration motor was an end-burning grain, with the ballistic control propellant sticks arranged in a specific geometry. The empty case is shown in Figure 8.3. The sticks were held in place by Teflon coated formers on the top and bottom of the grain. After assembly for casting, it was noticed that the top former did not hold the sticks rigid enough to prevent slumping during cure. A new former was fabricated, and used in the final casting.

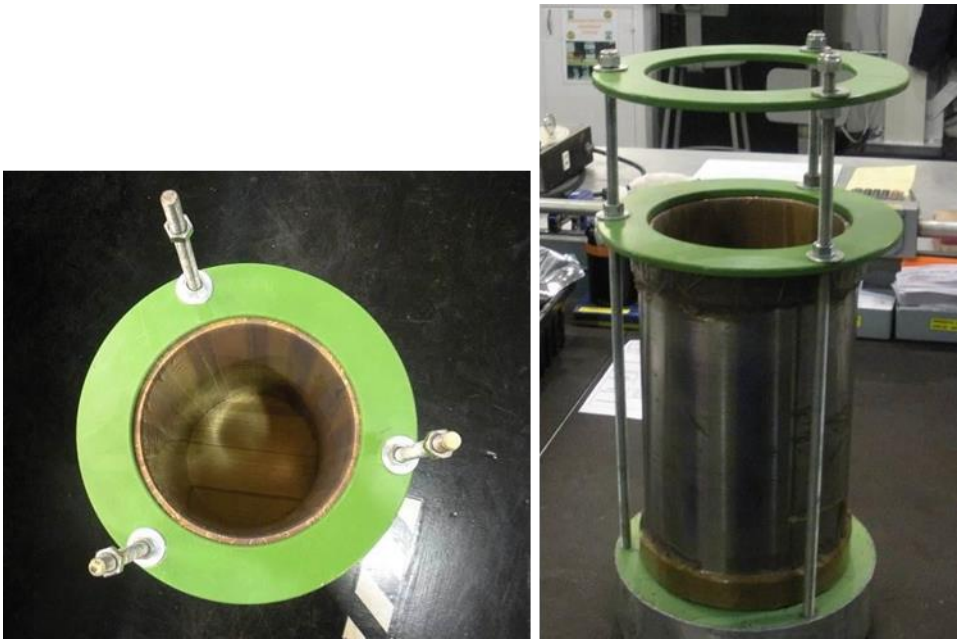


Figure 8.3. Feasibility Demonstration Motor Case

The BCP propellant was extruded by NSWC IHEODTD into 1/4" diameter sticks, and cut to 14-inches long. The sticks were shipped to Aerojet Rocketdyne for processing in the motor. The burning rate of this batch of propellant was checked from 500 to 4000 psi, and found to be identical to the test batch provided earlier. This points to excellent processing and ballistic control in the NSWC IHEODTD process for manufacturing this propellant. The sticks were cut to length and assembled into the demonstration case, with six sticks arranged symmetrically around the outside of the grain, one-inch away from the side wall, and one stick in the center.

Two identical 8.5 pound mixes were manufactured in one-gallon vertical Baker Perkins mixers. The mixes were taken up to the point of adding the curative, and held for 13 days while the tooling was being modified to better support the BCP sticks. Once ready, the curatives were added, and both mixes finished with low viscosity. The two mixes were then cast into the empty case, and the motor cured for 3 days at 135^{o}F. The propellant sample carton was cut and both mechanical properties and burning rate were tested. The data from this mix is provided in Table 8.1. Of major concern are the mechanical properties. The stress and strain are both considerably reduced from the checkout mix properties. The operators noted that the carton was extremely brittle, fragile, and difficult to cut.

Table 8.1. Motor-Loading Mix C27165 Properties

Property	Results
Formulation:	
Lacquer and curative, %	43.88
MBANF%, as-received	13.07
30-micron ground, %	41.93
MNA stabilizer	1.12
EOM Viscosity, kP	1.5
Strand burning rate, in/sec	
500 psi	0.18
1000 psi	0.36
2000 psi	0.79
2500 psi	1.16
Mechanical Properties, 72^{o}F	
Stress, psi	36
Strain, %	8.7
Modulus, psi	465

Concurrently, the motor grain was cut to length, and x-rayed. No defects, voids, fissures, or anomalies were noted in the completed grain. However, the grain was also brittle when cut.

Figure 8.4 shows the cut propellant grain, with the orange BCP sticks exposed.

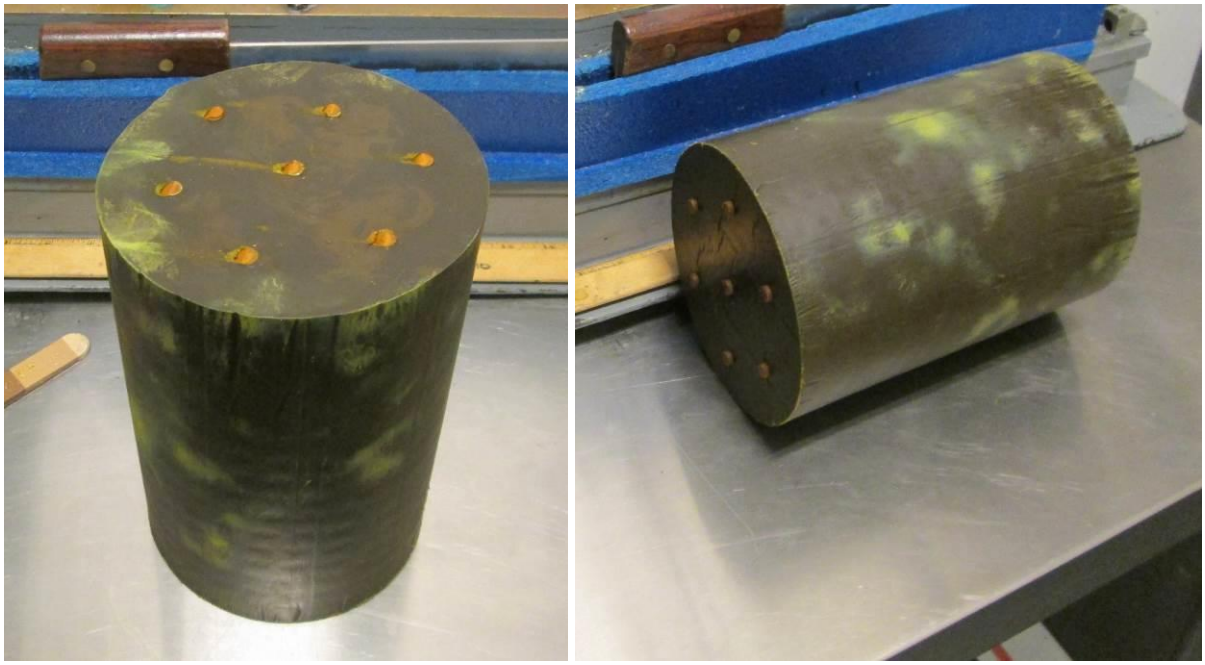
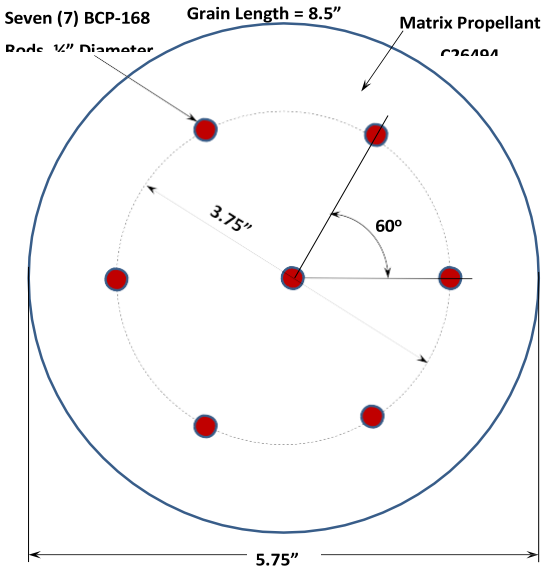


Figure 8.4. Finished Demonstration Grain

Based on the poor mechanical properties, an Engineering review of the batch properties was held. The structural engineer stated that he felt there was not enough margin in the propellant properties to survive ignition pressure. The ballistic engineer reviewed the properties, and indicated that he felt the motor would either not sustain combustion and extinguish, or it would quickly form cracks and over-pressurize. The revised ballistic prediction is shown in Figures 8.5 and 8.6. A safety review was held with management, and it was agreed by all that this motor was not safe to test.



Property	Matrix Value	Wire Value	Source
Propellant	C27163	BCP-168	
Density, lb_m/in^3	0.05890	0.06016	Thermochemistry
C*, ft/sec	4,812	4,723	Thermochemistry
Flame Temperature, °R	4,671	5,066	Thermochemistry
Reference Isp, lb_f-s/lb_m	233.7	233.5	Thermochemistry
Thrust Efficiency	0.95		Estimated
Throat Diameter, in	0.45 (c_d=1.0)		Obtain ~750 psia

Figure 8.5. Ballistic Prediction Input Parameters

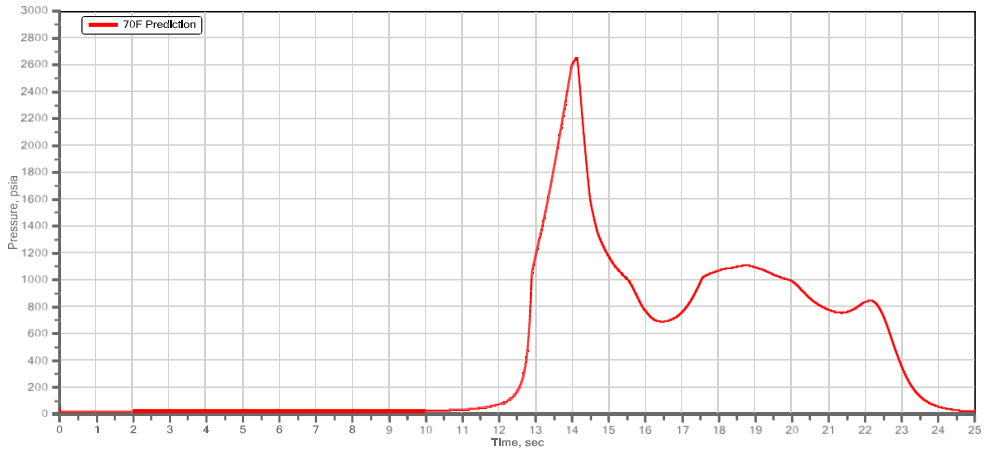


Figure 8.6. Predicted Pressure versus Time Trace

Looking back on the process, it is evident now that holding the propellant while the casting tooling was revised caused a significant issue. The MBANF solubility in the binder ingredients immediately became a key suspect. In a rough laboratory study at the end of this program, one-to-one mixtures of the MBANF with BTTN, R-18, and DEGDN were made and allowed to set over the weekend. Initially all of the containers had MBANF settle to the bottom. After setting 3 days, the MBANF/DEGDN combination was unchanged, but the other two showed signs of MBANF swelling and agglomeration, indicating that the material was at least slightly soluble in the lacquer ingredients. This solubility likely led to the poor, brittle mechanical properties of this propellant mix.

Due to schedule, funding, and material limitations, another test motor was not able to be loaded for this program. A great deal of technical information was learned on this program, but the end objective of a motor firing using the two technologies under evaluation was not realized.

Conclusions and Recommendations

Over the past five years of this effort, Aerojet Rocketdyne has supported NSWC IHEODTD in the evaluation of environmentally friendly replacements for RDX and lead. The team has evaluated MBANF as a potential RDX replacement in minimum-smoke rocket propellants. The sensitivity of MBANF is similar to RDX, and it provides similar performance in propellants. Propellant tailoring efforts were completed, and a propellant meeting all of the technical objectives except a hazard class 1.3 was developed. The evaluation of NSWC IHEODTD-developed lead-free extruded propellant for the ballistic control portion of the motor was also successfully completed, and recommendations made for the final material to be used in the demonstration. A subscale motor was successfully built, but due to unforeseen issues, the motor could not be tested for safety reasons.

In the future, for evaluation of new materials, solubility with propellant ingredients should be studied early in the program. Close interaction with the material supplier is also critical, particularly in relation to particle size and morphology. Aerojet Rocketdyne believes both of these materials have merit for future rocket propulsion systems.

Availability of starting materials is an issue with all energetic materials, and the MBANF

precursor, diaminofurazan (DAF), has similar availability issues. A program associated with WP-2143, performed by Nalas Engineering and funded by SERDP, investigated the viability of continuous production of DAF. The effort was partially successful but issues surrounding product purity have yet to be resolved.

Appendix A. Supporting Data

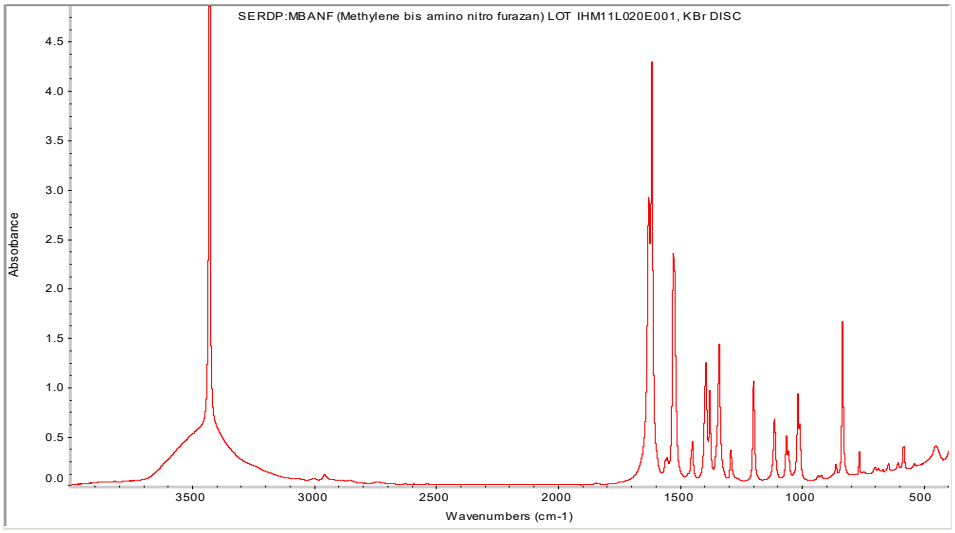


Figure A.1. FTIR Spectrum of MBANF

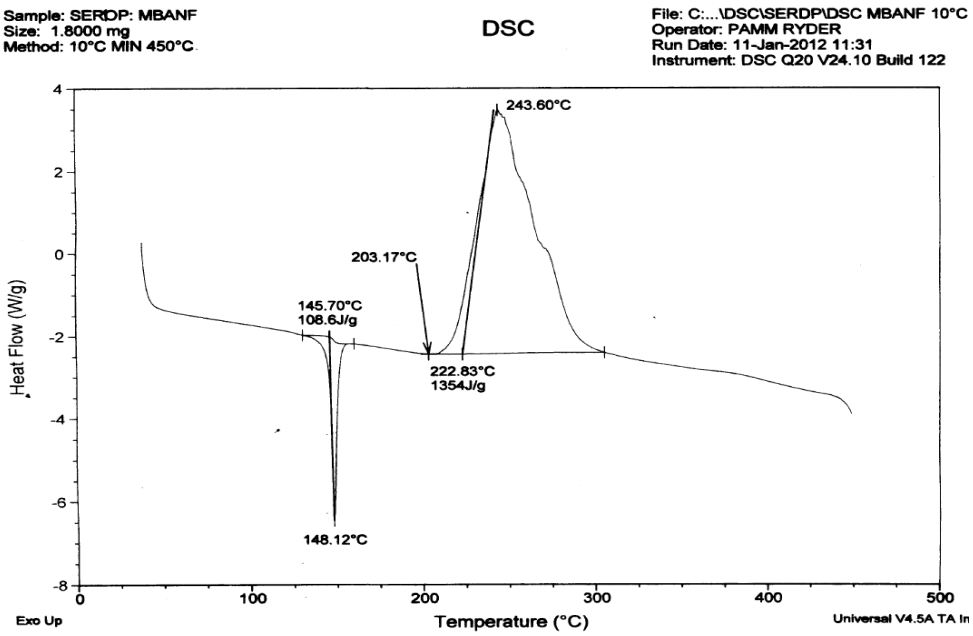
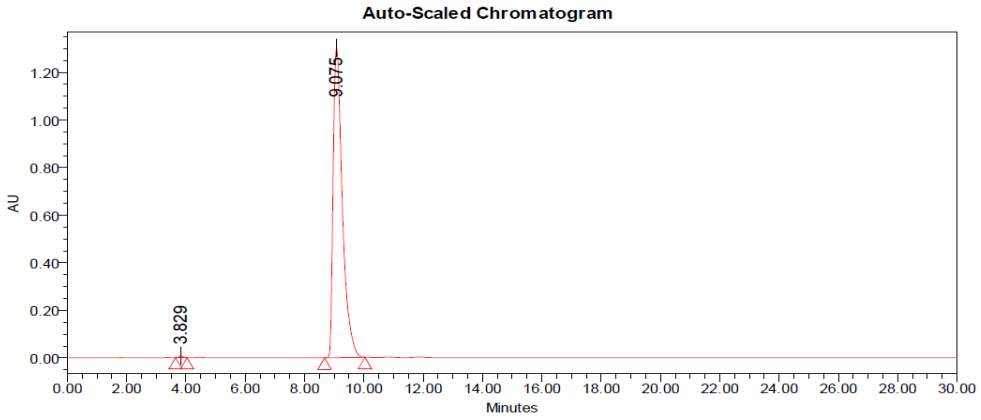


Figure A.2. DSC Trace of MBANF Sample

SAMPLE INFORMATION

Sample Name:	MBANF lot IHM11L020E001	Acquired By:	DianeRobinson
Sample Type:	Unknown	Sample Set Name:	DNFOA MBANF purity 011212
Vial:	3	Acq. Method Set:	new matl pda 2998 methset
Injection #:	1	Processing Method:	PDA Default Processing
Injection Volume:	10.00 ul	Channel Name:	2998 Ch4 323nm@1.2nm
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	2998 Ch4 323nm@1.2nm
Date Acquired:	1/12/2012 3:46:46 PM EST		
Date Processed:	1/13/2012 9:49:48 AM EST		



