EVALUATION OF A LOW TOXICITY RDX REPLACEMENT FOR MINIMUM SMOKE ROCKET PROPELLANT FORMULATIONS

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Technical Objective

First, an innovative tactical grain configuration, Exponent Modified Minimum Smoke (EMMS), will be used to eliminate the need for lead catalysts.

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 insensitive munitions (IM) requirements, and a reduction in toxicity compared to existing propellant ingredients. The key objectives are:

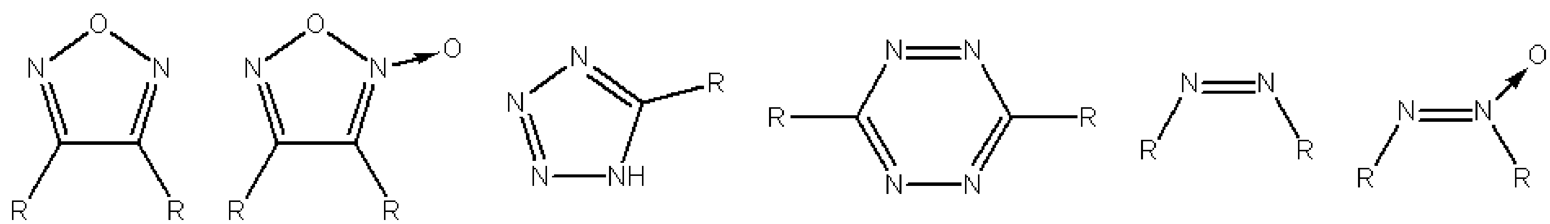
a) Demonstrate an RDX replacement with a reduction in toxicity, acceptable performance, and insensitivity,

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

RDX Replacement Candidates

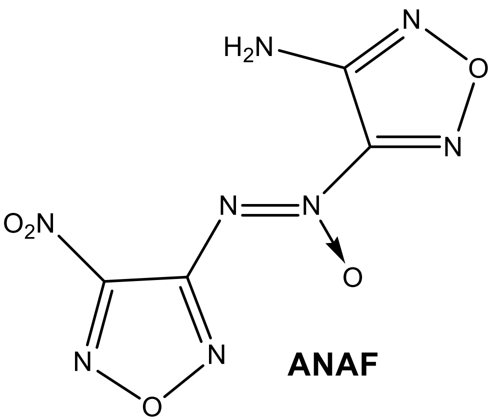
•For rocket propellant applications, density and heat of formation are paramount

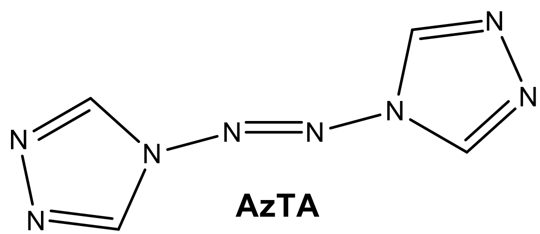
•Furazan, furoxan, tetrazole and tetrazine moieties have high predicted or measured heats of formation
•Heat of formation can be increased by addition of azo or azoxy bridges
•Multiple rings/macrocycles have shown increased thermal stability, decreased sensitivity
•Many of these materials have high predicted densities

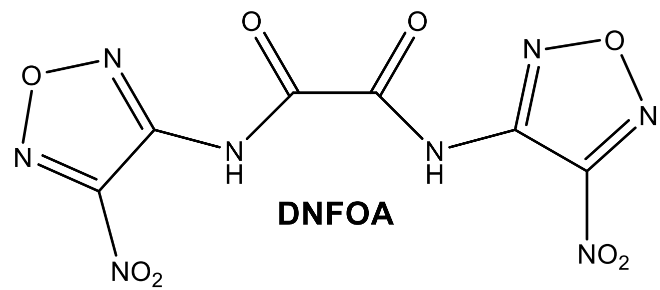


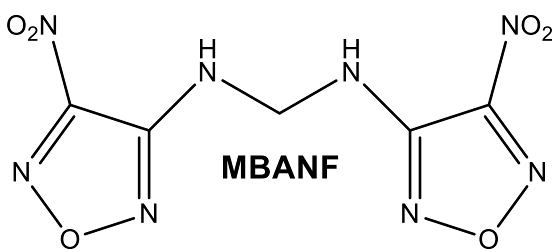
•DOE scientists have been making these molecules for DoD evaluation
•This library of compounds will be leveraged for this effort