Peak Results

	Name	RT	Area	Height	Amount	Units
1		3.829	69547	7808		
2		9.075	28140411	1302630		

Figure A.3. HPLC of MBANF Sample

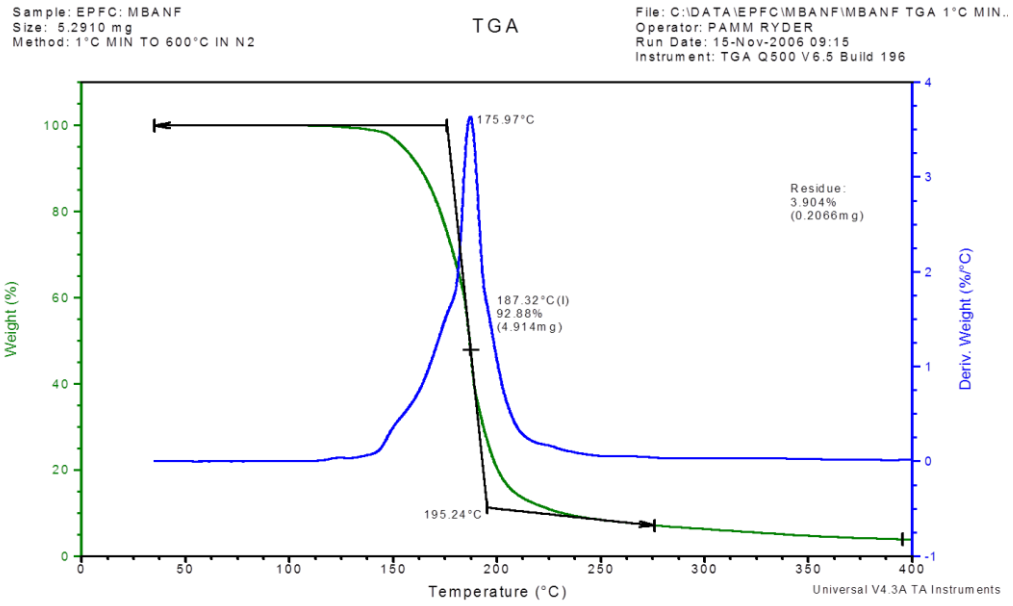


Figure A.4. TGA at 1°C/min for MBANF

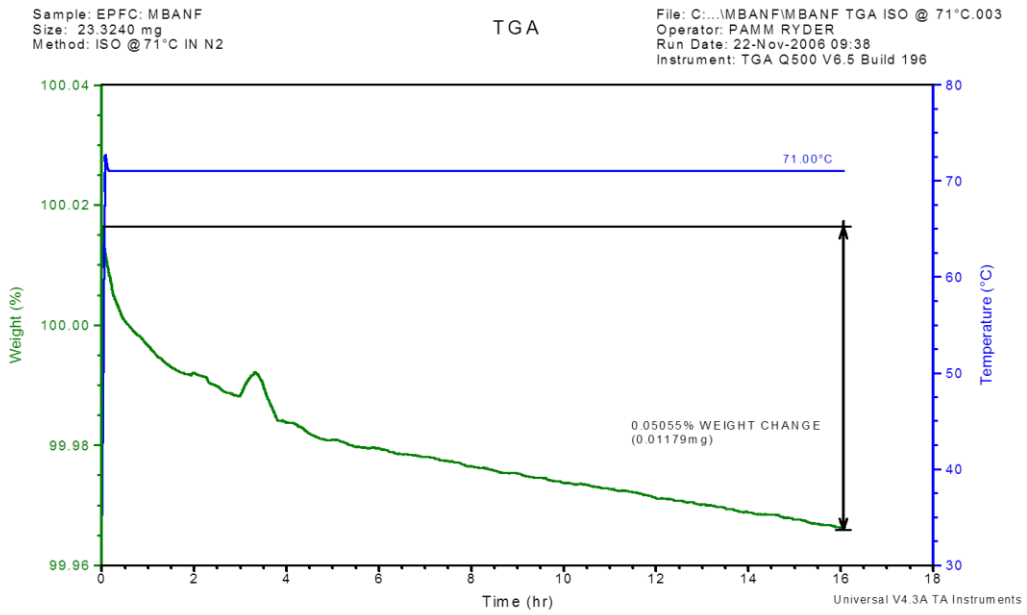


Figure A.5. Isothermal TGA of MBANF

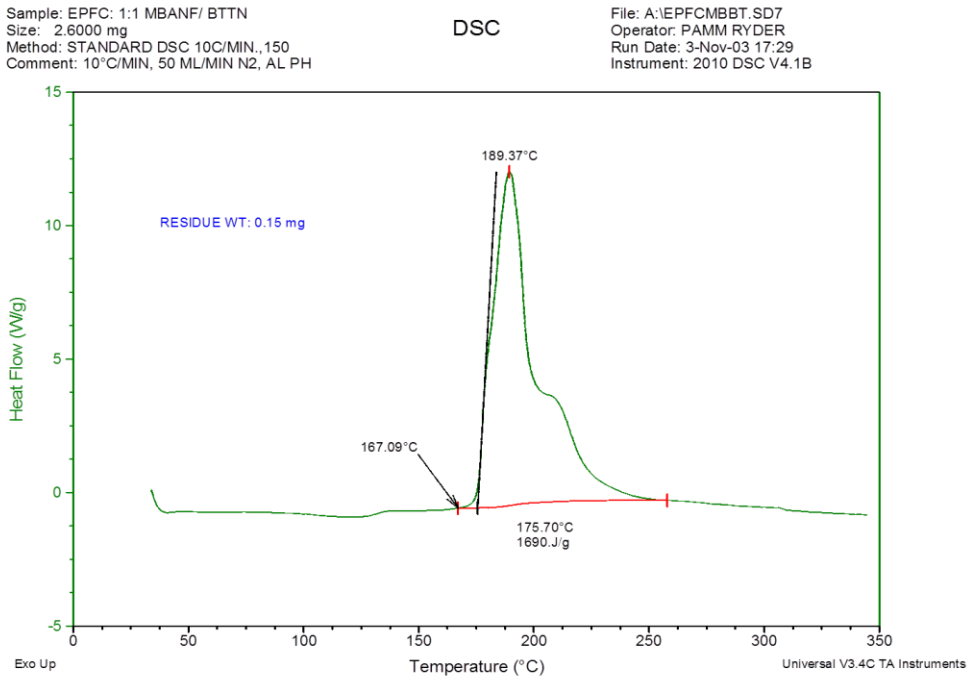


Figure A.6. DSC Compatibility MBANF and BTTN

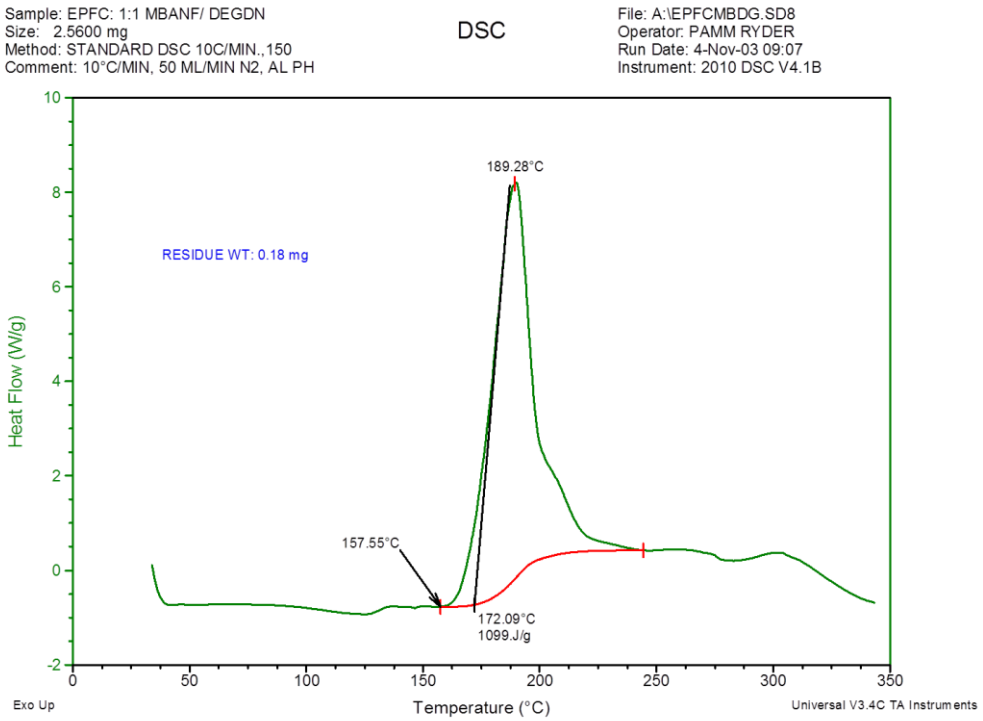


Figure A.7. DSC Compatibility of MBANF and DEGDN

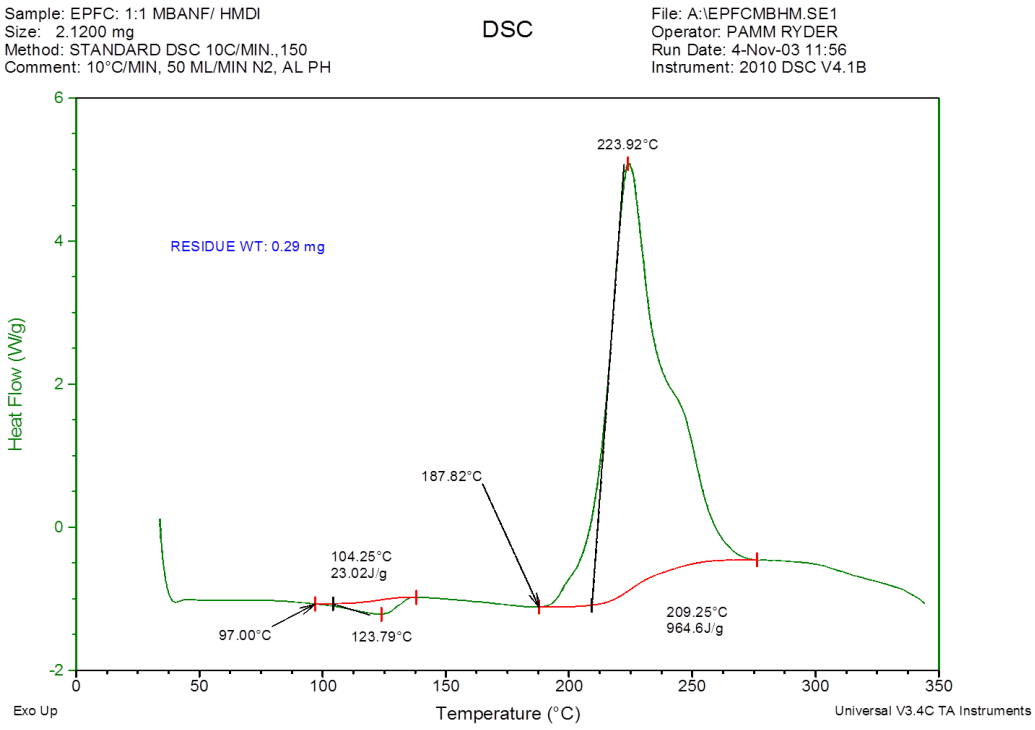


Figure A.8. DSC Compatibility of MBANF and HMDI

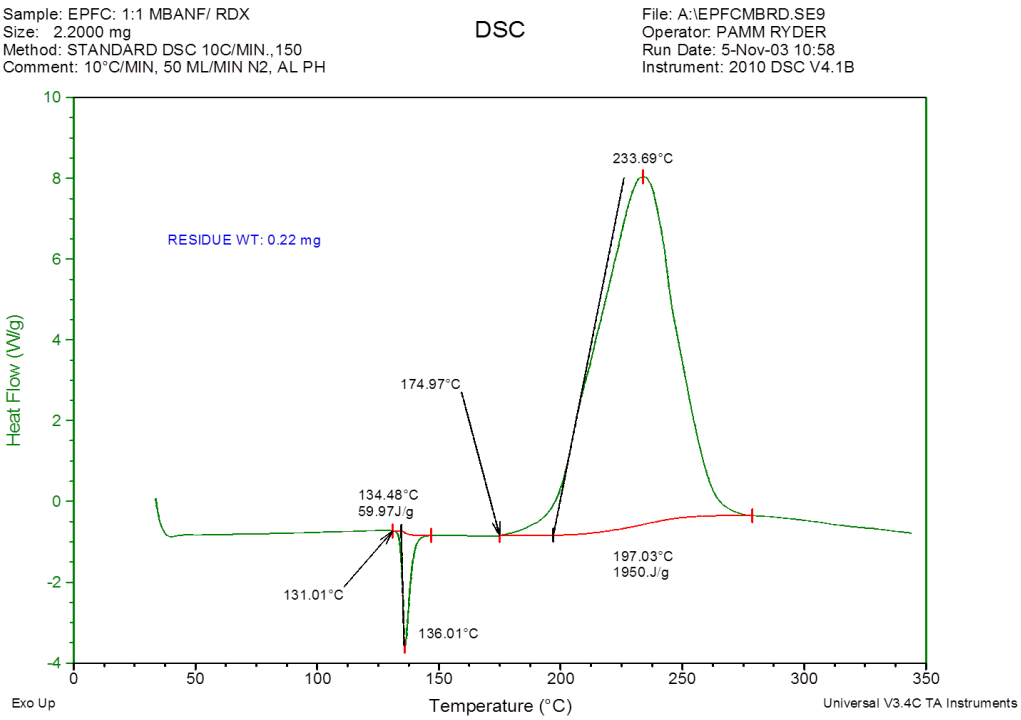


Figure A.9. DSC Compatibility of MBANF and RDX

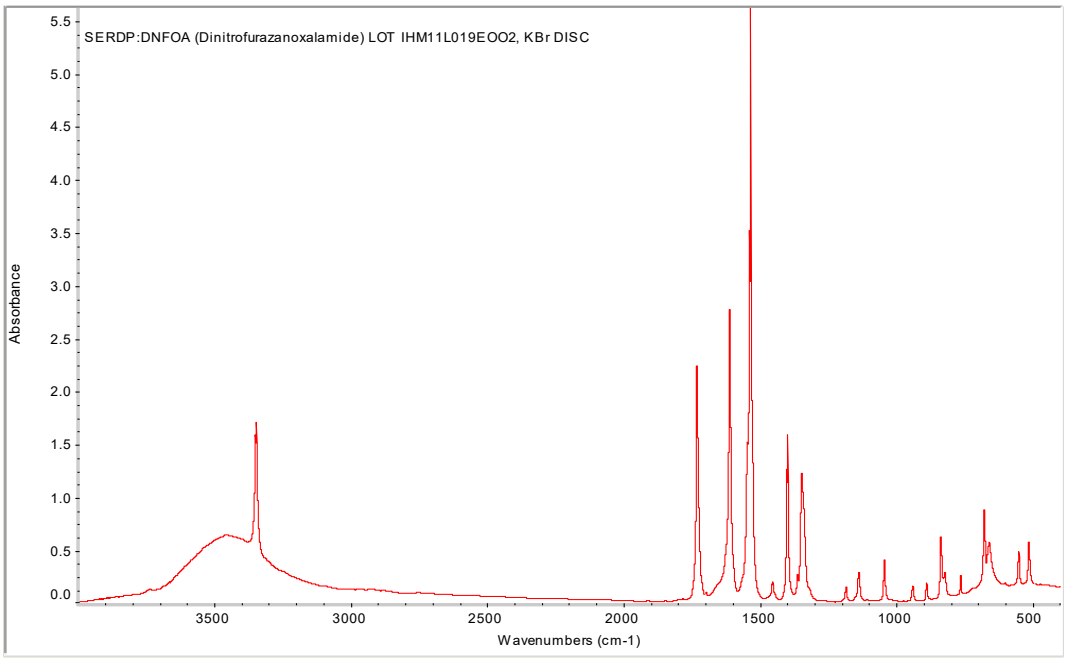


Figure A.10. FTIR Spectrum of DNFOA

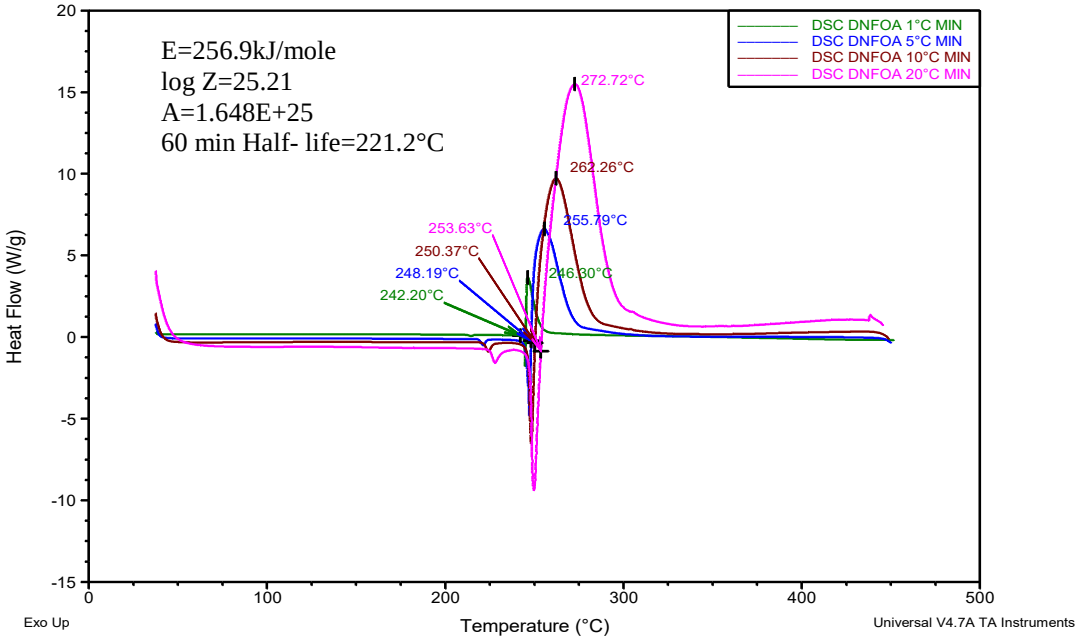


Figure A.11. Kinetics by DSC for DNFOA

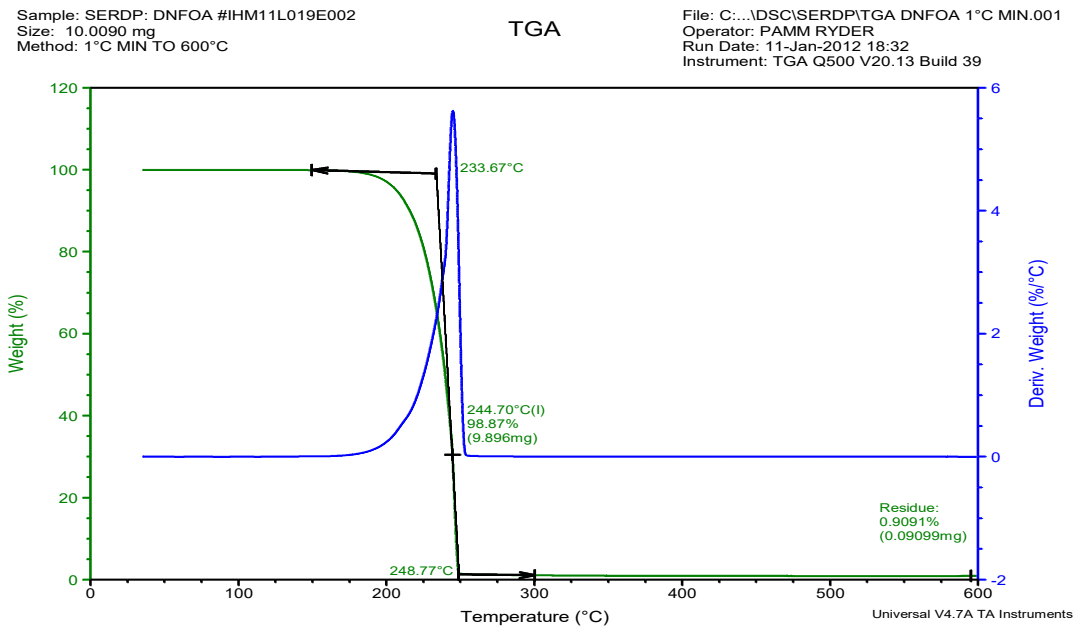


Figure A.12. TGA for DNFOA Heated at 1°C/min

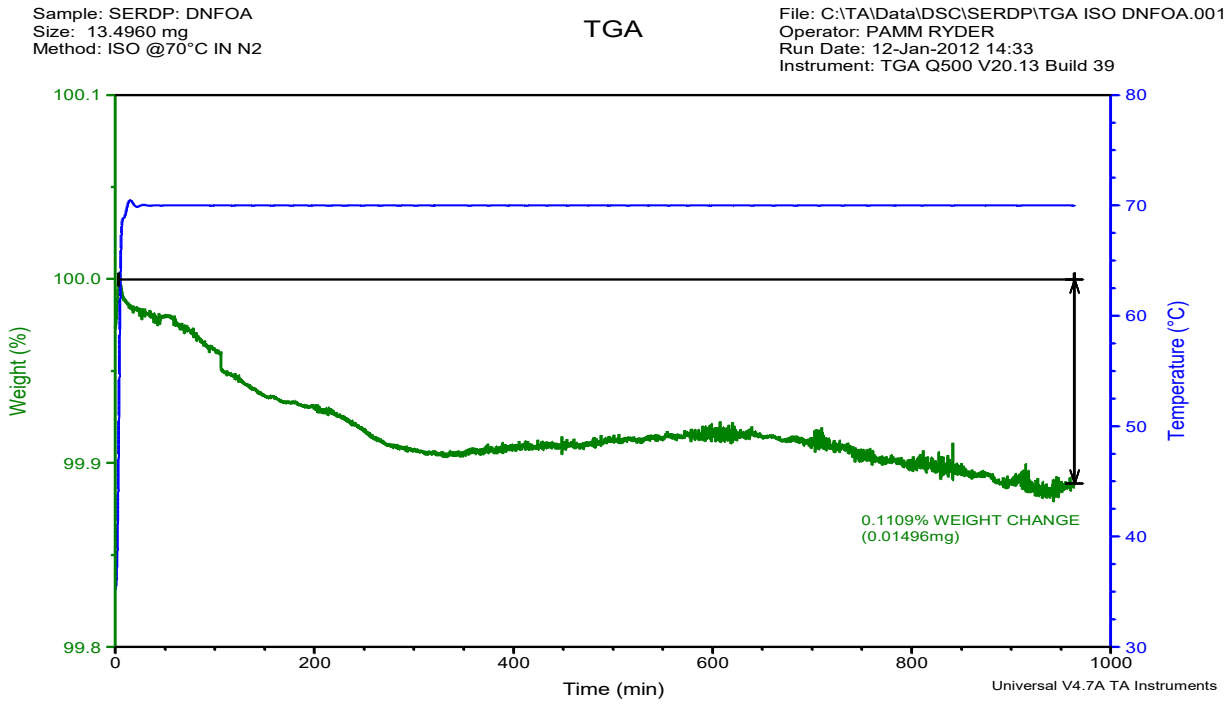


Figure A.13. Isothermal TGA for DNFOA

Summarize Results	**SERDP: Dinitrofurazanoxalamide**						
Date :	**1/10/2012**						
Group	Sample name	Weight	Carbon%	Nitrogen%	Hydrogen%	Sulphur%	Oxygen%
1	SULFANILAMMIDE	1.374	41.840	16.270	4.680	18.620	18.580
1	SULFANILAMMIDE	1.497	41.642	16.155	4.670	18.434	18.568
1	SULFANILAMMIDE	1.716	41.861	16.206	4.694	18.928	18.481
1	SULFANILAMMIDE	1.712	41.986	16.240	4.696	18.994	18.968
1	SULFANILAMMIDE	1.722	42.060	16.281	4.718	18.335	18.345
7 Sample(s) in Group No : 1							
Component Name	Theoretical	Average	STDev	cv%			
Carbon%	41.84	41.878	0.160	0.38%			
Nitrogen%	16.27	16.230	0.051	0.32%			
Hydrogen%	4.68	4.692	0.018	0.39%			
Sulphur%	18.62	18.662	0.292	1.57%			
Oxygen%	18.58	18.588	0.232	1.25%			
Group	Sample name	Weight	Carbon%	Nitrogen%	Hydrogen%	Sulphur%	Oxygen%
2	DNFOA IHM11L019E002	1.483	44.058	8.971	0.642	0.000	48.049
2	DNFOA IHM11L019E002	1.402	43.692	8.944	0.656	0.000	48.036
2	DNFOA IHM11L019E002	1.369	43.286	8.906	0.639	0.000	48.074
2	DNFOA IHM11L019E002	1.527	43.919	8.952	0.644	0.000	48.115
2	DNFOA IHM11L019E002	1.461	43.371	8.914	0.633	0.000	48.326
5 Sample(s) in Group No : 2							
Component Name		Average	STDev	cv%			
Carbon%		43.665	0.335	0.77%			
Nitrogen%		8.937	0.027	0.30%			
Hydrogen%		0.643	0.009	1.34%			
Sulphur%		0.000	0.000	0.00%			
Oxygen%		48.120	0.119	0.25%			

Figure A.14. CHNO Analysis Results for DNFOA

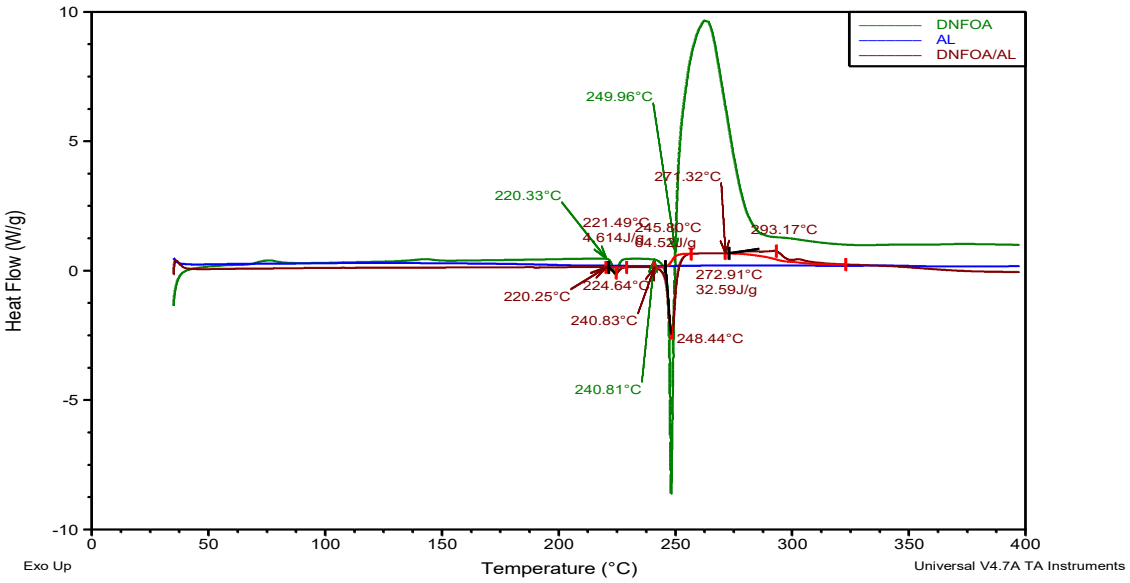


Figure A.15. DSC Compatibility - DNFOA and Aluminum

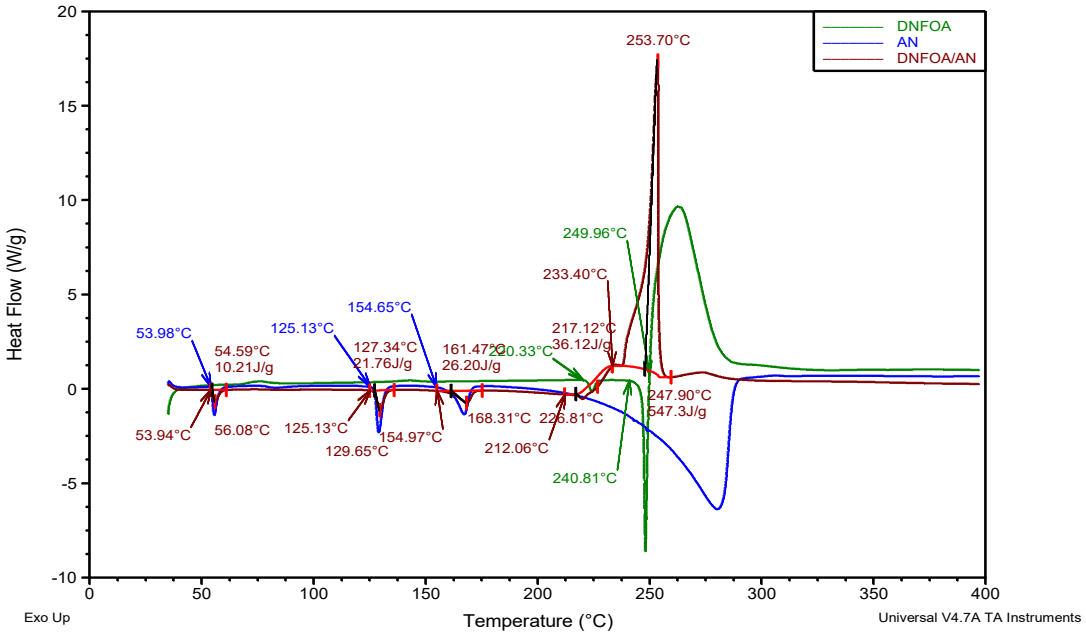


Figure A.16. DSC Compatibility - DNFOA and Ammonium Nitrate

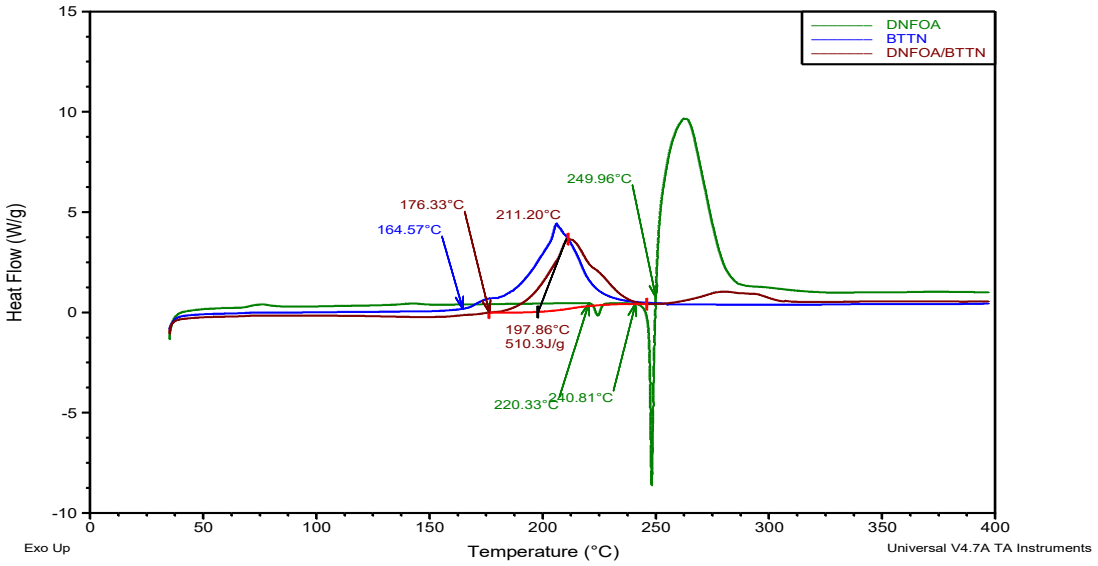


Figure A.17. DSC Compatibility - DNFOA and BTTN

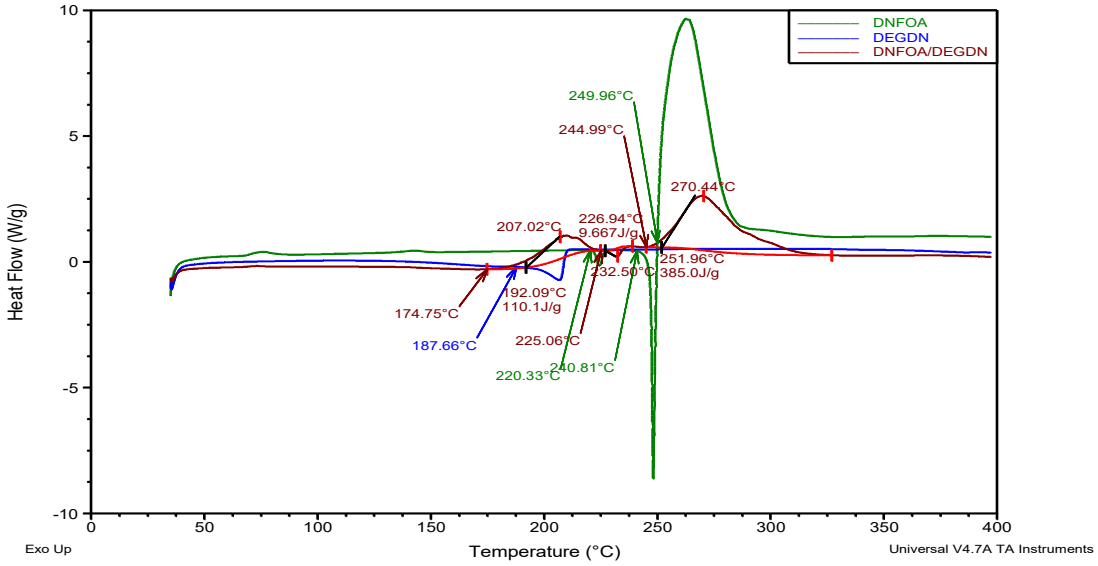


Figure A.18. DSC Compatibility - DNFOA and DEGDN

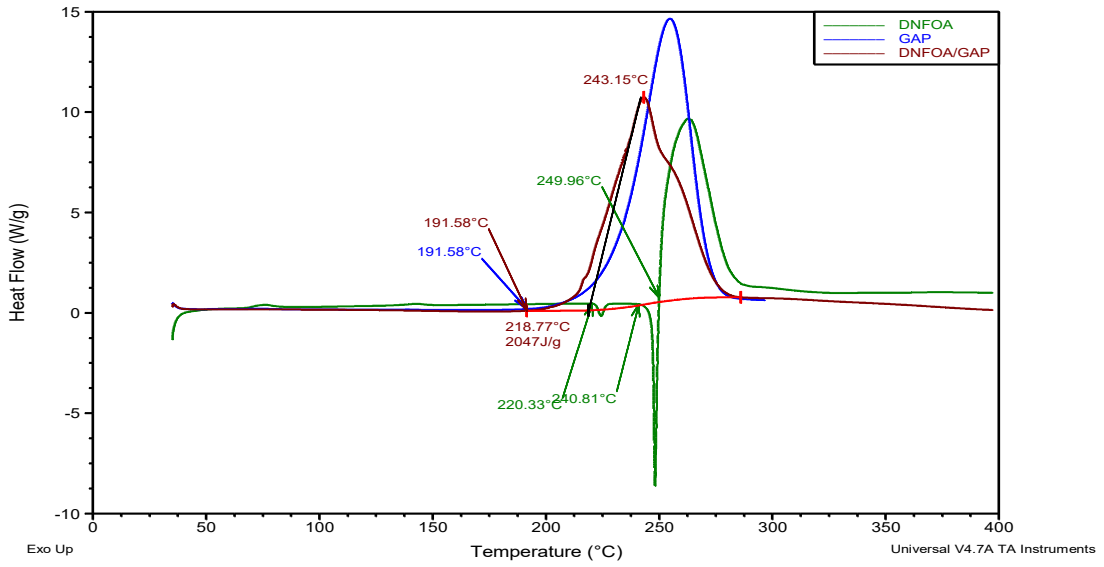


Figure A.19. DSC Compatibility - DNFOA and GAP

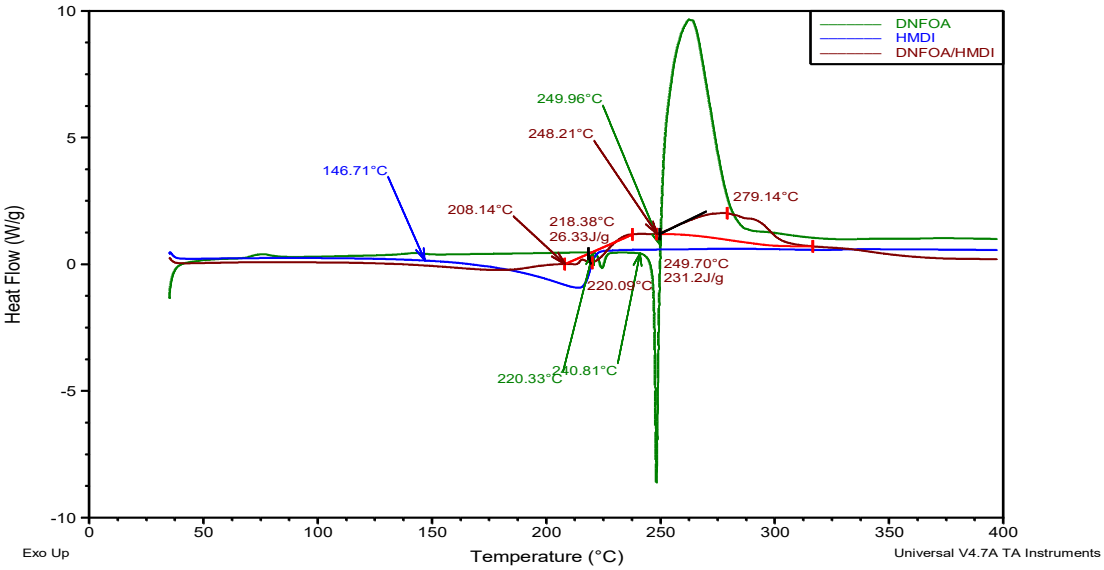


Figure A.20. DSC Compatibility - DNFOA and HMDI

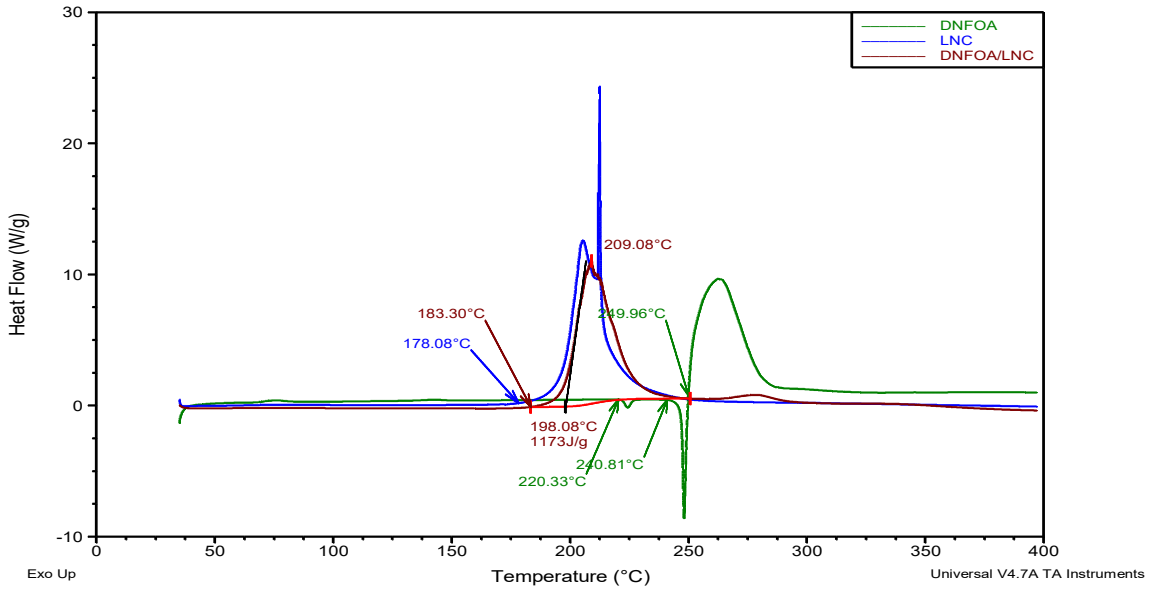


Figure A.21. DSC Compatibility - DNFOA and LNC

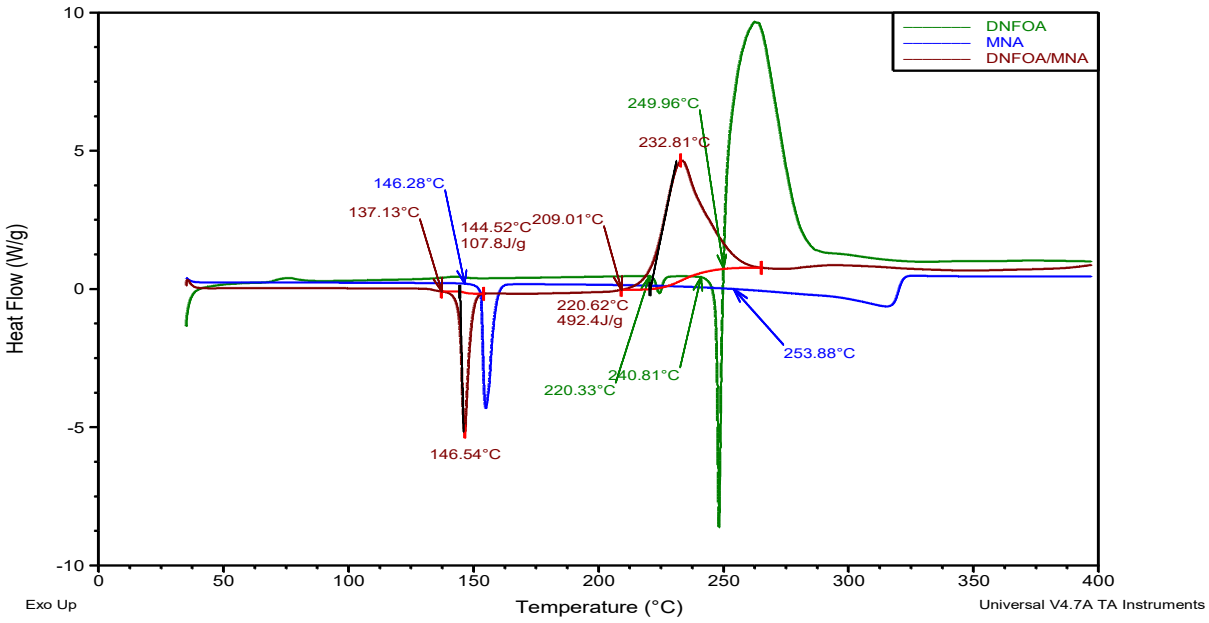


Figure A.22. DSC Compatibility - DNFOA and MNA

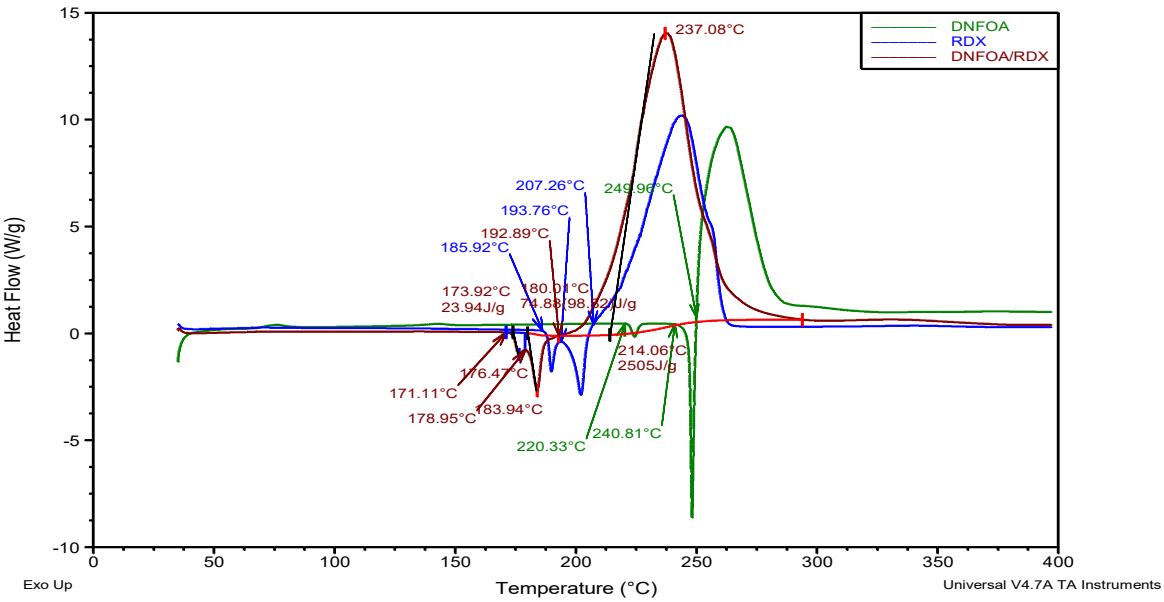


Figure A.23. DSC Compatibility - DNFOA and RDX

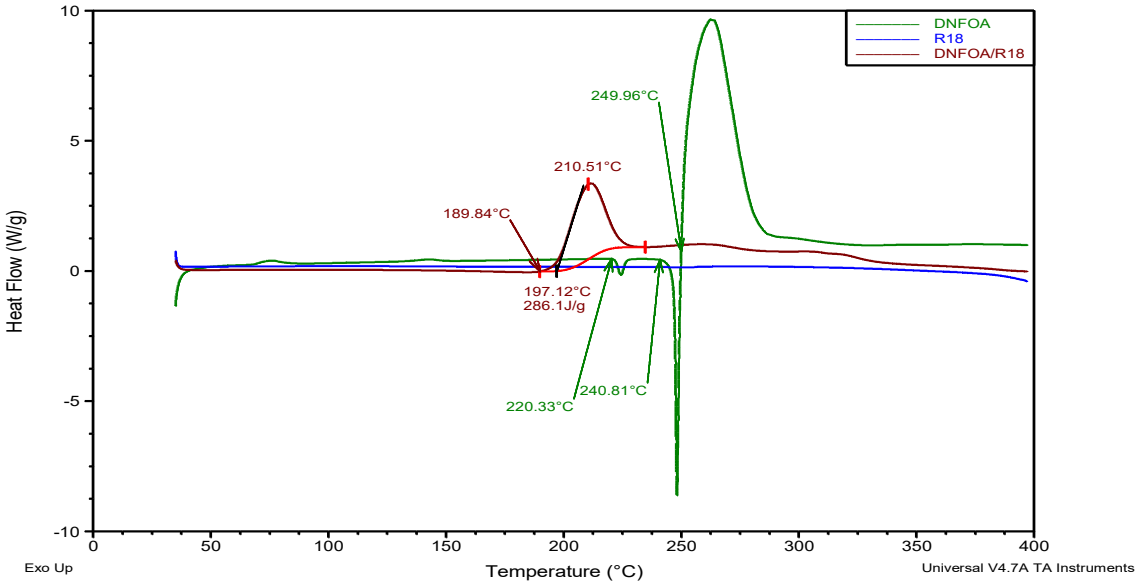


Figure A.24. DSC Compatibility - DNFOA and R18 Polymer

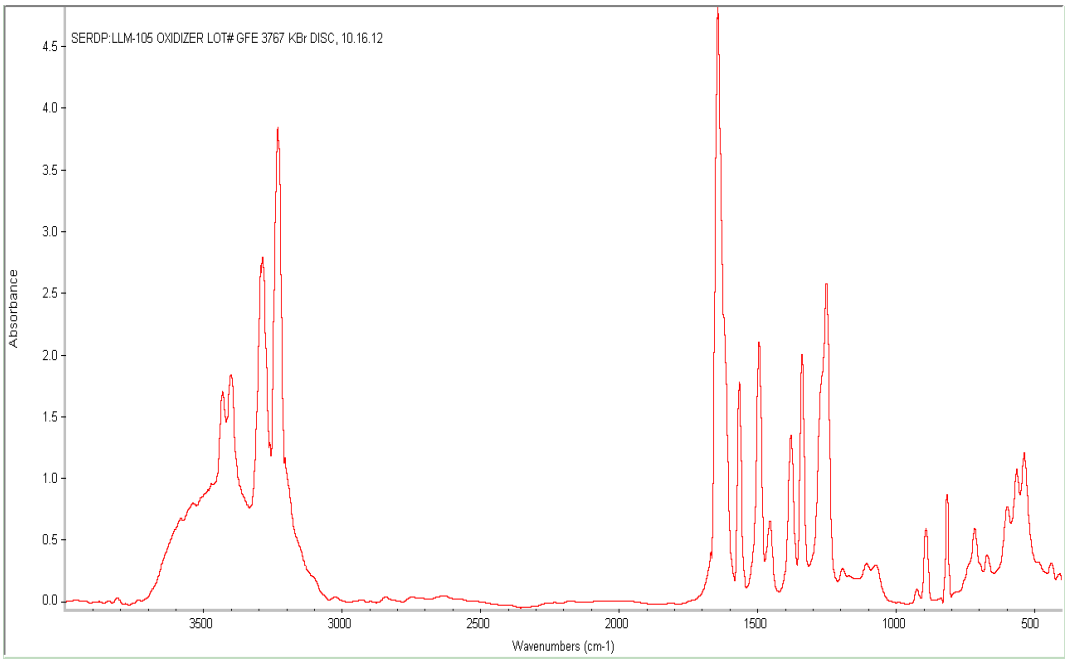


Figure A.25. FTIR Spectrum of LLM-105

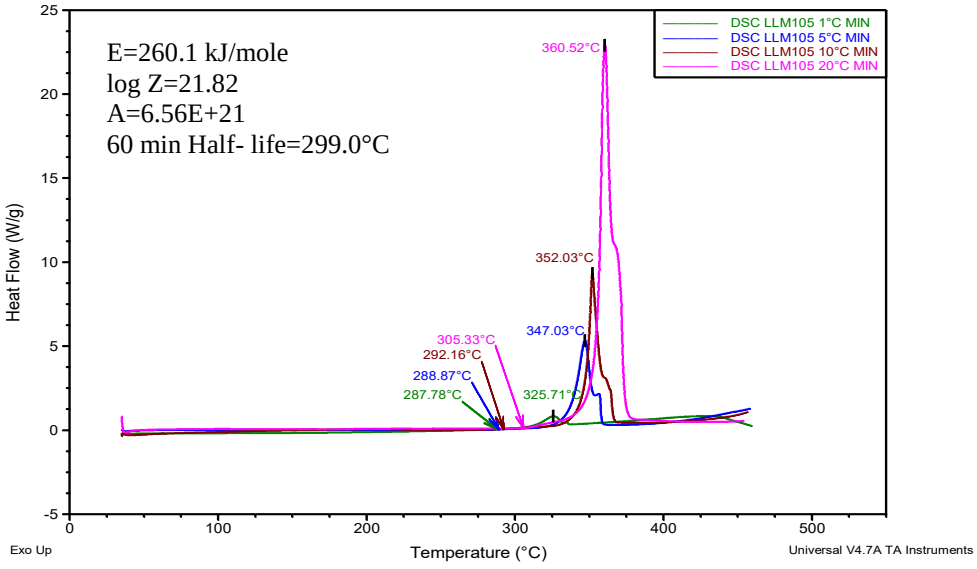


Figure A.26. Kinetics by DSC for LLM-105

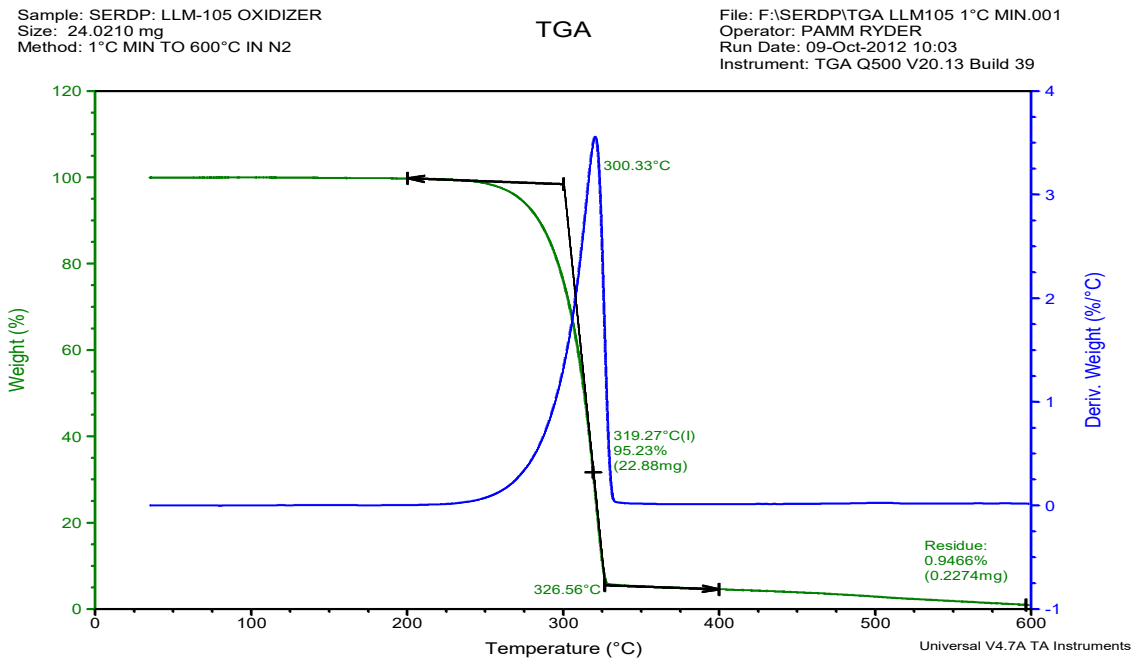


Figure A.27. TGA for LLM-105 Heated at 1°C/min

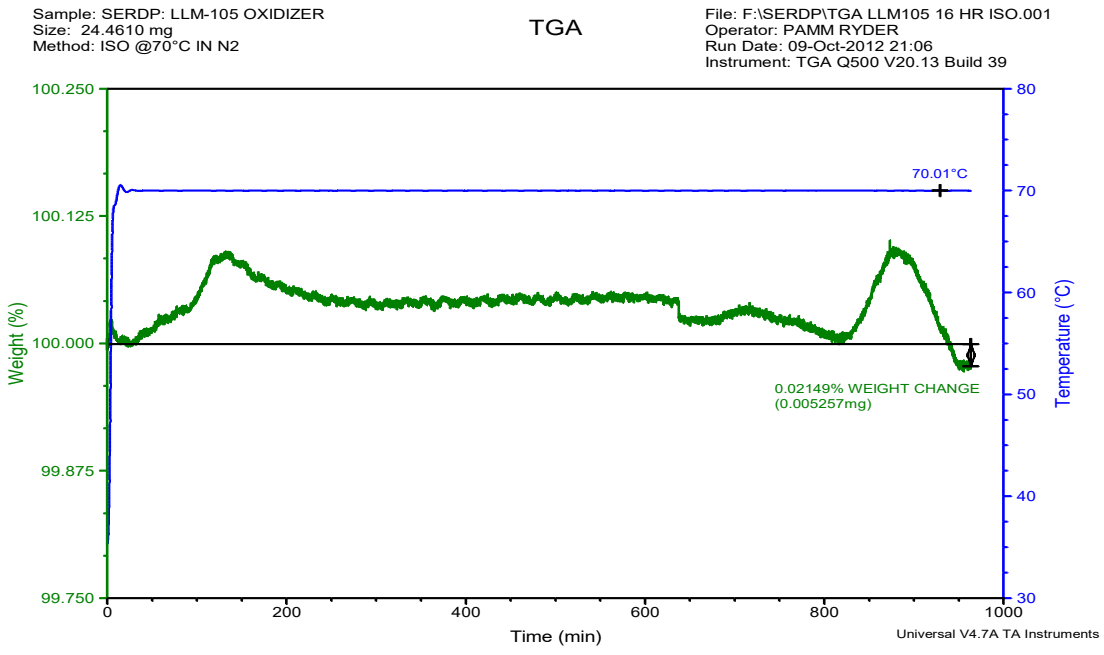


Figure A.28. Isothermal TGA for LLM-105

Summarize ResultsSERDP: LLM-105 OXIDIZER						
Date :	**10/16/2012**					
Group	Sample name	Weight	Nitrogen%	Carbon%	Hydrogen%	Oxygen%
1	SULFANILAMMIDE	1.728	16.270	41.840	4.680	18.580
1	SULFANILAMMIDE	1.799	16.413	41.818	4.596	19.382
1	SULFANILAMMIDE	1.722	16.341	41.798	4.470	18.580
1	SULFANILAMMIDE	1.863	16.591	42.112	4.517	18.935
1	SULFANILAMMIDE	1.568	16.692	41.984	4.439	18.580
5 Sample(s) in Group No : 1						
Component Name	Theoretical	Average	STDev	cv%		
Nitrogen%	16.27	16.461	0.176	1.07%		
Carbon%	41.84	41.910	0.134	0.32%		
Hydrogen%	4.68	4.540	0.098	2.16%		
Oxygen%	18.58	18.811	0.354	1.88%		
Group	Sample name	Weight	Nitrogen%	Carbon%	Hydrogen%	Oxygen%
2	LLM-105 OXIDIZER	1.449	40.128	22.237	1.705	34.812
2	LLM-105 OXIDIZER	1.523	40.097	22.171	1.844	34.228
2	LLM-105 OXIDIZER	1.758	40.241	22.232	1.835	34.245
2	LLM-105 OXIDIZER	1.853	40.212	22.215	1.823	34.087
2	LLM-105 OXIDIZER	1.598	40.015	22.131	1.792	34.079
5 Sample(s) in Group No : 2						
Component Name	Theoretical	Average	STDev	cv%		
Nitrogen%	38.89	40.138	0.091	0.23%		
Carbon%	22.22	22.197	0.045	0.20%		
Hydrogen%	1.85	1.800	0.056	3.13%		
Oxygen%	37.04	34.290	0.302	0.88%		