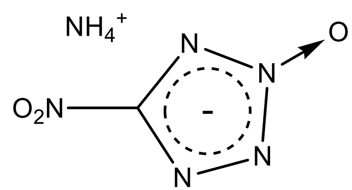
RDX Replacement Candidates

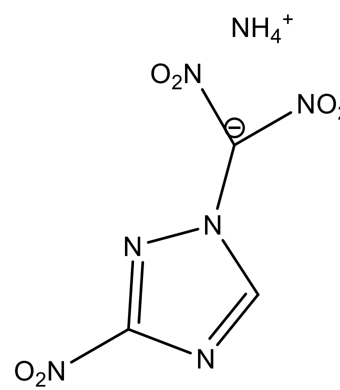

ANAF

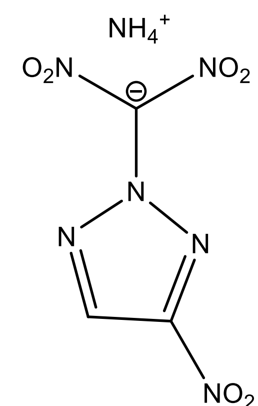

AzTA


DNFOA


MBANF


AONT


AGDNM NT124


AGDNM NT123

RDX Replacement Candidates

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
ADNM NT123	$C_3H_5N_7O_6$	235.12	0	---	1.8	---
ADNM NT124	$C_3H_5N_7O_6$	235.12	-35	---	1.7	---
AONT	$CH_4N_6O_3$	148.08	40	---	---	1.703

Baseline Propellant

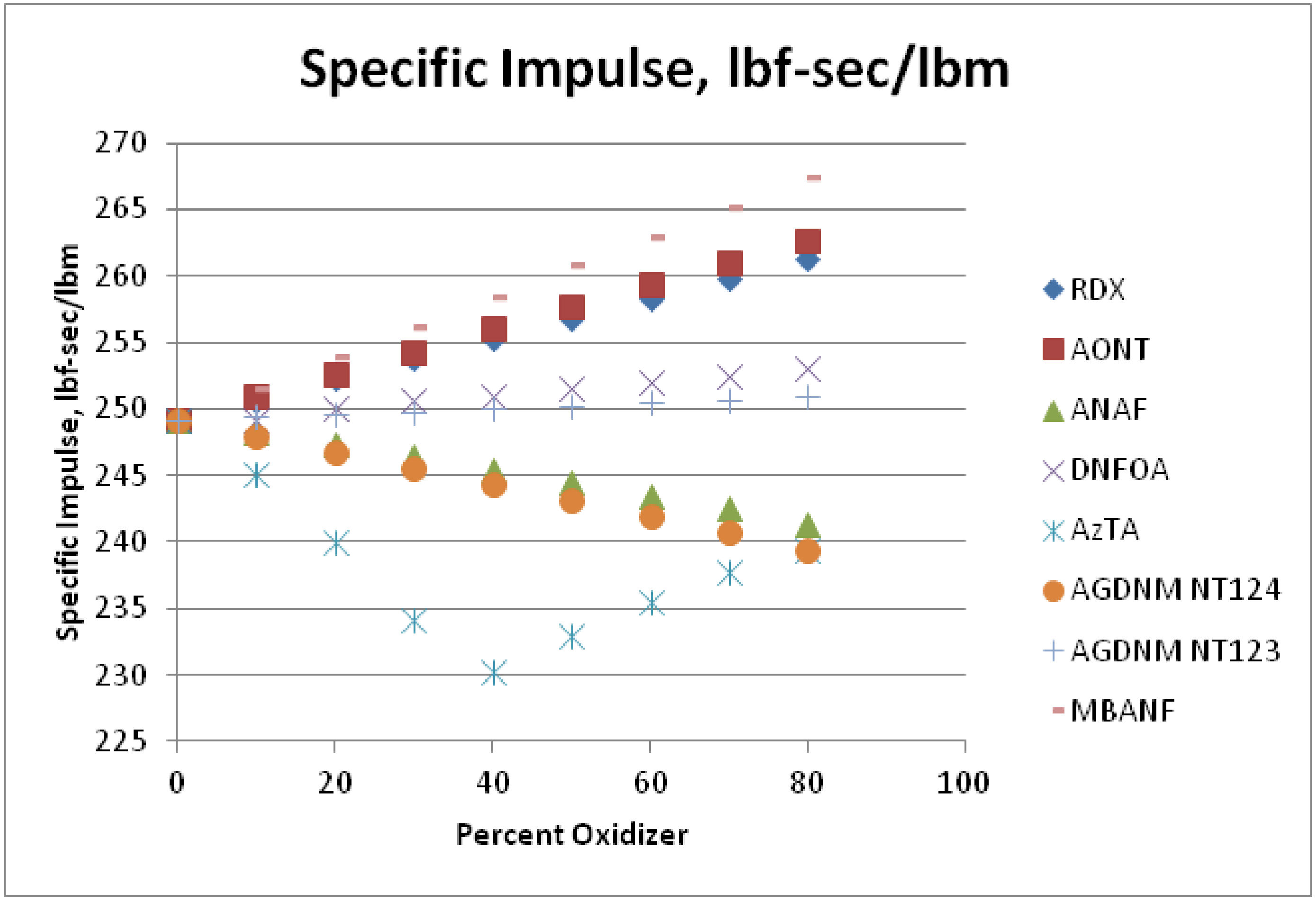
SOTA Minimum Smoke Propellant Characteristics