Figure A.29. Results of CHNO Analysis of LLM-105

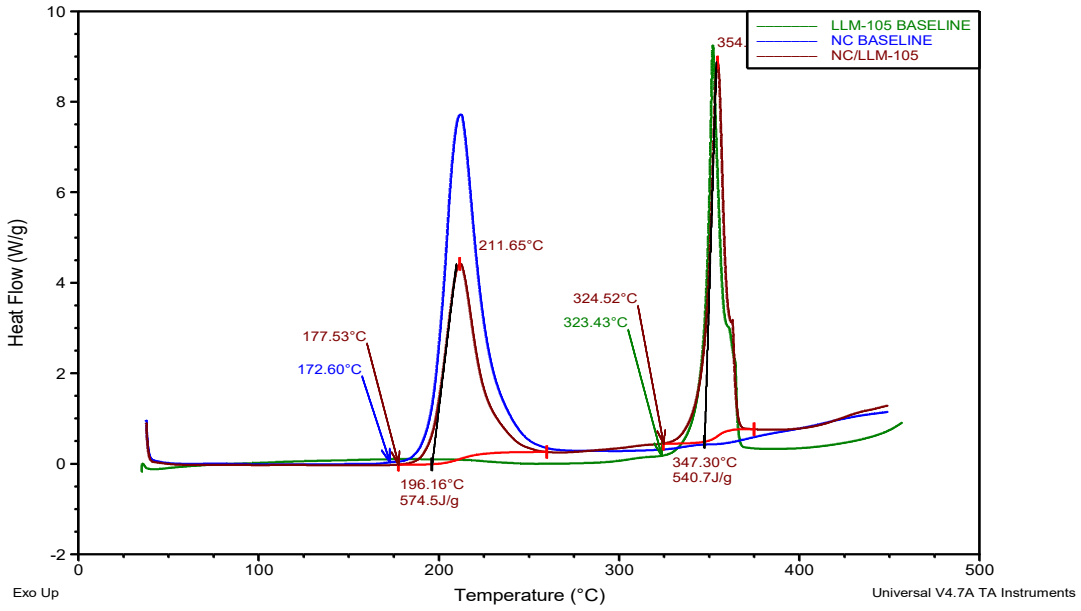


Figure A.30. DSC Compatibility - LLM-105 with Nitrocellulose

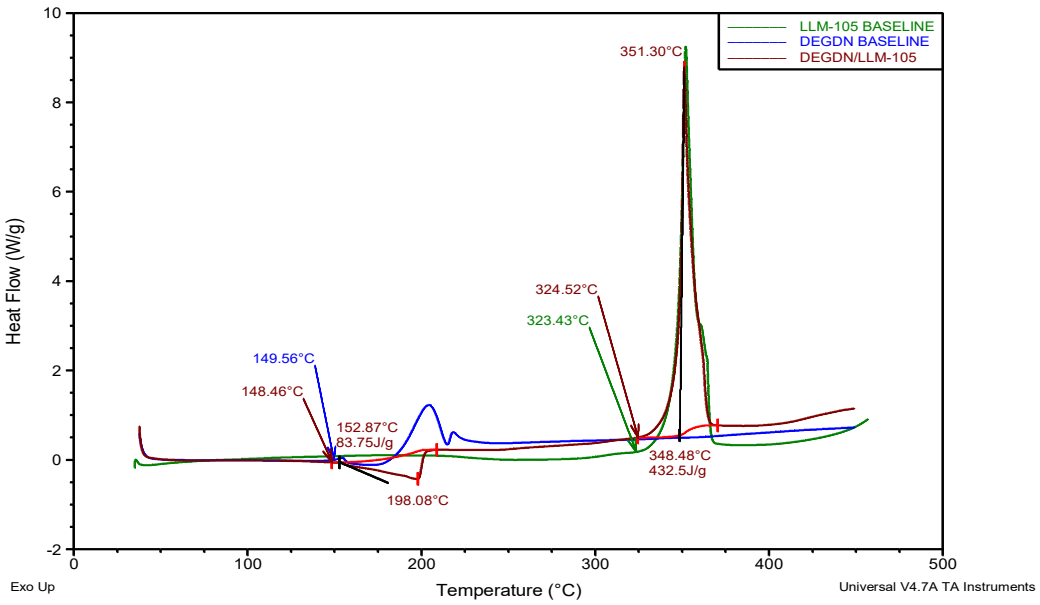


Figure A.31 DSC Compatibility - LLM-105 with DEGDN

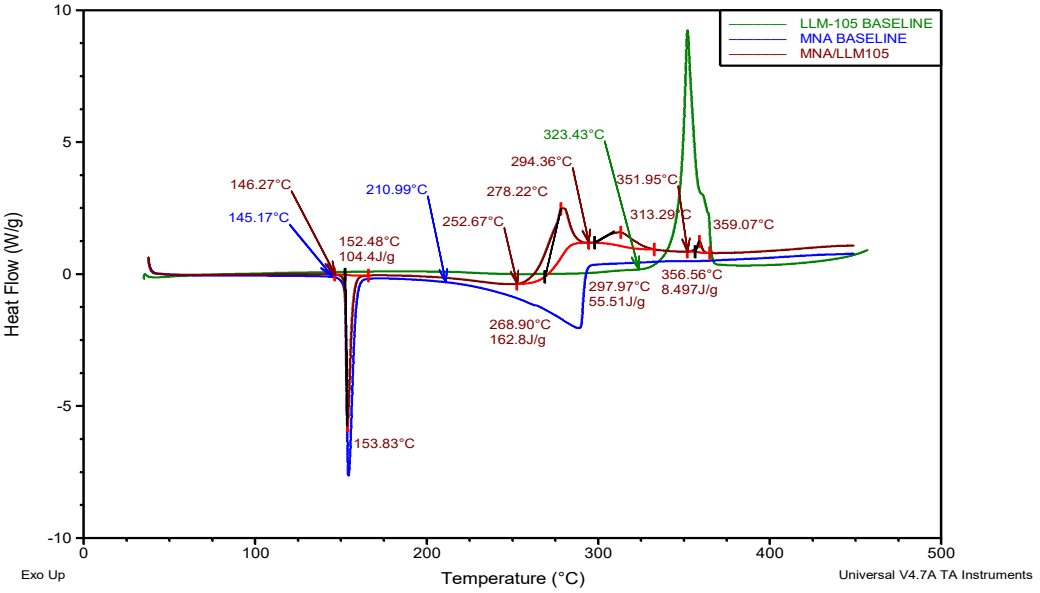


Figure A.32. DSC Compatibility - LLM-105 with MNA

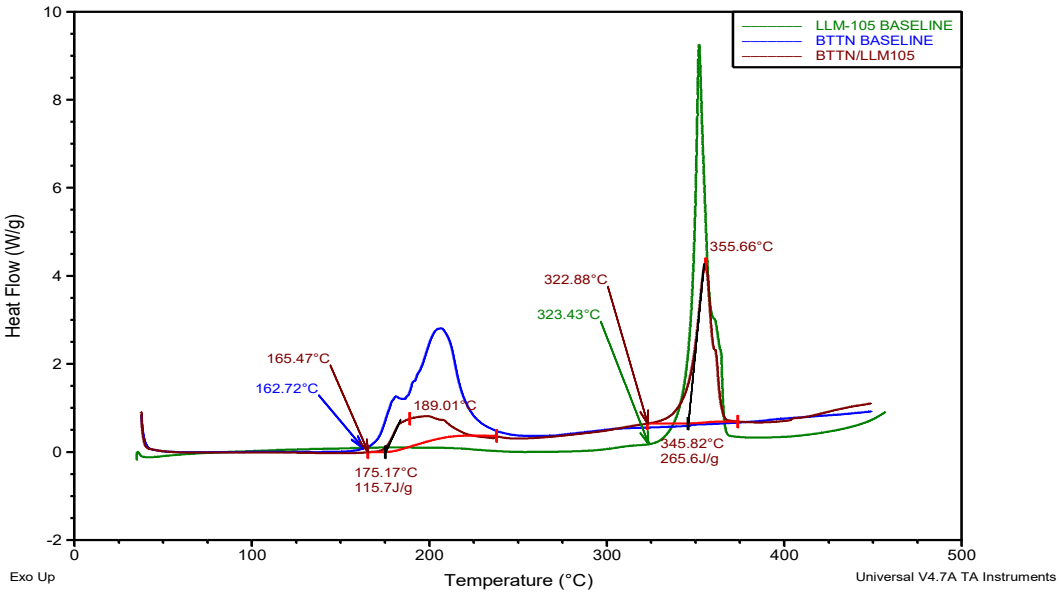


Figure A.33. DSC Compatibility - LLM-105 with BTTN

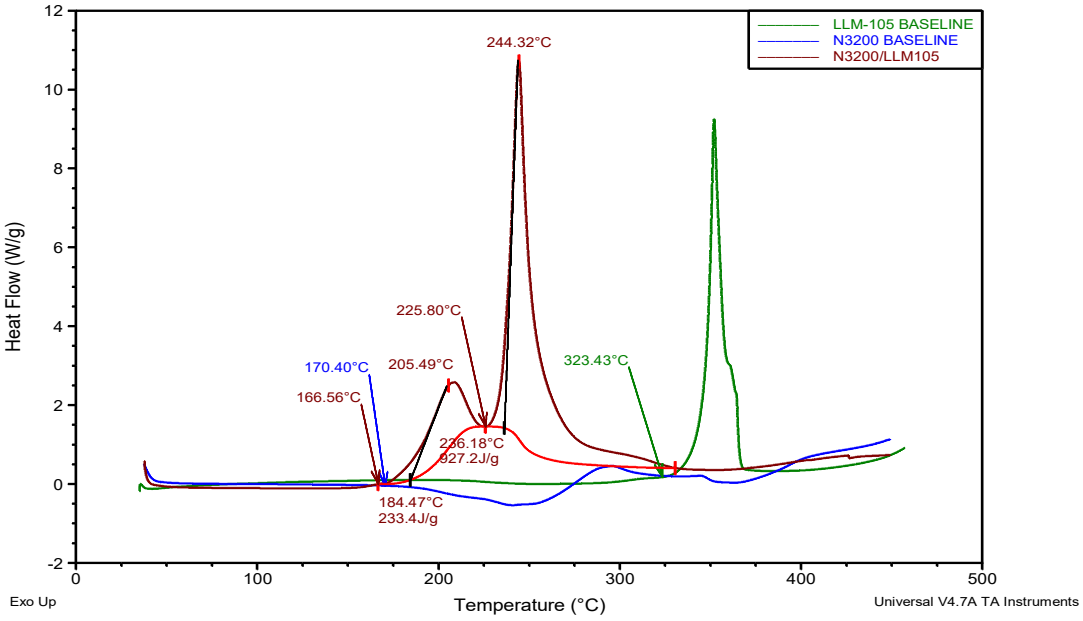


Figure A.34. DSC Compatibility - LLM-105 with N3200

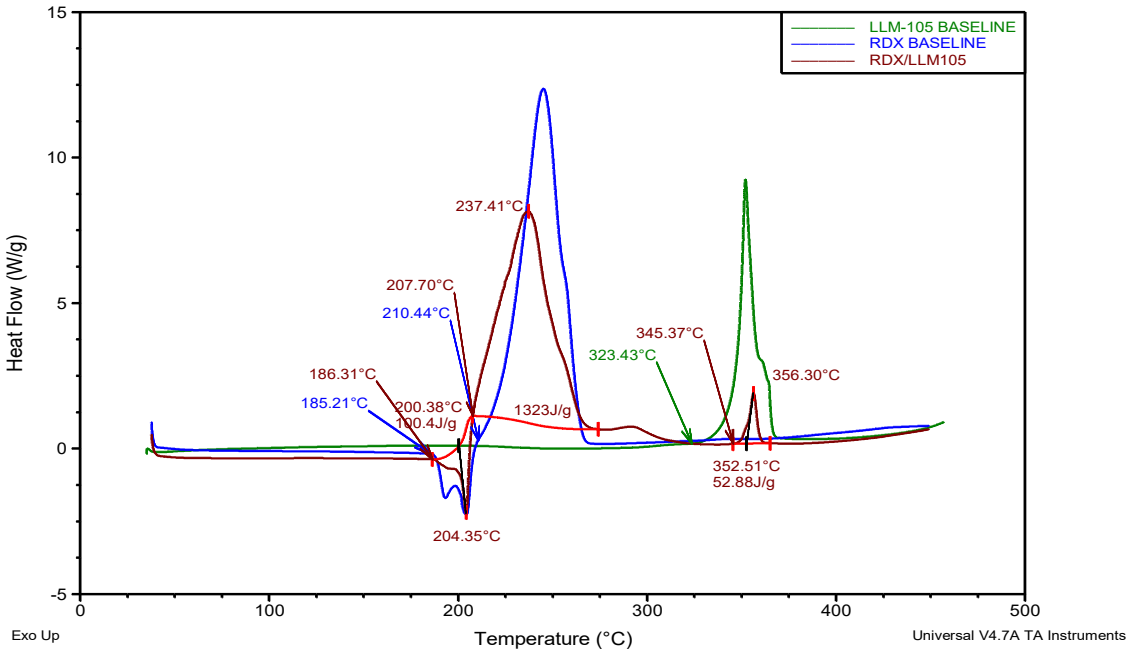


Figure A.35. DSC Compatibility - LLM-105 with RDX

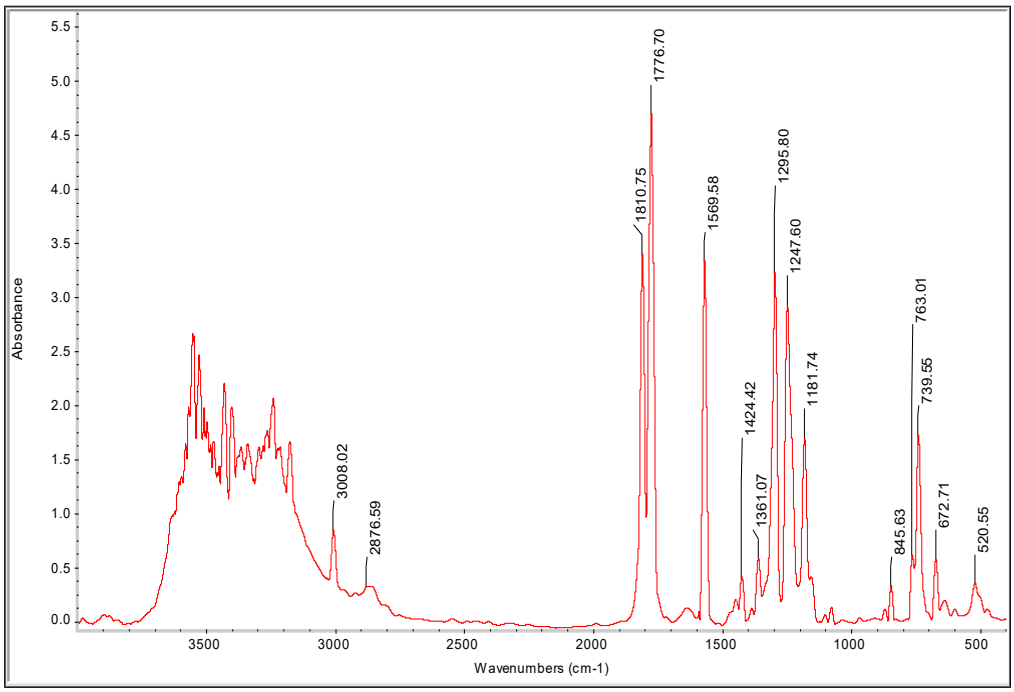


Figure A.36. FTIR Spectrum of DINGU

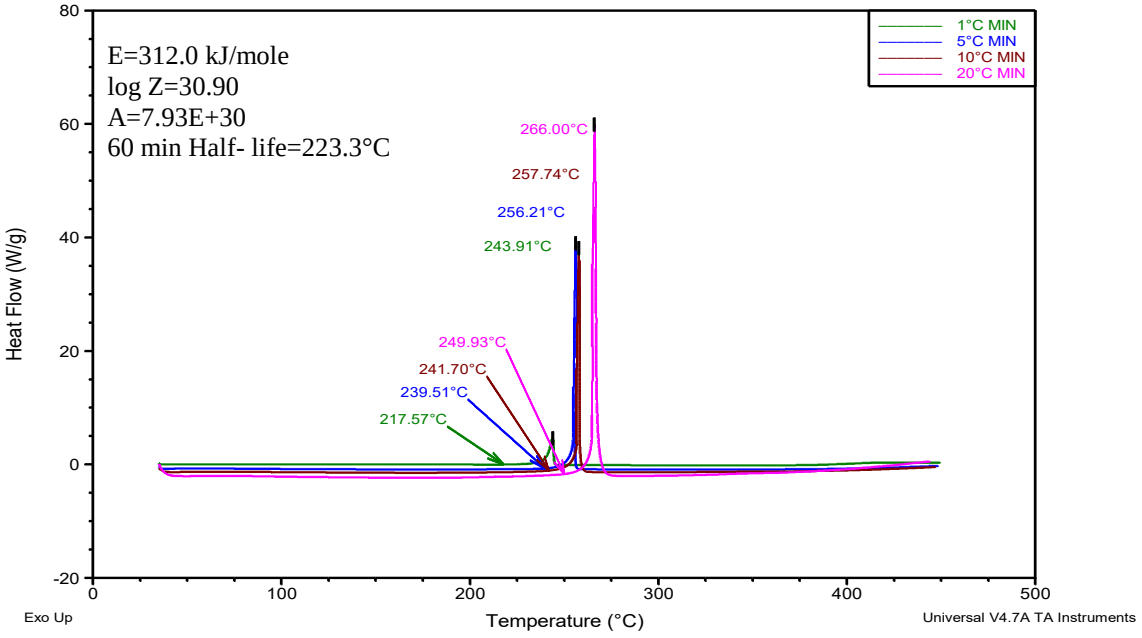


Figure A.37. Kinetics by DSC of DINGU

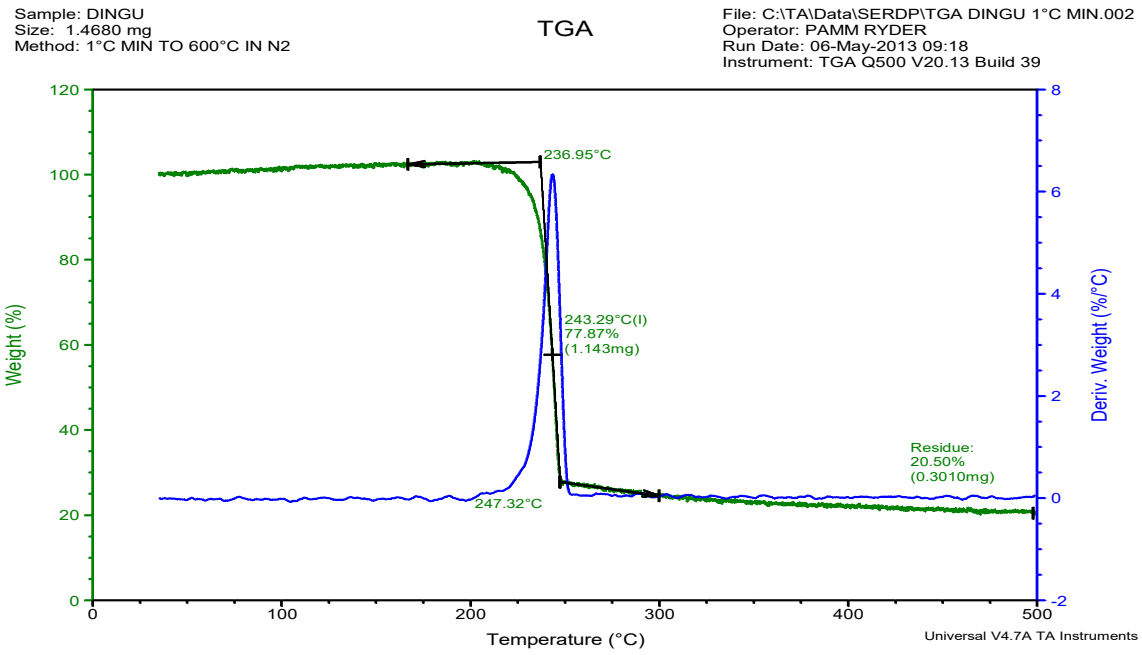


Figure A.38. TGA for DINGU Heated at 1°C/min

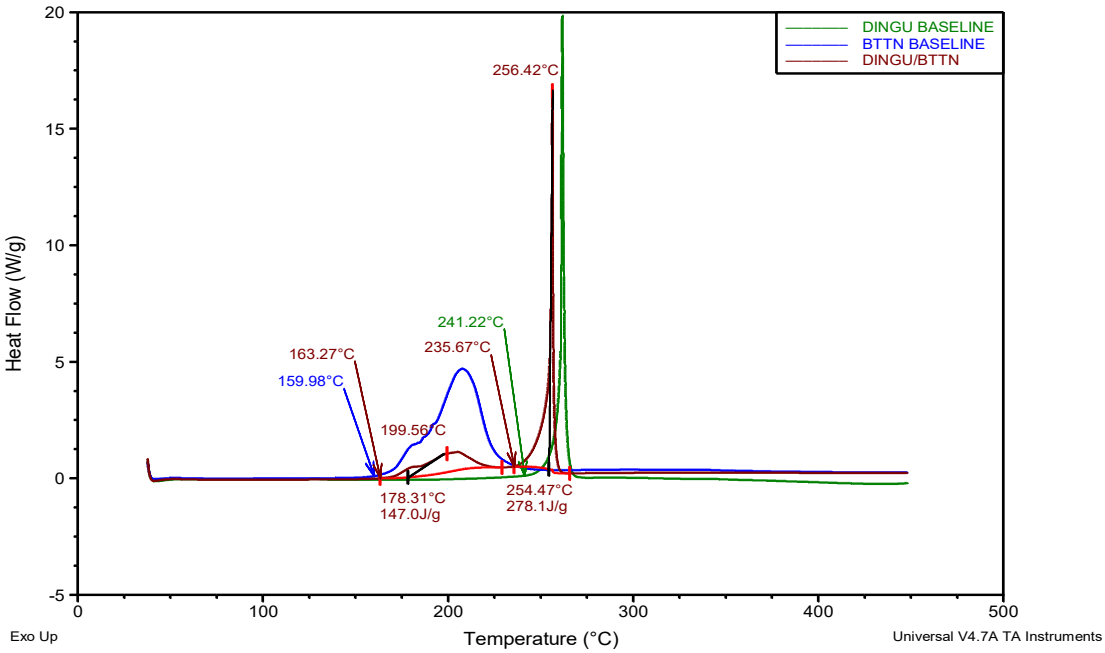


Figure A.39. DSC Compatibility - DINGU and BTTN

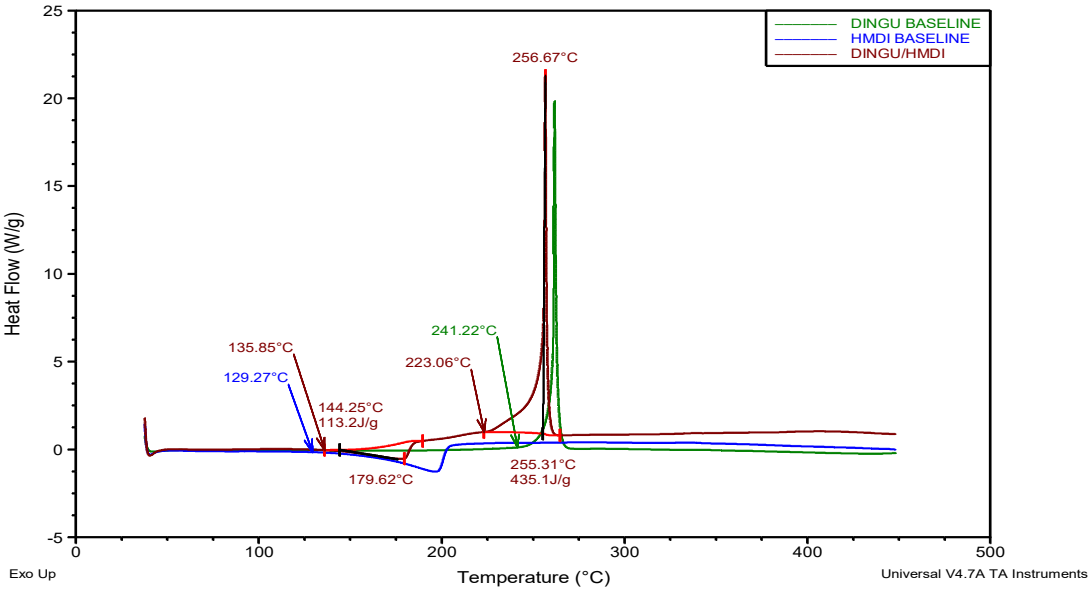


Figure A.40. DSC Compatibility - DINGU and HMDI Curative