Catalyst Type	SOTA 1	SOTA 2
	lead citrate	lead oxide
Burn rate, in/s	0.35	0.35
Pressure exponent	0.3	0.45
Density (lb/in^3)	0.062	0.0614
I_{sp}	246	246
I_{vol}	15.3	15.1

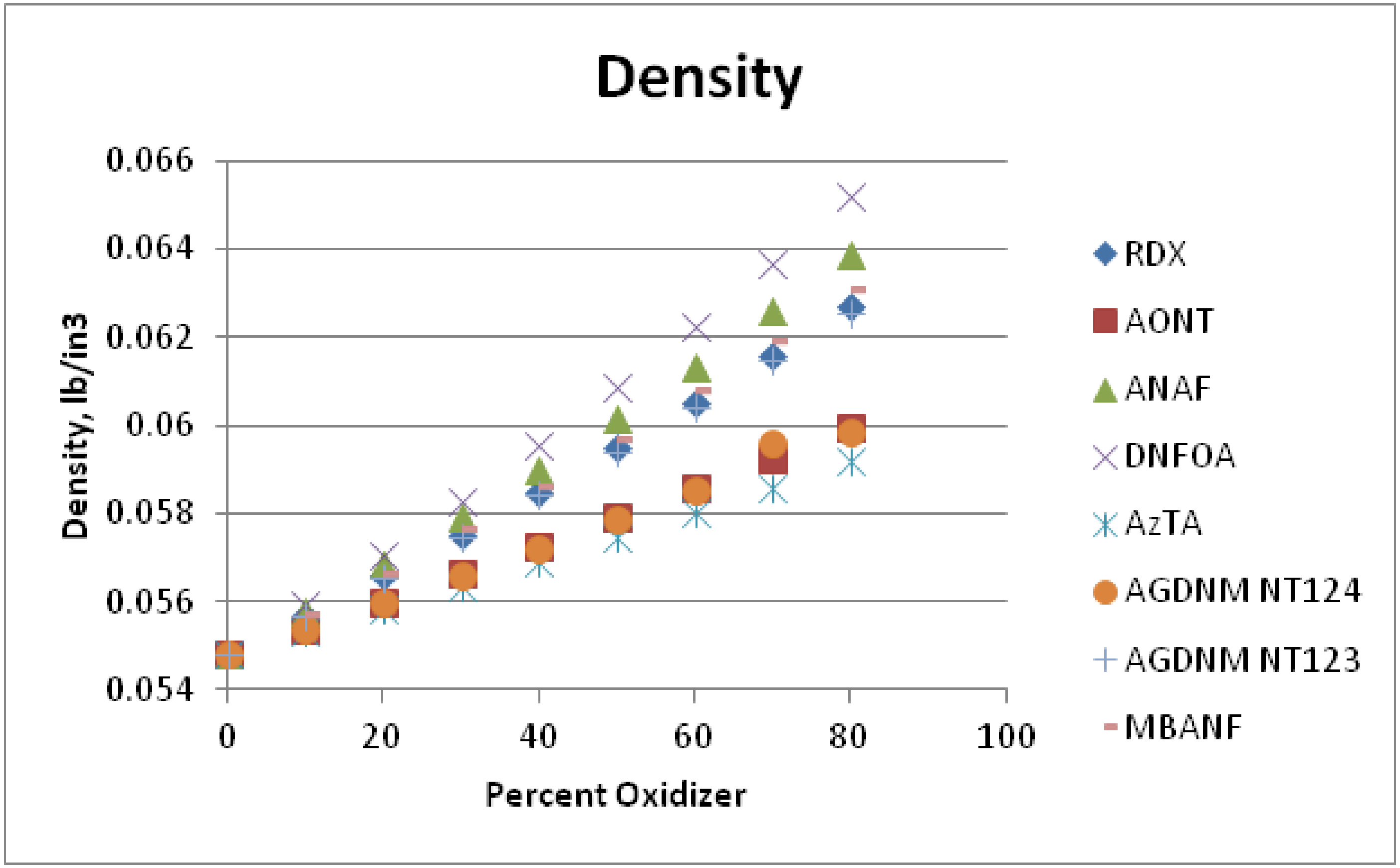
Representative Baseline Formulation

BTTN	17-20%
DEGDN	6.0-8.0%
NC	3.5-4.5%
MNA	0.75-1.5%
RDX	60-63%
Lead salt	2-7%
Carbon	0.4-1.0%
Zirconium carbide	0.9-1.1%
N-3200 curative	1.0-2.0%