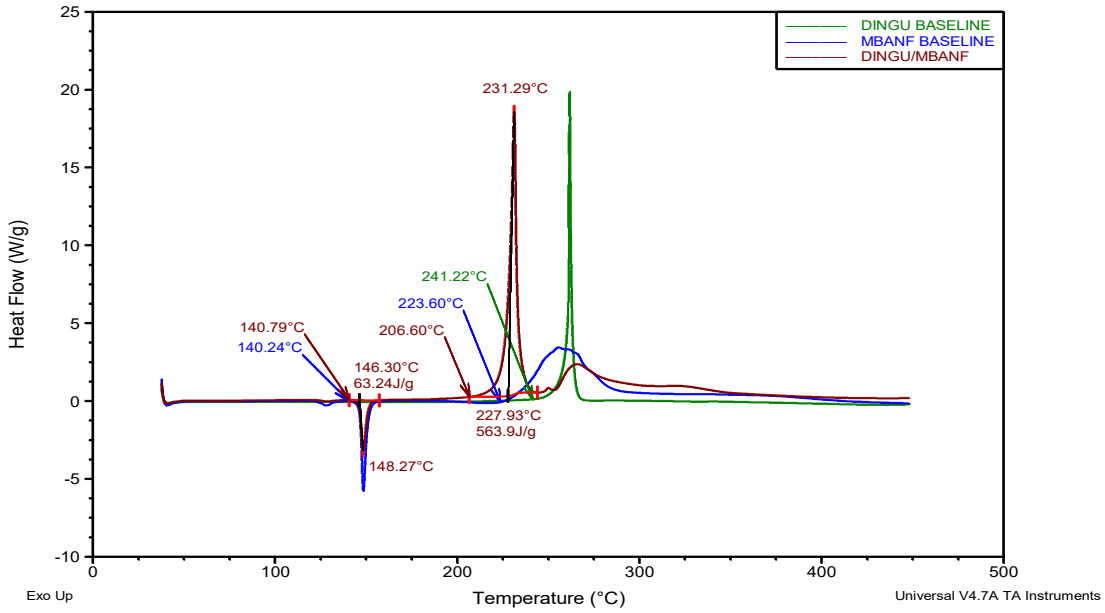


Figure A.41. DSC Compatibility - DINGU and MBANF

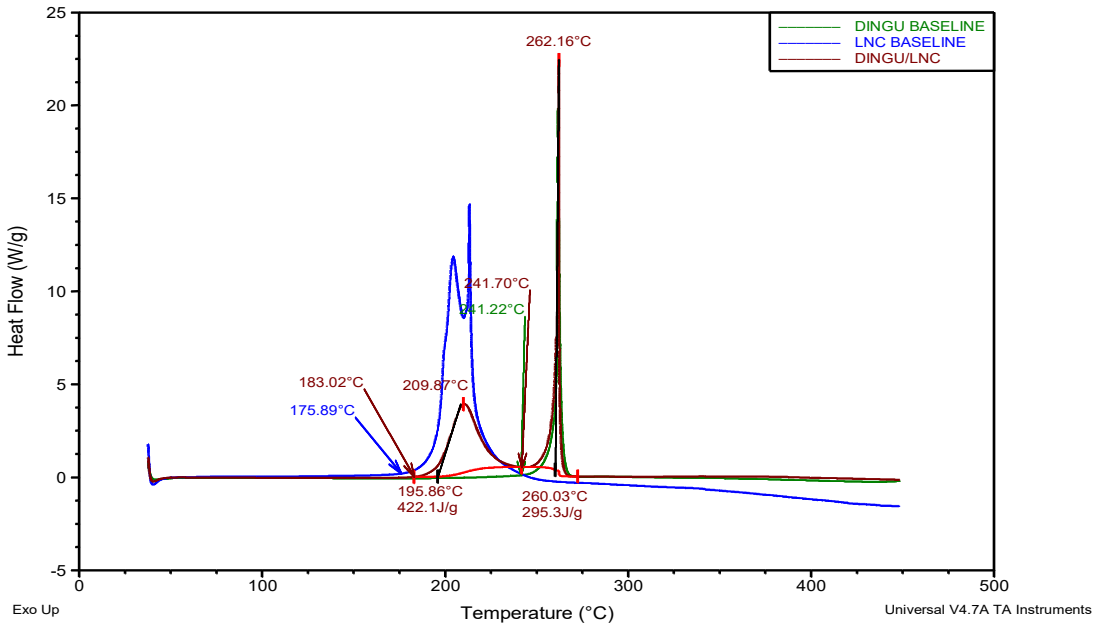


Figure A.42. DSC Compatibility - DINGU and LNC

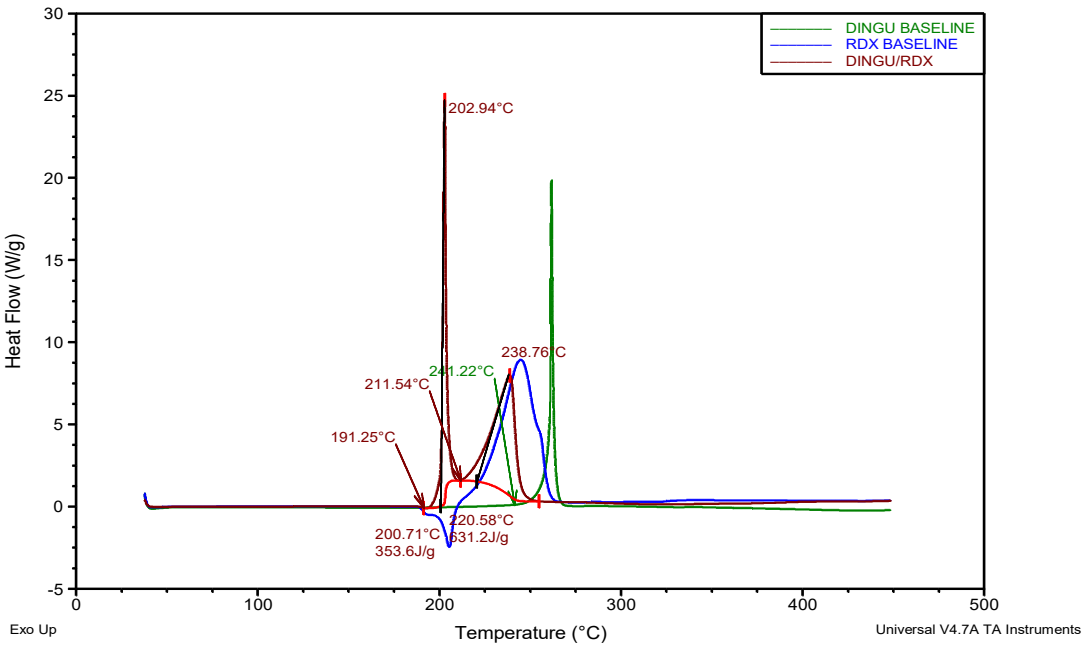
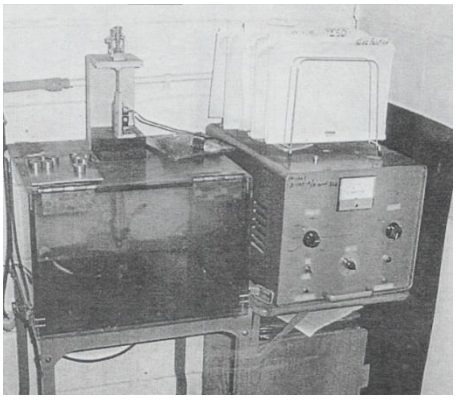


Figure A.43. DSC Compatibility - DINGU and RDX

Appendix B. Test Methods

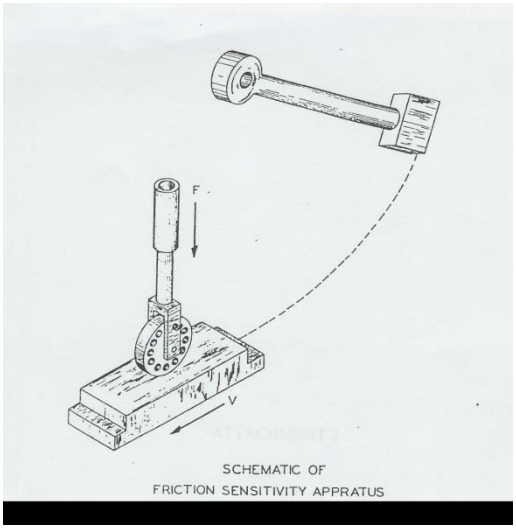
Electrostatic Discharge:

Aerojet Rocketdyne uses a pre-1974 ARC-built device referred to as the ESD tester to determine the sensitivity of energetic ingredients to static discharge. The device used applies a capacitive discharge of energy from 0.0013 Joules to 6 Joules at 5,000 volts to energetic ingredients in order to determine their sensitivity to static discharge. The sample is placed in a steel cup with 0.020 inch deep x 0.250 inch in diameter recess. The spark is discharged from a steel needle probe 1/16-inch above the 0.2 gram sample. This test is a screening tool to determine the proper controls needed to work with static sensitive energetic materials in the workplace.