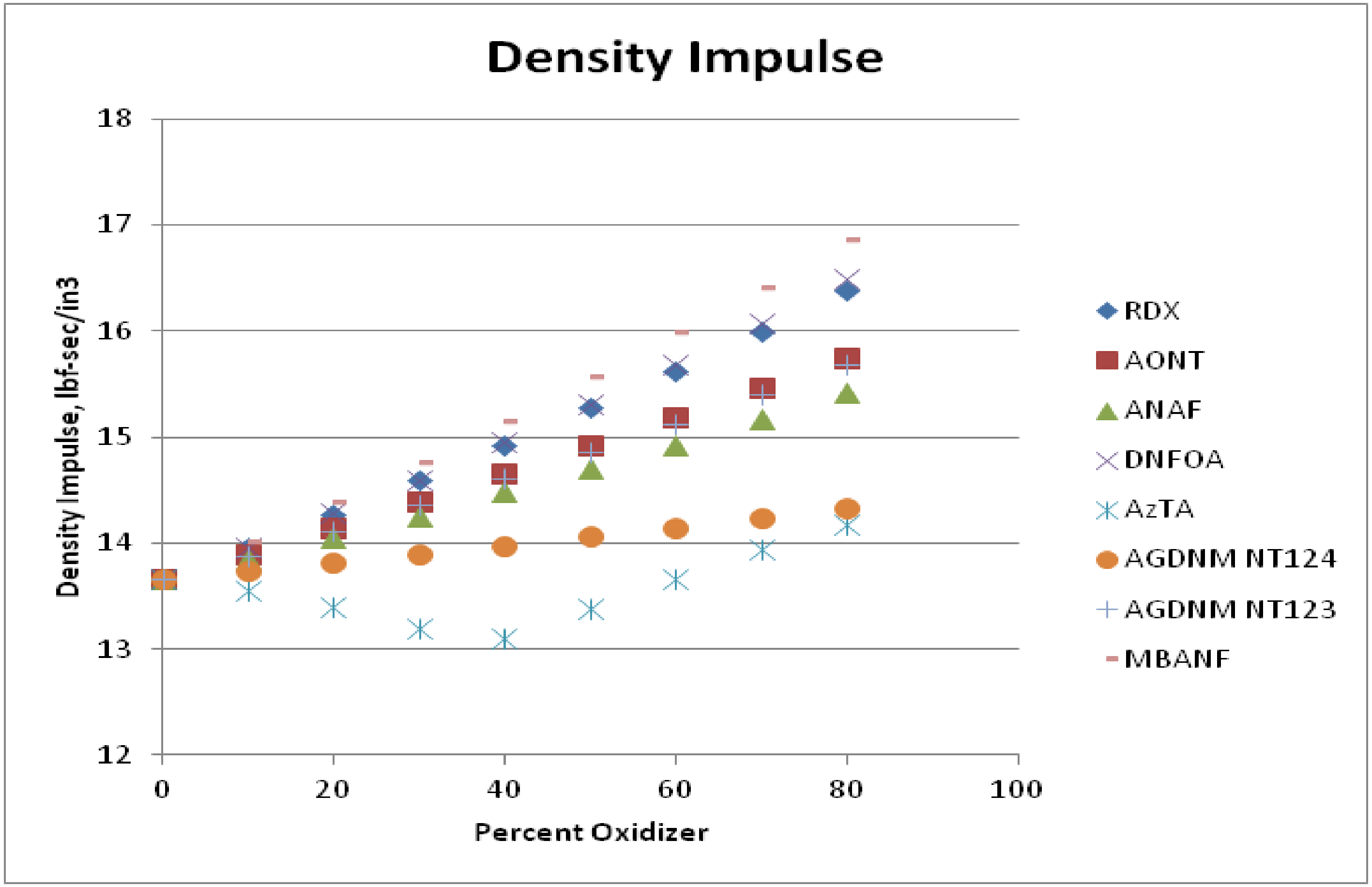
Predicted Propellant I_{sp}



Predicted Propellant Density



Predicted Propellant Volumetric I_{sp}



QSAR Models and Banding Criteria

TOPKAT—Human and ecological toxicity

EPI Suite 4.1—Physical properties

ECOSAR--Ecotoxicity

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

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Toxicity Assessment

Compound	Oral LD_{50} (mg/kg)	Inhalation LC_{50} (g/m^3-h)	Dermal	Ocular	Mutagenicity	Carcinogenicity
MBANF	2000	3.1E-03	Possible sensitizer	Moderate irritant	Positive	Possible weak carcinogen
DNFOA	124.6	7.2E-03	Possible sensitizer	Likely irritant	Positive	Indeterminate
ANAF	1900	1.4E-03	Probable sensitizer	Mild irritant	Positive	Positive
AzTA	7800	494.7	Negative	Possible moderate irritant	Positive	Positive
AGDNM NT123	865.4	5.8	Possible sensitizer	Likely irritant	Negative	Unlikely