Friction Sensitivity:

Sensitivity to friction is determined using an ABL Friction Tester. The sample is placed on a flat steel plate mounted on rollers and a stationary steel wheel suspended from a hydraulic cylinder. Pressure is applied to the wheel to a 2000 psi maximum. During testing, a heavy pendulum is dropped from various angles (45^{o} to 90^{o}) and allowed to strike the plate. The momentum at each angle translates to a given plate velocity. The data are reported as zero initiation level, which is the maximum pressure at a given drop angle at which 10 consecutive negatives are observed.



Impact Sensitivity:

Sensitivity to impact is determined on a Technoproducts Drop Weight Tester. Solid samples are tested in a brass cup into which a plunger is inserted. The samples are then tested by dropping weights (from 1 to 6 kg) from varying heights (0 to 50 cm). The data may be reported as E_{50} (the 50% probability point at which a positive is likely to occur) or as E_0 (the highest weight-height level at which 10 consecutive negative results are observed).

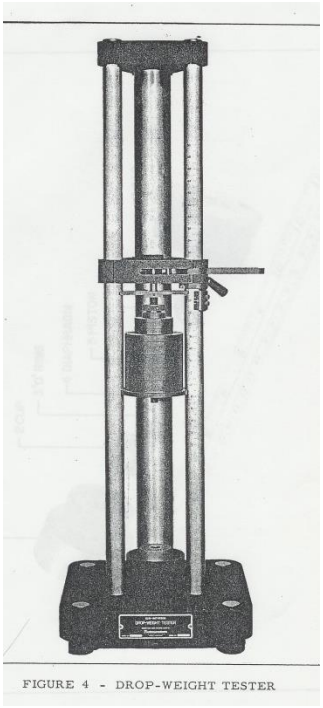
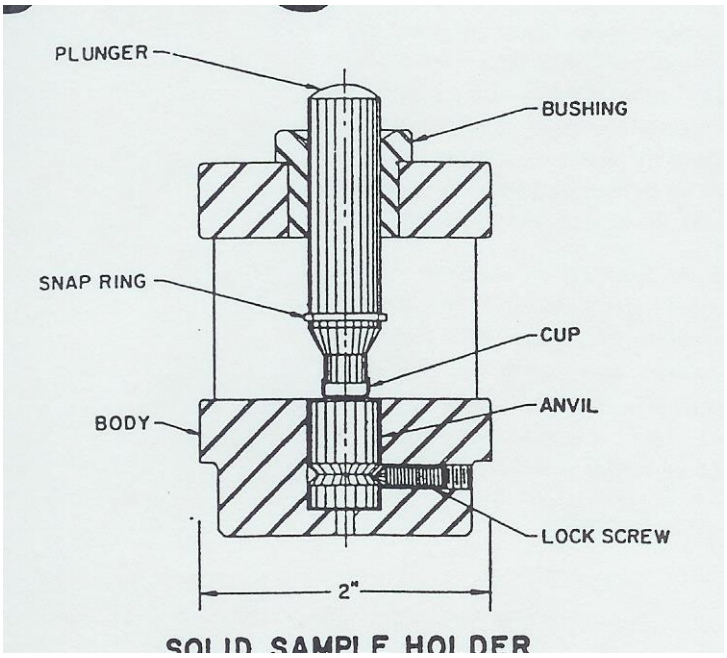


FIGURE 4 - DROP-WEIGHT TESTER



SOLID SAMPLE HOLDER

Rapid-Rise Autoignition:

The test sample is placedin a recess in a copper block, the temperature of which is monitored. The sample is heated at a rate of approximately 25°C/min. The temperature and time at which ignition occurs is recorded. The test is stopped if no reaction occurs by the time the sample reaches 350°C.

DSC Compatibility:

Materials being tested for compatibility are mixed at a 1:1 ratio inside of the DSC pan, the lid crimped on the pan, and the mixture is run at a rise rate of 10°C/min to 450°C. Any shift of an exotherm to a lower temperature by more than 10°C indicates incompatibility.

Small Scale Gap Test (or IHE Gap test):

Aerojet Rocketdyne uses the MIL-STD 1751 Method 1042, Explosive Shock Sensitivity Test, for performing shock sensitivity testing.

End-of-Mix Viscosity:

Propellant samples are evaluated for viscosity by using a Brookfield viscometer equipped with an “F” spindle, at a rotation of 1 revolution per minute. The dial reads viscosity in kilopoise.

Strand Burning Rate:

Burning rate in solid strands is measured using a nitrogen-pressurized burner capable of holding pressures from 14.7 to 5000 psi. The strands are roughly ¼” square, and 5 inches long. The distance between the timing wires is 3.5 inches, and the operator monitors the time to burn at pressure. At Aerojet Rocketdyne, the strands are inhibited with thick vacuum grease prior to burning to prevent flashing.

Appendix C. Final Toxicology Assessment

U.S. ARMY PUBLIC HEALTH CENTER
8252 Blackhawk Road, Aberdeen Proving Ground, Maryland 21010-5403

Toxicology Report No. S. 0049740-13
U.S. Department of Defense
Strategic Environmental Research and Development Program
(SERDP)
April 2018

Toxicology Assessment for Eliminating Lead, RDX, and AP in a Castable Exponent-Modified Minimum Smoke (EMMS)-Configured Propellant while Maintaining Performance (SERDP Project WP-2143)

Prepared by William S. Eck, PhD.

Approved for public release; distribution unlimited

ARIMS Designation: 500c

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14. ABSTRACT

This report is an assessment of the impacts on human health and ecotoxicity of formulations for minimum-smoke propellants intended to remove RDX and other toxic components of current propellant formulation. The compounds under consideration are generally predicted by QSAR modeling to be less toxic than RDX. Inhalation toxicity appears to be high form MBANF, DNFOA, and ANAF, but these predictions may be due to poor fit to the QSAR models. Most of the compounds under consideration are expected to pose dermal or ocular hazards, and are predicted to be mutagenic in the Ames assay. In vitro evaluation of these compounds is recommended.

15. SUBJECT TERMS

RDX replacements, MBANF, DNFOA, ANAF, lead replacements, ammonium perchlorate replacements, human health evaluation, environmental evaluation, AzTA, AGDNM NT123, AGDNM NT124, AONT, DINGU, DNGU.

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GLOSSARY

APHC	U.S. Army Public Health Center
ATSDR	Agency for Toxic Substances and Disease Registry
BCF	Bioconcentration Factor
CAD	Cartridge-Activated Device
EMMS	Exponent-Modified Minimum Smoke
ESOH	Environment, safety, and occupational health
GHS	Globally Harmonized System
IPR	In-Progress Review
LOAEL	Lowest Adverse Effect level
NASA	National Aeronautics and Space Administration (U.S.)
NIOSH	National Institute for Occupational Safety and Health
NIS	Sodium-iodide symporter
NOAEL	No Observed Adverse Effect level
RDX	1,3,5-Trinitronitramine or “Cyclonite”
SERDP	Strategic Environmental Research and Development Program (DoD)

TOXICOLOGY REPORT NO. S.0049740-13
TOXICOLOGY ASSESSMENT for ELIMINATING LEAD, RDX, and AP in a CASTABLE EPONENT-MODIFIED MINIMUM SMOKE (EMMS)-CONFIGURED PROPELLANT WHILE MAINTAINING PERFORMANCE
(SERDP PROJECT WP-2143)
APRIL 2018

1 Summary

1.1 Overview

This project is being undertaken to find replacements for 1,3,5-Trinitronitramine or "Cyclonite (RDX) and other identified toxic components in a current formulation of minimum-smoke rocket propellant. Eight new compounds are being evaluated for performance and environmental impact. This report is a preliminary assessment of the Environment, Safety, and Occupational Health (ESOH) impacts of these new compounds. This information will be factored into the selection process for development of a new propellant formulation.

1.2 Purpose

The purpose of this study is to provide ESOH information on new or replacement energetic compounds for Department of Defense (DoD) use. This information is critical to the Research, Development, Testing, and Evaluation (RDT&E) of alternatives under the DoD Strategic Environmental Research and Development Program (SERDP) program and is necessary for work unit program evaluation.

Research, development, testing, training, and use of substances potentially less hazardous to human health and the environment is vital to the readiness of the DoD. Safeguarding the health of Service Personnel, Civilians, and the environment requires an assessment of alternatives before they are fielded. Continuous assessments begun early in the RDT&E process can save significant time and effort during RDT&E, as well as over the life cycle of the items developed. In addition, residues of pyrotechnics, propellants, explosives, and incendiaries have been found in soil, air, surface, and ground water samples, creating environmental problems and interfering with training activities.

The Strategic Environmental Research and Development Program is dedicated to finding replacements for substances causing environmental and/or occupational risks to health. The DoD seeks to develop new experimental propellants that are less toxic than present formulations for minimum-smoke propellants yet have comparable performance.

1.3 Conclusions

All compounds under consideration appear to be less toxic than RDX. While inhalation toxicity appears to be high for methanediamine (MBANF), ethanediamide (DNFOA), and 4-[2-(4-nitro-1,2,5-oxadiazol-3-yl)-2-oxidodiazenyl]-1,2,5-oxadiazol-3-amine (ANAF), this may be due to poor fit to the QSAR models as these values appear to not correlate to the projected oral toxicity. Most of the compounds under consideration are potential dermal or ocular hazards, which could

pose a problem in the manufacturing environment, but this could be addressed by engineering controls or personal protective equipment. Many of the compounds are projected to be mutagenic.

In terms of environmental toxicity, these compounds are generally predicted to be less toxic than RDX. The MBANF, DNFOA, and ANAF are expected to present only a moderate ability to migrate through ground water, while the others present a significant transport threat to ground and surface water. Bioaccumulation is expected to be low for all compounds, but biodegradation is predicted to be poor, with persistence in the environment lasting weeks to months.

1.4 Recommendations

Compounds selected for scale-up should be tested for toxicity in accordance with ASTM International Guideline E-2552 in appropriate systems.

2 References

See Appendix A for list of references

3 Authority

Military Interdepartmental Purchase Request (MIPR) No. N0017411MP10443. This Toxicology Assessment addresses, in part, the ESOH requirements required by DoD Directive 4715.1E, ESOH, 2005. This investigation was carried out as project WP-2143 for the DoD, SERDP. The Principle Investigator is Dr. Bradley Sleadd, Naval Surface Warfare Center, Indian Head Division, Indian Head, MD.

4 Background

Current regulations require assessment of human health and environmental effects arising from exposure to substances in soil, surface water, and ground water. Applied after an item has been fielded, these assessments can reveal the existence of adverse environmental and human health effects that must be addressed, often at substantial cost. It is more efficient to begin the assessment of exposure, effects, and environmental transport of military-related compounds/ substances early in the RDT&E process in order to avoid unnecessary costs, conserve physical resources, and sustain the health of our forces and others potentially exposed.

In an effort to support this preventive approach, the U.S. Army Public Health Center (APHC) has been tasked with creating a phased process to reduce adverse ESOH effects impacting readiness, training, and development costs. This is an on-going effort, and this report represents the status of information available for this work unit as of the date of publication. Summary interpretations of this information have been provided to the sponsor in support of SERDP, In-Progress Reviews (IPR).

5 Statement of Problem

The propellant formulations currently used in rocket propulsion systems contain a significant amount of RDX, lead, and ammonium perchlorate. The RDX is environmentally persistent and toxic, causing seizures in humans and mammals, and may be carcinogenic. An RDX-free formulation for a minimum-smoke propellant would be a significant ESOH enhancement of this propellant system. Lead is a notorious systemic toxicant, and ammonium perchlorate has adverse health effects on pregnant and nursing women, fetuses, and infants. A formulation for a minimum-smoke propellant free of these toxicants would be a significant ESOH enhancement of this propellant system.

6 Methods

In order to determine the human health and ecological impact of compounds employed in these formulations, it is necessary to correctly identify each compound and to determine its physical, chemical, and toxicological properties. The primary means of identification employed for each compound in this program is its Chemical Abstracts Service Registry Number (CAS RN) (see Table 1). While all compounds do not necessarily have a single CAS RN, the CAS RN is an unambiguous way of accessing information for chemical substances. In some cases where a compound is newly-discovered or novel, a CAS RN may not be assigned. The CAS RN is readily used as a keyword for searching online databases and is often cross-referenced with both systematic and non-systematic (i.e., “common” or trivial) names for chemical substances. In some cases, synonyms and trade names are also used to identify structures.

This report addresses compounds investigated as part of this work unit through the end of Fiscal Year 2016; finalization of the report was hampered by uncertain funding status for the project and technical difficulties.at Indian Head. Basic physical and chemical properties are usually determined by consulting tertiary sources when such information is available. When such information is not available, it is estimated using Quantitative Structure-Activity Relationship (QSAR) models where possible. The properties necessary to assess fate and transport in the environment (FTE) include:

- Molecular weight (MW).
- Henry’s law constant (K_H).
- Octanol-water partition coefficient (log K_{OW}).
- Water solubility
- Boiling point (bp).
- Organic carbon partition coefficient (log K_{OC}).
- Vapor pressure (vp).

Information on combustion, explosion, and thermal decomposition products is also collected, if available. Toxicological information needed to estimate potential human health risks includes reported toxicity effects of oral, inhalation, dermal, and ocular exposures; potential for developmental or reproductive toxicity, mutagenesis and carcinogenesis; and modes and mechanisms of toxicity. Toxicological information is derived directly from primary sources whenever possible.

Table 1. Compounds under evaluation

Compound	CAS RN
MBANF	146859-30-5
DNFOA	454182-52-6
ANAF	159013-86-2
AzTA	Unknown
AGDNM NT123	Unknown
AGDNM NT124	Unknown
AONT	Unknown
DINGU/DNGU	55510-04-8

Sources used in this search may include publications from the U.S. Department of Health and Human Services Agency for Toxic Substances and Disease Registry (ATSDR) and *The Merck Index* (O'Neil, 2006), the Defense Technical Information Center (DTIC®), Food and Agriculture Organization of the United Nations (FAO), the World Health Organization (WHO), the International Agency for Research on Cancer (IARC), the International Chemical Safety Cards (ICSC) developed by the National Institute for Occupational Safety and Health (NIOSH), and the U.S. National Library of Medicine's Toxicology Data Network (TOXNET®) that provides access to information from the National Institutes of Health (NIH) and the U.S. Environmental Protection Agency (USEPA). The TOXNET is a suite of individual databases including ChemIDPlus® (CIDP) (i.e., chemical and registration numbers, and chemical identification and structure, searches respectively), Hazardous Substances Data Bank (HSDB®), Chemical Carcinogenesis Research Information System (CCRIS), Developmental and Reproductive Toxicology (DART/ETIC), Directory of Information Resources Online (DIRLINE®), Genetic Toxicology (GENE-TOX), Haz-Map (database linking chemicals, jobs and diseases), Household Products Databank (HPD) (potential health effects of chemicals in common household products), Integrated Risk Information System (IRIS), International Toxicity Estimates for Risk (ITER), Toxicology Information Online (TOXLINE®), Toxic Release Inventory (TRI), and Lactation Database (LactMed; database of drugs and other chemicals to which breastfeeding mothers may be exposed). The USEPA ECOTOXicology Database System (ECOTOX) and the National Institute of Environmental Health Sciences (NIEHS) National Toxicology Program (NTP)

databases were used. Primary sources are identified and retrieved using PubMed®, the Ovid® Technologies Journals, and the EBSCOhost® Research Database. Commercial suppliers are sometimes contacted for results of in-house research that may not appear in the open literature. (DTIC® is a registered trademark of the Defense Technical Information Center, TOXNET®, ChemIDPlusLite®, ChemIDPlus®, HSDB®, DIRLINE®, TOXLINE®, PubMed® are registered trademarks U.S. National Library of Medicine; OVID®, is a registered trademark of Ovid Technologies, Inc.; and EBSCOhost® is a registered trademark of EBSCO Publishing.)

Table 2. Categorization Criteria used in the Development of Environmental Safety and Occupational Health Severity (modified from (Howe et al. 2006)

	Low	Moderate	High
ENVIRONMENTAL PERSISTENCE	Readily biodegrades (<28 days)	Degradation ½ life: water <40 days , soil <120 days	Degradation ½ life: water >40 days soil > 120 days
TRANSPORT	Water sol. < 10 mg/L log K_{OC} > 2.0	Water sol. 10-1000 mg/L log K_{OC} 2.0-1.0	Water sol. > 1000 mg/L log Koc <1.0
BIOACCUMULATION	log K_{OW} <3.0	log K_{OW} 3.0-4.5	log K_{OW} >4.5
TOXICITY	No evidence of carcinogenicity/ mutagenicity; Subchronic LOAEL > 200 mg/kg-d	Mixed evidence for carcinogenicity/mutagenicity (B2, 2); Subchronic LOAEL 5-200 mg/kg-d	Positive corroborative evidence for carcinogenicity /mutagenicity; LOAEL < 5 mg/kg-d
ECOTOXICITY	Acute LC_{50}/LD_{50} >1 mg/L or 1500 mg/kg; Subchronic EC_{50} >100 µg/L or LOAEL >100 mg/kg-d	Acute LC_{50}/LD_{50} 1-0.1 mg/L or 1500-150 mg/kg; Subchronic EC_{50} 100-10 µg/L or LOAEL – 10-100 mg/kg-d	Acute LC_{50}/LD_{50}<100 µg/L or <150 mg/kg; Subchronic LOAEL <10 mg/kg-d

Notes:
mg/L - milligrams per liter
LOAEL - lowest-observed adverse effect level
LC_{50} – concentration expected to result in 50 percent lethality to a population of test animals.
mg/kg-d - milligram per kilogram per day
µg/L - microgram per liter

Environmental persistence, bioaccumulation, human health toxicity, and ecotoxicity were assigned to general categories of risk (e.g., low, moderate, or high) using criteria modified from Howe et al. (2006). Table 2 describes the criteria used in the categorization, though the relative proportions of each substance were also factored into the final assessment. The Globally Harmonized System, which is another classification scheme for toxicity, is discussed in Appendix B.

If no experimental data was identified in the literature, toxicity values for the various parameters were predicted using QSAR software where possible. Modeling packages include US EPA's EPI Suite™ 4.0 (USEPA 2008a), ECOSAR™ (USEPA 2007) and TOPKAT 6.2® (BIOVIA Inc.). EPI Suite™ and ECOSAR™ are trademarks of the USEPA; TOPKAT is a registered trademark of BIOVIA, Inc.

Compounds that are salts, organometallics, or consist of multiple subunits cannot be estimated using currently-available QSAR models. To overcome this limitation, the toxicity of each component species is calculated and converted to the equivalent mole-based toxicity measure. The most toxic species on a molar basis is then identified, and it is assumed that it will be the controlling species for toxicity. The molar toxicity is then reconverted to mass by using the formula mass of the original compound.

7 Results

7.1 Physical and Chemical Properties

Physical and chemical properties are summarized in Table 3. When data was not found, "ND" (no data) is inserted. In some cases the property named is not applicable ("n/a") to the substance being described. For example, if the compound is a nonvolatile solid or an inorganic salt, vapor pressure, K_{OW}, K_{OC}, and the Henry's Law constant (K_H) are typically negligible.

7.2 Summaries

Summaries of toxicity data for each of the formula components are presented in Table 4; summary assessments of human health and environmental toxicity are presented in Tables 5 and 6. Each characterization is generally based on the criteria provided in Table 2. The final risk characterization also incorporates assessment of the uncertainty associated with available data, the amount of each compound present in the formulation, the nature of potential exposure associated with use of the end item, and the professional judgment of the toxicologist.

7.3 N,N'-bis(4-nitro-1,2,5-oxadiazol-3-yl)-methanediamine [MBANF]

7.3.1 General Information

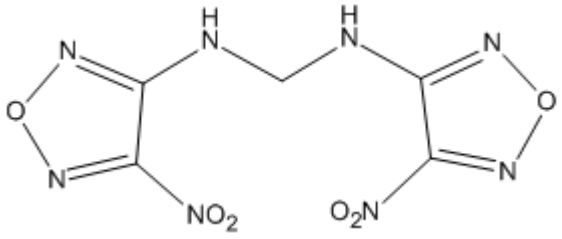

Fig. 1. MBANF

7.3.2 Toxicology Data

7.3.2.1 Oral

The MBANF was tested in the Neutral Red Update test and found to have a predicted LD_{50} of 148 mg/kg, placing it right at the border between moderate and low toxicity (USAPHC 2013b).

The Toxicology Prediction by Komputer Assisted Technology (TOPKAT) modeling predicts an oral LD_{50} in rats of 2000 mg/kg (the limit dose for toxicity) with high confidence. The TOPKAT predicts a chronic Lowest –observed-adverse-effect level (LOAEL) of 11.4 mg/kg-day at a high level of confidence. This predicted level of toxicity corresponds to an assessment of Low to Moderate acute oral toxicity.

7.3.2.2 Inhalation

No experimental data was found. The TOPKAT predicts a rat inhalation LC_{50} of 3.1×10^{-3} g/m^3-hour at a low level of confidence. This predicted level of toxicity corresponds to an assessment of High for inhalation toxicity, and Category 1 in the GHS system. These characterizations may be the result of a poor predictive capability of the QSAR systems.

7.3.2.3 Dermal

No experimental data was found. The TOPKAT modeling predicts MBANF is unlikely to be a skin irritant, but may be a skin sensitizer at a low level of confidence.

7.3.2.4 Ocular

No experimental data was found. The TOPKAT modeling predicts MBANF will likely be a moderate ocular irritant, but at low confidence.

7.3.2.5 Development and Reproduction

No experimental data was found. The TOPKAT modeling predicts MBANF is unlikely to be a developmental or reproductive toxicant at moderate confidence.

7.3.2.6 Genotoxicity

The MBANF was tested via the Ames procedure (USAPHC 2013a) and found to have low genotoxic potential. However, the compound exhibited cytotoxicity toward all test strains at concentrations as low as 18 µg/L.

7.3.2.7 Carcinogenicity

No experimental data were found. The TOPKAT modeling for MBANF is mixed, but is suggestive of a weak carcinogen.

7.3.2.8 Ecotoxicology

No experimental data were found. The information below is based on modeling using the Estimation Program Interface (EPI) Suite 4.0, Ecological Structure Activity Relationships (ECOSAR), and TOPKAT models.

7.3.2.8.1 Fate and Transport

The MBANF is only moderately soluble in water, and has an extremely low octanol-water partition coefficient, Henry's Law constant, and estimated Bioconcentration Factor (BCF). The carbon adsorption coefficient is moderate to low. Taken together, these values indicate this compound to be only a moderate ground water transport risk, with little tendency to bioaccumulate.

7.3.2.8.2 Ecotoxicity

No experimental data were found. Analysis by ECOSAR indicates this compound is not sufficiently soluble in aqueous systems to present a significant toxicity threat to aquatic species; LC_{50} values exceed the solubility of the compound. The Microtox®[1] test indicates the aquatic toxicity of MBANF will be about 0.126 mg/L, making it moderately toxic (USAPHC 2013). This finding is consistent with the observation of cytotoxicity in the Ames assay.

7.3.2.8.3 Degradation/Treatment

No experimental data were found. The EPI Suite predicts this compound is not readily biodegradable, with persistence in the environment of weeks to months, and removal by wastewater treatment plants is expected to be poor (<2 percent).

[1]Microtox is a registered trademark of Modern Water Inc., New Castle, DE.

7.4 N^1, N^2-bis(4-nitro-1,2,5-oxadiazol-3-yl)-ethanediamide [DNFOA]

7.4.1 General Information

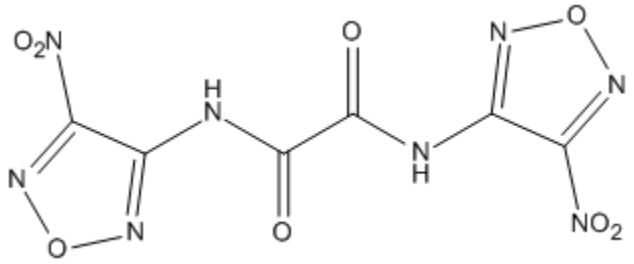

Fig 2. DNFOA

7.4.2 Toxicology Data

This compound contains functional groups that were poorly represented by toxicological data within the TOPKAT system, with the compound's parameters exceeding the Optimum Prediction Space for virtually every model system tested; values obtained from TOPKAT should be treated with the appropriate degree of skepticism.

7.4.2.1 Oral

The TOPKAT modeling predicts a rat oral LD_{50} of 124.6 mg/kg at low confidence. The chronic oral LOAEL is predicted to be 1.1 mg/kg at low confidence. This predicted level of toxicity corresponds to an assessment of Moderate acute oral toxicity.

7.4.2.2 Inhalation

No experimental data were found. The TOPKAT modeling predicts an inhalation LC_{50} of 7.2 x 10^{-3} g/m^3-hour at low confidence. This predicted level of toxicity corresponds to an assessment of High for inhalation toxicity, and Category 1 in the GHS system. These characterizations may be the result of a poor predictive capability of the QSAR systems.

7.4.2.3 Dermal

No experimental data were found. The TOPKAT modeling predicts DNFOA will not be a skin irritant, but is likely to be a severe sensitizer, although at low confidence.

7.4.2.4 Ocular

No experimental data were found. The TOPKAT modeling predicts DNFOA will be a severe ocular irritant at low confidence.

7.4.2.5 Development and Reproduction

No experimental data were found. The TOPKAT modeling predicts DNFOA is unlikely to be a developmental or reproductive toxicant.

7.4.2.6 Genotoxicity

Williams (USAPHC 2012) tested DNFOA in the Ames system, finding that it was cytotoxic at levels above 20 µg/mL, but not mutagenic.

7.4.2.7 Carcinogenicity

No experimental data were found. The TOPKAT modeling for carcinogenicity is indeterminate, with available models equally predicting opposite outcomes.

7.4.2.8 Ecotoxicology

7.4.2.8.1 Fate and Transport

At an estimated 308 mg/L, water solubility for DNFOA is moderate, but the log K_{OW} and Henry's Law constant are both low, as is the log K_{OC}. Together, these values indicate this compound is likely to remain soluble in ground water, with little tendency to bind to particles in the soil. The low bioconcentration factor indicates it is unlikely to accumulate in the food chain. Overall, this compound is assessed to be a moderate ground water threat.

7.4.2.8.2 Ecotoxicity

The Microtox test predicts the aquatic toxicity of DNFOA will be about 2.85 mg/L, making it moderately toxic (USAPHC 2013b).

The TOPKAT predicted an EC_{50} for *Daphnia* of 4.0 mg/L with low confidence, but was unable to make a prediction for the fathead minnow due to lack of suitable compounds comprising the training set.

The EPI Suite predicted that this compound has insufficient solubility to cause toxicity in green algae, *Daphnia*, and fish.

7.4.2.3 Degradation/Treatment

The EPI Suite modeling indicates this compound is unlikely to be biodegraded, suggesting environmental persistence of weeks to months. Removal by wastewater treatment facilities is expected to be poor (<2 percent).

7.5 4-[2-(4-nitro-1,2,5-oxadiazol-3-yl)-2-oxidodiazenyl]-1,2,5-oxadiazol-3-amine [ANAF]

7.5.1 General Information

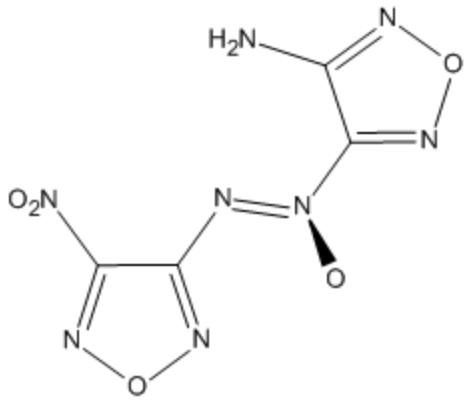

Figure 3: ANAF

7.5.2 Toxicology Data

7.5.2.1 Oral

No experimental data were found. The TOPKAT modeling predicts a rat oral LD_{50} of 1800 mg/kg at high confidence. The chronic LOAEL is predicted to be 41.0 mg/kg at high confidence. This predicted level of toxicity corresponds to an assessment of Moderate acute oral toxicity.

7.5.2.2 Inhalation

No experimental data were found. The TOPKAT modeling predicts a rat inhalation LC_{50} of 1.4 x 10^{-3} g/m^3-hour with low confidence. This predicted level of toxicity corresponds to an assessment of High for inhalation toxicity, and Category 1 in the GHS system. These characterizations may be the result of a poor predictive capability of the QSAR systems.

7.5.2.3 Dermal

No experimental data were found. The TOPKAT modeling predicts this compound will not be a skin irritant; however, it is predicted to be a severe skin sensitizer at low confidence.

7.5.2.4 Ocular

No experimental data were found. TOPKAT modeling suggests ANAF will be a mild ocular irritant at low confidence.

7.5.2.5 Development and Reproduction

No experimental data were found. The TOPKAT modeling predicts ANAF is unlikely to be a developmental or reproductive toxicant, at low confidence.

7.5.2.6 Genotoxicity

No experimental data were found. The TOPKAT modeling predicts ANAF will be mutagenic in the Ames test at high confidence.

7.5.2.7 Carcinogenicity

No experimental data were found. The TOPKAT modeling is mixed but suggests ANAF may be a weak carcinogen.

7.5.2.8 Ecotoxicology

7.5.2.8.1 Fate and Transport

With an estimated aqueous solubility of 7.57×10^5 mg/L and a low K_{OC} of 0.02, ANAF is expected to have a significant ability to migrate through ground water and may be a threat to surface and drinking water. The low vapor pressure and Henry's Law Constant indicate ANAF will not be volatile, and will be present in the atmosphere only in particulate form. Because of the very low vapor pressure, potential inhalation exposures are anticipated to be due to inhalation of particulates, not inhalation of vapor. The bioconcentration factor is low, so accumulation in the food chain is not anticipated.

7.5.2.8.2 Ecotoxicity

No experimental data were found.

The TOPKAT modeling predicts an EC_{50} for ANAF in *Daphnia* of 0.56 mg/L, corresponding to moderate toxicity. The TOPKAT was unable to make a prediction for fathead minnow due to lack of a suitable model.

The ECOSAR made predictions for ANAF using both the aromatic amine and neutral organic models. The aromatic amine model predicts the LC_{50} values for fish will exceed the solubility of the compound, but the 48-hour LC_{50} for *Daphnia* is predicted to be 6.3 mg/L, and the 96-hour

EC_{50} for green algae is predicted to be 18.5 mg/L, corresponding to low toxicity in both test species. Neutral organics toxicity predictions were all solubility-limited.

7.5.2.8.3 Degradation/Treatment

No experimental data were found. The EPI Suites predicts ANAF will not be readily biodegradable, with persistence in the environment for weeks to months, and removal by wastewater treatment facilities is predicted to be poor (<2 percent).

7.6 Azobistriazole (AzTA)

7.6.1 General Information

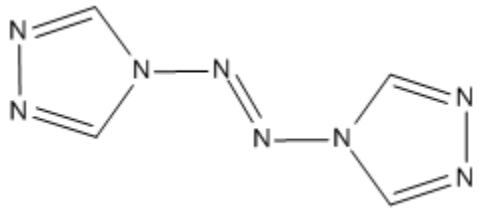

Figure 4: AzTA

7.6.2 Toxicology Data

7.6.2.1 Oral

No experimental data were found. The TOPKAT modeling predicts an oral LD_{50} in rats of 7.7 g/kg at high confidence. The chronic LOAEL is predicted to be 494.7 mg/kg-day at low confidence. This predicted level of toxicity corresponds to an assessment of Low acute oral toxicity.

7.6.2.2 Inhalation

No experimental data were found. The TOPKAT modeling predicts an inhalation LC_{50} in rats of 3.1 g/m^3-hour at high confidence. This predicted level of toxicity corresponds to an assessment of High for inhalation toxicity, and Category 3 in the GHS system.

7.6.2.3 Dermal

No experimental data were found. The TOPKAT modeling predicts AzTA will be neither a dermal irritant nor sensitizer.

7.6.2.4 Ocular

No experimental data were found. The TOPKAT modeling predicts AzTA is possibly a moderate ocular irritant.

7.6.2.5 Development and Reproduction

No experimental data were found. The TOPKAT modeling predicts AzTA will not be a developmental or reproductive toxicant.

7.6.2.6 Genotoxicity

No experimental data were found. The TOPKAT predicts AzTA will be mutagenic in the Ames test at high confidence.

7.6.2.7 Carcinogenicity

No experimental data were found. The TOPKAT modeling predicts AzTA is likely to be carcinogenic.

7.6.2.8 Ecotoxicology

7.6.2.8.1 Fate and Transport

With an estimated aqueous solubility of 1.86×10^4 mg/L and a log K_{OC} of 0.65, AzTA is expected to have a significant ability to migrate through ground water and may be a threat to surface and drinking water. The low vapor pressure and Henry's Law Constant indicate that AzTA will not be volatile, and will be present in the atmosphere only in particulate form. The low log K_{OW} indicates a low tendency to bioaccumulate or bioconcentrate.

7.6.2.8.2 Ecotoxicity

No experimental data were found. The TOPKAT modeling of AzTA predicts an EC_{50} in *Daphnia* of 27.6 mg/L. A prediction for fathead minnow could not be made due to lack of a suitable model.

EPA's ECOSAR program models AzTA as a non-fused triazole. The 96-hour EC_{50} for green algae is 419.68 mg/L, the 48-hour LC_{50} in *Daphnia* is 215.12 mg/L, and the 96-hour LC_{50} in fish is 23,320 mg/L (no effect at saturation).

7.6.2.8.3 Degradation/Treatment

No experimental data were found. The EPI Suite modeling predicts AzTA will not be readily biodegradable, with environmental persistence of weeks. AzTA is also predicted to be poorly removed (less than 2 percent) by wastewater treatment plants.

7.7 Ammonium dinitro (4-nitro-2*H*-1,2,3-triazol-2-yl)methanide [AGDNM NT123]

7.7.1 General Information

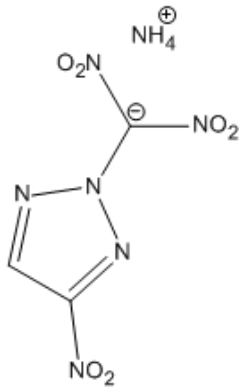

Figure 5. AGDNM NT123

7.7.2 Toxicology Data

7.7.2.1 Oral

No experimental data were found. The TOPKAT modeling of AGDNM NT123 predicts an oral LD_{50} in rats of 865.4 mg/kg at high confidence. The chronic LOAEL is predicted to be 17.6 mg/kg-day at high confidence. This predicted level of toxicity corresponds to an assessment of Moderate acute oral toxicity.

7.7.2.2 Inhalation

No experimental data were found. The TOPKAT modeling of AGDNM NT123 predicts an inhalation LC_{50} of 5.8 g/m^3-hour at high confidence. This predicted level of toxicity corresponds to an assessment of Low for inhalation toxicity, and Category 3 in the GHS system.

7.7.2.3 Dermal

No experimental data were found. The TOPKAT modeling predicts AGDNM NT123 is unlikely to be an irritant, but may be a sensitizer at high confidence.

7.7.2.4 Ocular

No experimental data were found. The TOPKAT modeling predicts AGDNM NT123 may be a severe ocular irritant at low confidence.

7.7.2.5 Development and Reproduction

No experimental data were found. The TOPKAT modeling predicts AGDNM NT123 will not be a developmental or reproductive toxicant at high confidence.

7.7.2.6 Genotoxicity

No experimental data were found. The TOPKAT modeling predicts AGDNM NT123 will not be mutagenic in the Ames assay at high confidence.

7.7.2.7 Carcinogenicity

No experimental data were found. The TOPKAT modeling for carcinogenicity is unlikely to be carcinogenic at moderate confidence.

7.7.2.8 Ecotoxicology

7.7.2.8.1 Fate and Transport

Based upon an estimated solubility of 2.52×10^5 mg/L and a log K_{OC} of 0.629, AGDNM NT123 is expected to have a significant ability to migrate through ground water and may be threat to surface or drinking water. The low vapor pressure estimate and Henry's Law constant indicate that any AGNDM NT123 present in the atmosphere will exist in particulate form. The low log K_{OW} indicates a low tendency to bioconcentrate or bioaccumulate.

7.7.2.8.2 Ecotoxicity

No experimental data were found. The TOPKAT modeling of AGDNM NT123 predicts an EC_{50} in *Daphnia* of 121.7 mg/L, but was unable to make a prediction for fathead minnow due to lack of a suitable model.

ECOSAR models AGDNM NT123 as both a non-fused triazole and as a neutral organic. The triazole model predicts a 96-hour EC_{50} in green algae of 228.0 mg/L, a 48-hour LC_{50} in *Daphnia* of 3.163×10^4 mg/L, and a 96-hour LC_{50} in fish of 6135 mg/L. The corresponding values in the neutral organic model are 5604 mg/L, 5.369×10^4 mg/L and 1.41×10^5 mg/L.

7.7.2.8.3 Degradation/Treatment

No experimental data were found. The EPI Suite modeling predicts AGDNM NT123 will not be readily biodegradable, with persistence in the environment of weeks to months. The AGDNM NT123 is also predicted to be poorly removed (less than 2 percent) by wastewater treatment processes.

7.8 Ammonium dinitro (3-nitro-1*H*-1,2,4-triazol-1-yl)methanide [AGDNM NT124]

7.8.1 General Information

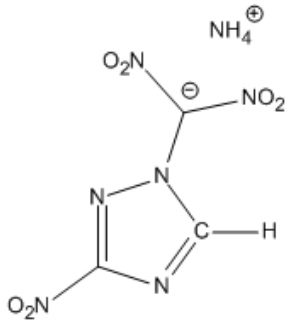

Fig. 6. AGDNM NT124

7.8.2 Toxicology Data

7.8.2.1 Oral

No experimental data were found. The TOPKAT modeling predicts an oral LD_{50} in rats of 1.0 g/kg at high confidence. The chronic LOAEL is predicted to be 17.6 mg/kg-day at high confidence. This predicted level of toxicity corresponds to an assessment of Moderate acute oral toxicity.

7.8.2.2 Inhalation

No experimental data were found. The TOPKAT modeling predicts an inhalation LC_{50} of 4.9 g/m^3-hour at high confidence. This predicted level of toxicity corresponds to an assessment of Low for inhalation toxicity, and Category 3 in the GHS system.

7.8.2.3 Dermal

No experimental data were found. The TOPKAT modeling predicts AGDNM NT124 is unlikely to be a skin irritant, but is probably a sensitizer at moderate confidence.

7.8.2.4 Ocular

No experimental data were found. The TOPKAT modeling predicts AGDNM NT124 is likely to be an ocular irritant at low confidence.

7.8.2.5 Development and Reproduction

No experimental data were found. The TOPKAT modeling predicts AGDNM NT124 will not be a developmental or reproductive toxicant at high confidence.

7.8.2.6 Genotoxicity

No experimental data were found. The TOPKAT modeling predicts AGDNM NT124 will not be mutagenic in the Ames assay at high confidence.

7.8.2.7 Carcinogenicity

No experimental data were found. The TOPKAT modeling of AGDNM NT124 for carcinogenicity is indeterminate.

7.8.2.8 Ecotoxicology

7.8.2.8.1 Fate and Transport

With an estimated aqueous solubility of 1×10^6 (default limit) and log K_{OC} of 0.21, AGDNM NT124 is expected to have a significant ability to migrate through ground water, and may be a threat to surface and drinking water. The vapor pressure and Henry's Law constant indicate AGDNM NT124 may exist in the atmosphere as a vapor-particulate mix. The log K_{OW} indicates a low tendency to bioconcentrate.

7.8.2.8.2 Ecotoxicity

No experimental data were found. The TOPKAT modeling predicts an EC_{50} in *Daphnia* of 121.7 mg/L; a prediction could not be made for fathead minnows due to lack of a suitable model.

The ECOSAR models AGDNM NT124 as both a non-fused triazole and as a neutral organic. In the triazole model, the 96-hour EC_{50} in green algae is predicted to be 487.8 mg/L, the 48-hour LC_{50} in *Daphnia* is predicted to be 1.1×10^5 mg/L, and the 96-hour LC_{50} in fish is predicted to be 1.79×10^4 mg/L. The corresponding values in the neutral organic model are 1.63×10^4 mg/L, 2.12×10^5 mg/L, and 6.12×10^5 mg/L.