AGDNM NT124	1000	4.9	Probable sensitizer	Possible irritant	Negative	Indeterminate
AONT	645.8	6.4	Possible sensitizer	Possible irritant	Positive	Indeterminate
RDX	100	0.75	Negative	Irritant	Negative	Possible

Ecotoxicity Assessment

Compound	Aquatic	Invertebrates	Plants	Mammals	Birds
MBANF					
DNFOA					
ANAF					
AzTA					
AGDNM NT123					
AGDNM NT124					
AONT					
RDX					

Blue color indicates no data or unknown.

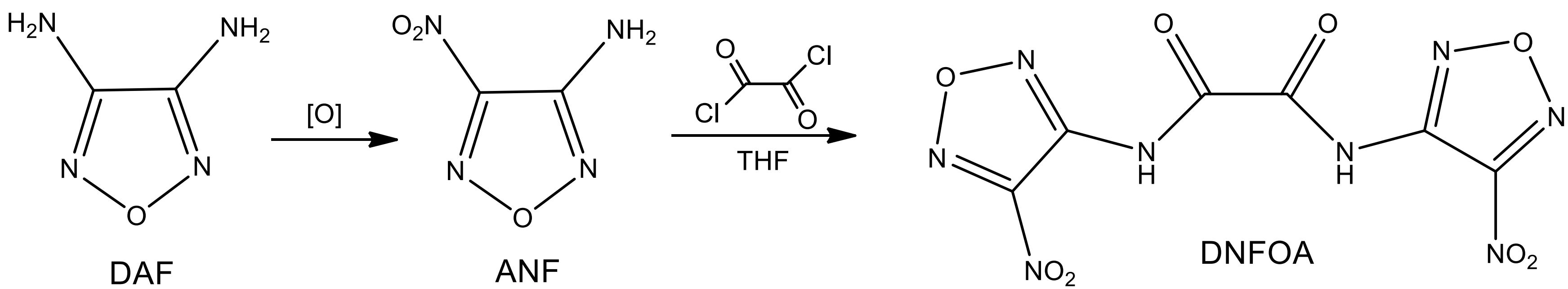
Rank Comparison for RDX Replacement

- Ranking is based on acute toxicity and mutagenicity/carcinogenicity projections.
  1) AGDNM NT124
  2) AGDNM NT123
  3) MBANF
  4) AONT
  5) DNFOA
  6) AzTA
  7) ANAF
- Modeling projections should only be regarded as tentative because energetics of these types are generally not well-handled by currently-available QSAR modeling tools.