7.8.2.8.3 Degradation/Treatment

No experimental data were found. The EPI Suite model predicts AGDNM NT124 will not be readily biodegradable, with persistence in the environment for weeks to months. The AGDNM NT124 is also predicted to be poorly removed (less than 2 percent) by wastewater treatment processes.

7.9 Ammonium 5-nitro-2H-tetraol-2-olate [AONT]

7.9.1 General Information

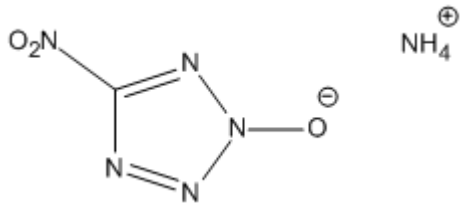

Figure 7. AONT

7.9.2 Toxicology Data

7.9.2.1 Oral

No experimental data were found. The TOPKAT predicts an oral LD_{50} in rats of 645.8 mg/kg at high confidence. The chronic LOAEL is predicted to be 36.0 mg/kg-day at low confidence. This predicted level of toxicity corresponds to an assessment of Moderate acute oral toxicity.

7.9.2.2 Inhalation

No experimental data were found. The TOPKAT predicts an inhalation LC_{50} in rats of 6.4 g/m^3-hour at moderate confidence. This predicted level of toxicity corresponds to an assessment of Low for inhalation toxicity, and Category 3 in the GHS system.

7.9.2.3 Dermal

No experimental data were found. The TOPKAT predicts AONT to be a possible skin sensitizer at moderate confidence.

7.9.2.4 Ocular

No experimental data were found. The TOPKAT predicts AONT to possibly be a severe ocular irritant.

7.9.2.5 Development and Reproduction

No experimental data were found. The TOPKAT predicts AONT will not be a developmental or reproductive toxicant at high confidence.

7.9.2.6 Genotoxicity

No experimental data were found. The TOPKAT predicts AONT will be mutagenic in the Ames assay at high confidence.

7.9.2.7 Carcinogenicity

No experimental data were found. The TOPKAT modeling of carcinogenicity is indeterminate.

7.9.2.8 Ecotoxicology

7.9.2.8.1 Fate and Transport

With an aqueous solubility estimated at 1.5×10^5 mg/L and a predicted log K_{OC} of 0.145, AONT is expected to have a significant ability to migrate through ground water and may be a threat to surface or drinking water. The low vapor pressure and Henry's Law constant suggest that in the atmosphere, AONT will exist as a vapor-particulate mix. The value of the log K_{OW} indicates a low tendency to bioconcentrate.

7.9.2.8.2 Ecotoxicity

No experimental data were found. The TOPKAT predicts an EC_{50} in *Daphnia* of 7.7 mg/L at low confidence; a prediction could not be made for fish due to lack of a suitable model.

The ECOSAR models AONT in the neutral organics class, and predicts a 96-hour EC_{50} for green algae of 1.24×10^4 mg/L, a 48-hour LC_{50} in *Daphnia* of 1.65×10^5 mg/L, and a 96-hour LC_{50} in fish of 5.48×10^5 mg/L. The last two values are expected to exceed the solubility limit of the compound.

7.9.2.8.3 Degradation/Treatment

No experimental data were found. The EPI Suite modeling predicts AONT will not be readily biodegradable, with persistence in the environment of weeks to months. The AONT is also predicted to be poorly removed (less than 2 percent) by wastewater treatment plants.

7.10 1,4-Dinitroglycoluril [DINGU/DNGU]

7.10.1 General Information

The systematic name for this compound is tetrahydro-1,4-dinitroimidazo[4,5-d]imidazole-2,5-(1H,3H)-dione. A second common short name is DNGU. DINGU is a class 1.1d explosive.

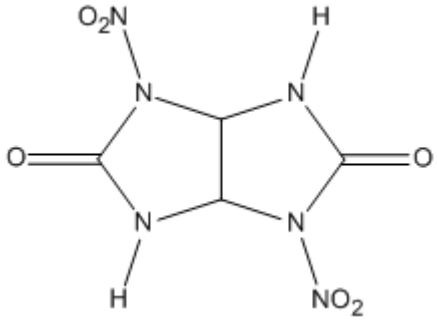

Fig. 8. DINGU

7.10.2 Toxicology Data

No experimental toxicological data were found for this compound; all estimates below are based on QSAR modeling.

7.10.2.1 Oral

The TOPKAT modeling predicts an oral LD_{50} in rats of 43.1 mg/kg at high confidence. A chronic LOAEL could not be predicted because the value calculated was greater than the calculated LD_{50}. This predicted level of toxicity corresponds to an assessment of Moderate acute oral toxicity.

7.10.2.2 Inhalation

The TOPKAT modeling predicts an inhalation LC_{50} in rats of 0.39 g/m^3-hour at low confidence. This predicted level of toxicity corresponds to an assessment of Moderate for inhalation toxicity, and Category 1 in the GHS system.

7.10.2.3 Dermal

The TOPKAT modeling predicts DINGU to be a probable skin irritant, but unlikely sensitizer, at low confidence.

7.10.2.4 Ocular

The TOPKAT modeling predicts DINGU to be a possible mild ocular irritant.

7.10.2.5 Development and Reproduction

The TOPKAT modeling predicts DINGU to be a developmental or reproductive toxicant at low confidence.

7.10.2.6 Genotoxicity

The TOPKAT modeling predicts DINGU will not be mutagenic in the Ames assay, but at low confidence.

7.10.2.7 Carcinogenicity

The TOPKAT modeling for carcinogenicity is indeterminate overall, but models with higher levels of confidence predict DINGU is a likely carcinogen.

7.10.2.8 Ecotoxicology

7.10.2.8.1 Fate and transport

With high aqueous solubility and a low log K_{OC}, DINGU is likely to represent a ground water transport risk, and may pose a threat to surface and drinking water. Volatility from water is expected to be negligible. The DINGU is expected to exist in the atmosphere only in particulate form, but would be readily degradable by hydroxyl radicals in the atmosphere. With a log bioconcentration factor (BCF) of less than 0.5 (EPI Suite 4.1 prediction), bioaccumulation is not expected.

7.10.2.8.2 Ecotoxicity

No experimental data were found. The TOPKAT modeling predicts an EC_{50} in *Daphnia* of >1000 g/L, and an LC_{50} in fish of 5200 mg/L, at low and moderate confidence, respectively.

The EPA's EPI Suite 4.1 program models DINGU as a neutral organic, with a 96-hour EC_{50} in green algae of 6.78×10^6 mg/L, a 48-hour LC_{50} in *Daphnia* of 1.47×10^7, and a 96-hour LC_{50} in fish of 4.45×10^7 mg/L, all of which are expected to be greater than the solubility of DINGU.

7.10.2.8.3 Degradation/Treatment

The EPA's EPI Suite 4.1 program predicts DINGU will not be readily biodegradable in the environment, with persistence of weeks to months. Removal by physical processes in standard waste water treatment plants is expected to be minimal (less than 2 percent).

8 Discussion

8.1 Environmental Impact

The proposed compounds have fate and toxicity aspects that are variable, many have profiles that suggest they would result in lower risk from environmental use and releases. Acute toxicity is low for many compounds, and preliminary information suggests that impact on species at the base of the food chain would be minimal. For several compounds, there may also be concern over mutagenicity and developmental effects. There is some concern over environmental persistence, ground and surface water transport; however, these data were modeled and uncertain. Please see specific information for each compound as presented below.

8.2 Compound Summaries

8.2.1 MBANF

The MBANF has been tentatively selected for further development. *In vitro* data have been obtained for estimation of acute toxicity, mutagenicity, and aquatic toxicity. Additional information on basic experimental physical property data are needed to validate model predictions for this compound, especially octanol-water partition coefficient and solubility data. The MBANF is projected to have moderate-high acute toxicity, and moderate aquatic toxicity. The Ames testing for mutagenicity is negative. Additional testing, to include biodegradation testing, may be indicated pending the outcome of these preliminary assays and the prospects for future development of this compound. If this compound is selected for advanced development, *in vivo* determination of acute toxicity is recommended.

8.2.2 DNFOA

The DNFOA is a candidate for advanced development. *In vitro* testing indicates it is somewhat less acutely toxic than MBANF, with lower aquatic toxicity. However, data gaps and areas of uncertainty for this compound remain significant due to the lack of experimental data and low confidence in the modeling predictions. If this compound is selected for advanced development, *in vivo* determination of acute toxicity is indicated, as well as biodegradation testing and determination of basic physical-chemical properties.

8.2.3 ANAF

Basic experimental physical-chemical property data are needed to validate model predictions for ANAF, especially octanol-water partition coefficient and solubility data. Recommended toxicology tests include an Ames mutagenicity test, neutral red uptake (acute toxicity), and the Microtox assay (aquatic toxicity). Additional testing, to include biodegradation testing, may be indicated pending the outcome of these preliminary assays and the prospects for future development of this compound.

8.2.4 AzTA

Toxicity modeling of AzTA suggests potential for adverse effects from exposure would be low by the oral and inhalation routes, and ecotoxicity also appears to be low. Modeling indicates developmental and reproductive toxicity is also low, however there is an indication that AzTA is mutagenic in the Ames test, and is quite possibly carcinogenic. Recommend at an Ames test and corresponding mammalian mutagenicity testing be conducted *in vitro* to assess carcinogenic potential.

8.2.5 AGDNM NT123

Modeling for oral and inhalation is suggestive that toxicity would appear to be relatively low for this compound. The primary concerns appear to be transport in ground and surface water and occupational health concerns relating to dermal and ocular toxicity. Experimental data on physical properties and a basic battery of *in vitro* testing should be conducted if this compound is selected for further development. Additional testing may be required as development proceeds.

8.2.6 AGDNM NT124

Oral and inhalation toxicity modeling suggests risks are relatively low for this compound. The primary concern would appear to be possible transport in ground and surface water and occupational health concerns relating to dermal and ocular toxicity. Experimental data on physical properties and a basic battery of *in vitro* testing should be conducted if this compound is selected for further development. Additional testing may be required as development proceeds.

8.2.7 AONT

Oral and inhalation toxicity are predicted to be low; the primary concerns would appear to be in the occupational health area where skin sensitization is a possibility. Determination of mutagenicity in the Ames test would appear to be the most urgent testing need, but a standard *in vitro* testing battery is suggested.

8.2.8 DINGU

Only QSAR modeling predictions are available for this compound. Oral toxicity appears to be high, while inhalation toxicity is moderate. There is a moderate risk for dermal and ocular effects in occupational exposures, but DINGU is not expected to be a dermal sensitizer. Ecotoxicity is low, but environmental persistence is long at weeks to months, with little prospect of biodegradation. Carcinogenicity is unknown.

A basic *in vitro* screen of Ames test, neutral red uptake, and Microtox assay are recommended. In addition to standard acute toxicity tests, follow-on *in vivo* testing should include a micronucleus test to help determine mutagenic effects in mammalian systems. A developmental/reproductive toxicity assessment *in vivo* may also be necessary at some point in the future.

8.3 Regulations and Standards

No regulations or standards were found for any of the compounds considered in his report.

8.4 Summary and conclusions

Toxicity modeling for all compounds under consideration suggests they are less toxic than RDX, yet considerable uncertainty exists. While inhalation toxicity appears to be high for MBANF, DNFOA, and ANAF, this may be due to poor fit to the QSAR models as these values appear to not correlate to the projected oral toxicity. Most of the compounds under consideration are potentially dermal or ocular hazards, which could pose a problem in the manufacturing environment, but this could be addressed by engineering controls or personal protective equipment. Many of the compounds are projected to be mutagenic.

In terms of environmental toxicity, these compounds are generally predicted to be less toxic than RDX. The MBANF, DNFOA, and ANAF are expected to present only a moderate ability to migrate through ground water, while the others present a significant transport threat to ground and surface water. Bioaccumulation is expected to be low for all compounds, but biodegradation is predicted to be poor, with persistence in the environment lasting weeks to months.

9 Recommendations

In accordance with the principles of ASTM E2552, initial testing should be rapid and low cost as appropriate to the stage of development. Recommendations for initial *in vitro* testing are outlined in the summary of each compound.

10 Point of Contact

The Point of Contact for this report is Dr. William Eck, e-mail: usarmy.apg.medcom-phc.mbx.tox-info@mail.mil, phone: 410-436-3980.

Table 3. List of Physical and Chemical Properties

Compound	MW	bp (°C)	Aqueous solubility (mg/L)	log K_{ow}	log K_{oc}	Henry's Law Constant (atm-cubic meter per mole (m^3/mol) @ 25ºC	Vapor Pressure (mmHg) @ 25°C
MBANF[1]	272.14	418.45	278	0.12	2.14	1.073E-10	8.32E-10
DNFOA[1]	314.13	579.14	308.4	-0.21	1.54	1.249E-15	9.32E-13
ANAF[1]	242.11	584.0[2]	298.3	0.795[2]	2.23	3.95E-14	1.26E-13[2]
AzTA[1]	164.13	298.09	1.86E+04	-1.40	0.65	3.97E-09	3.41E-04
AGDNM NT123[1,3]	235.12	359.73	2.52E+05	-1.46	0.63	7.54E-12	6.44E-06
AGDNM NT124[1,3]	235.12	359.73	1E+06	-2.21	0.21	1.85E-12	6.44E-06
AONT	131.05	271.54	1.5E+05	-2.24	0.14	6.17E-10	5.37E-04
DINGU	232.11	470.3	3000[2]	-1.25[2] -3.98	0.66[2] -0.95	1.43E-17	2.26E-09
RDX*	222.15	ND	130[4]	1.6[4]	ND	2.08E-08[4]	8.02E-06[4]

*RDX data are included for purpose of comparison
Notes: dec=decomposes; n/a=not applicable
mmHg - millimeters of mercury
1=Values derived from EPI Suite 4.1 modeling unless otherwise indicated.
2=SciFinder value.
3=Values based upon the neutral form of the anion.
4=ChemIDPlusLite, 2011.

Table 4. Toxicity Data

Compound	Acute Oral (mg/kg)	Chronic Oral LOAEL (mg/kg-d)	Inhalation LC_{50} (g/m^3-h)	Dermal	Ocular	Mutagenicity	Carcinogenicity
MBANF[1]	2000	11.4	3.1E-03	Possible sensitizer	Moderate irritant	Negative[2]	Possible weak carcinogen
DNFOA[1]	124.6	1.1	7.2E-03	Possible sensitizer	Likely severe irritant	Negative[3]	Indeterminate
ANAF[1]	1800	41.0	1.4E-03	Possible sensitizer	Possible mild irritant	Positive	Possibly weakly carcinogenic
AzTA[1]	7800	494.7	3.1	Negative	Possible moderate irritant	Positive	Positive
AGDNM NT123[1]	865.4	17.6	5.8	Possible sensitizer	Possible severe irritant	Negative	Probable negative
AGDNM NT124[1]	1000	17.6	4.9	Probable sensitizer	Possible irritant	Negative	Indeterminate
AONT[1]	645.8	36.0	6.4	Possible sensitizer	Probable severe irritant	Positive	Indeterminate
DINGU	43.1	nd	0.393	Probable irritant	Possible mild irritant	Negative	Possible
RDX*	59(mouse) 100(rat) 500(rabbit)	0.3 (NOAEL)	ND (Lethal effects in swine)	Negative	Irritant	Negative	Possible

Notes:
1=All predictions based upon TOPKAT modeling unless otherwise indicated.
2=USAPHC, 2013
3=USAPHC, 2012.

Table 5. Toxicity Assessment

Compound	Oral	Inhalation	Dermal	Ocular	Carcinogenicity	Comments
MBANF	Low-Mod	High	Mod	Mod	Unk	
DNFOA	Mod	High	Mod	Mod-High	Unk	
ANAF	Mod	High	Mod	Low	Low-Mod	
AzTA	Low	Low	Low	Mod	High	
AGDNM NT123	Mod	Low	Mod	Mod	Low	
AGDNM NT124	Mod	Low	Mod	Mod	Unk	
AONT	Mod	Low	Mod	Mod	Unk	
DINGU	High	Mod	Mod	Low	Mod	
RDX*	Mod	Unk	Low	High	Low-Mod	

Evaluations are based on weight of evidence, physicochemical properties and professional judgment using criteria set forth in Table 2.

Table 6. Ecotoxicity Assessment

Compound	Aquatic	Invertebrate	Plants	Mammalian	Avian	Comments
MBANF	Mod	Low	Unk	Low-Mod	Unk	
DNFOA	Low	Low	Unk	Mod	Unk	
ANAF	Low	Low-Mod	Unk	Low-Mod	Unk	
AzTA	Low	Low	Unk	Low	Unk	
AGDNM NT123	Low	Low	Unk	Mod	Unk	
AGDNM NT124	Low	Low	Unk	Mod	Unk	
AONT	Low	Low	Unk	Mod	Unk	
DINGU	Low	Low	Unk	High	Unk	Persistent
RDX*	Low	Low	Low	High	High	

Evaluations are based on weight of evidence and professional judgment using criteria set forth in Table 2.

Appendix A

References

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Appendix B:
Globally Harmonized System

The acronym GHS is the acronym for the Globally Harmonized System of Classification and Labeling of Chemicals. The GHS attempts to establish international consensus for defining health, physical, and environmental hazards of chemicals; creating a classification process for comparison with defined hazard criteria; and communicating hazard information and protective measures on labels and Safety Data Sheets (SDS), formerly known as Material Safety Data Sheets (MSDS). The GHS attempts to reduce differences among levels of protection for workers established by the different countries and reduce regulatory burden and barriers to commerce while establishing consistent standards for classification. The GHS is the result of an international mandate adopted in the 1992 United Conference on Environment and Development, often called the “Earth Summit”. The harmonization and classification of chemicals was one of six program areas endorsed by the U.N. General Assembly to strengthen International efforts
in the environmentally sound management of chemicals.

While there are several aspects of the GHS, the one most important area for our purposes is classification of chemicals into various hazard categories based upon their effects and the route of exposure. Tabular extracts of the criteria for acute toxicity (both oral and inhalation), dermal, and ocular effects are included below. More information can be found in the original source (OSHA 2012).

Table B-1. GHS Acute Toxicity

	Category 1	Category 2	Category 3	Category 4	Category 5
Oral (mg/kg)	≤5	>5 ≤50	>50 ≤300	>300 ≤2000	Criteria: -Anticipated LD50 between 2000 and 5000 mg/kg -Indication of significant effects in humans. -Any mortality in Category 4 -Significant clinical signs in Category 4 -Indications from other studies. *If assignment to a more hazardous class is not warranted.
Dermal (mg/kg)	≤50	>50 ≤200	>200 ≤1000	>1000 ≤2000	
Gases (ppm)	≤100	>100 ≤500	>500 ≤2500	>2500 ≤5000	
Vapors (mg/L)	≤0.5	>0.5 ≤2.0	>2.0 ≤10	>10 ≤20	
Dusts & Mists (mg/L)	≤0.05	>0.05 ≤0.5	>0.5 ≤1.0	>1.0 ≤5	

Table B-2. GHS Skin Corrosion/Irritation

Skin Corrosion Category 1			Skin Irritation Category 2	Mild Skin Irritation Category 3
Destruction of dermal tissue; visible necrosis in at least one animal.			Reversible adverse effects in dermal tissue Draize score: ≥ 2.3, <4.0, or persistent inflammation	Reversible adverse effects in dermal tissue Draize score: ≥ 1.5, <2.3
Subcategory 1A Exposure < 3 minutes Observation < 1 hour	Subcategory 1B Exposure < 1 hour Observation < 14 days	Subcategory 1C Exposure < 4 hours Observation < 14 days		

Table B-3: GHS Eye Effects

<table>
<tr><td>Category 1
Serious Eye Damage</td><td colspan="2">Category 2
Eye Irritation</td></tr>
<tr><td rowspan="2">Irreversible damage 21 days after exposure

Draize score:
Corneal opacity ≥ 3
Iritis ≥ 1.5</td><td colspan="2">Reversible adverse effects on cornea, iris, conjunctiva

Draize score:
Corneal opacity ≥ 1
Iritis > 1
Redness ≥ 2
Chemosis ≥ 2</td></tr>
<tr><td>Irritant
Subcategory 2A
Reversible in 21 days</td><td>Mild irritant
Subcategory 2B
Reversible in 7 days</td></tr>
</table>

Table B-4. GHS Acute and Chronic Aquatic Toxicity

<table>
<tr><td>Acute Category I
Acute toxicity ≤ 1.00 mg/L</td><td>Acute Category II
Acute toxicity > 1.00 but ≤10.0 mg/L</td><td colspan="2">Acute Category III
Acute toxicity > 10.0 but < 100 mg/L</td></tr>
<tr><td>Chronic Category I
Acute toxicity ≤ 1.00 mg/L and lack of rapid biodegradability and log Kow ≥ 4, unless BCF < 500.</td><td>Chronic Category II
Acute toxicity > 1.00 mg/L but ≤ 10.0 mg/L and lack of rapid biodegradability, and log Kow ≥ 4, unless BCF < 500 and unless chronic toxicity > 1 mg/L.</td><td>Chronic Category III
Acute toxicity > 10.0 mg/L but ≤ 100.0 mg/L and lack of rapid biodegradability and log Kow ≥ 4, unless BCF < 500 and unless chronic toxicity > 1 mg/L.</td><td>Chronic Category IV
Acute toxicity > 100.0 mg/L and lack of rapid biodegradability and log Kow ≥ 4, unless BCF < 500 and unless chronic toxicity > 1 mg/L.</td></tr>
</table>