RDX Replacement Down-select Matrix

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

DNFOA Synthesis



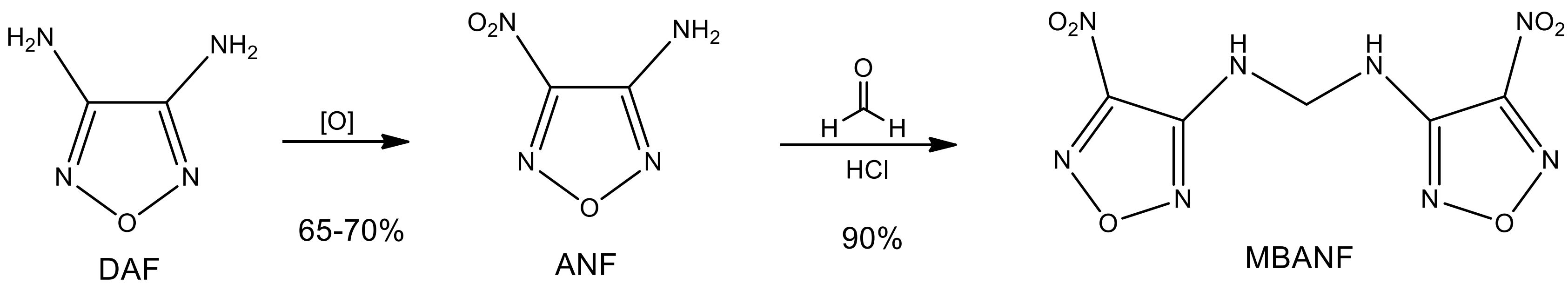
Synthesis is problematic

- Low conversion of ANF-hydrolysis of oxalyl chloride?

Needle morphology

- Recrystallization or milling required

MBANF Synthesis



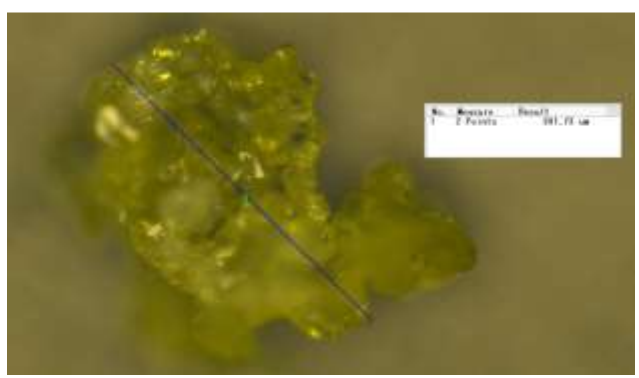
High yields!

Very productive-

- 100 grams of product from 500 mL reactor volume

Free flowing crystalline aggregates; 75-300 µm

- Formulation may de-aggregate; studies ongoing



RDX Replacement SSST Comparison

Material	*RDX*	*MBANF*	*DNFOA*
Impact, kg-cm	**49**	**220**	**150**
Friction, psi at 90º drop angle	**1200**	**1800**	**1800**
ESD, joules	**0.38**	**6**	**0.19**
Autoignition, ºC		**213**	**247**

- Samples of DNFOA and MBANF have been sent to USAPHC for *in vitro* studies
- Additional characterization of both materials by Aerojet is ongoing
- MBANF has been shown to be compatible with other proposed ingredients
- DNFOA compatibility studies are in progress

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MBANF evaluated by Aerojet in min-smoke propellants

Potential high-performance Class 1.3 propellant demonstrated

Mix Number	C22626	C22653	C22736
PGN premix /BTTN/DEGDN AN (150um/40um) MBANF	10/10/10.7 24/25 16	10/10/10.7 12/20 33	10/10/10.7 24/23 16
EOM Viscosity, kP	3	25.5	5
I_{sp}, sec Density, lb/in^3	246.5 0.05892	249.6 0.0594	246.5 0.05892
Mechanical properties	Not tested	Not tested	Good σ = 60 psi/ε = 17%
IHE gap, cards	+60/-70	+90	Not loaded

- MBANF selected to go forward
- Scale up to multiple kilograms by end of FY14
- IHC obtained
- Intermediate scale formulation efforts underway

Questions?