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

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ABSTRACT

Minimum smoke rocket motors used in the DoD arsenal contain environmentally harmful materials such a lead salts, Cyclotrimethylenetrinitramine (RDX), and in some cases ammonium perchlorate. Special handing of these materials during manufacturing, remediation where environmental contamination has occurred, and evaluation and treatment of personnel exposed to these materials presents enormous cost burdens to DoD. Particularly relevant is contamination of historic test ranges and the associated clean-up costs. Thus, finding new alternatives which eliminate environmentally harmful materials but maintain performance is of high importance.

In response to SERDP WPSON-11-02, “ENVIRONMENTALLY BENIGN, INSENSITIVE, CASTABLE, HIGH-PERFORMANCE, MINIMUM-SMOKE ROCKET PROPELLANT”, a proposal was submitted and accepted; WP-2143, **“**Eliminating Lead, RDX, and AP in a Castable, EMMS-Configured Propellant while Maintaining Performance”. A part of this program is the identification, synthesis and scale-up of a replacement for RDX that has the following properties: 1) less toxic than RDX, 2) less sensitive than RDX, 3) high density and heat of formation, 4) high volumetric specific impulse, 5) compatibility with other propellant ingredients and 6) ease of synthesis and scale up.

Several initial candidates have been selected for evaluation, and thermo-chemical calculations have been performed to predict their performance in a baseline minimum-smoke rocket propellant formulation. Predictive QSAR evaluation of the environmental fate and toxicity of the candidates has also been conducted. These criteria, along with an evaluation of the scalability of the ingredient synthesis and preliminary shock sensitivity and compatibility studies, will result in the eventual down-selection of one or two candidates for synthesis at the 100-200 gram scale and subsequent small scale formulation. This report will describe the initial data related to the evaluation criteria and rationale for down-selection of the RDX replacement molecule(s).

This effort was performed under contract WP-2143 with the Strategic Environmental Research and Development Program.

INTRODUCTION

Minimum smoke rocket motors used in the DoD arsenal contain environmentally harmful materials such a lead salts, Cyclotrimethylenetrinitramine (RDX), and in some cases ammonium perchlorate. Special handing of these materials during manufacturing, remediation where environmental contamination has occurred, and evaluation and treatment of personnel exposed to these materials presents enormous cost burdens to DoD. Particularly relevant is contamination of historic test ranges and the associated clean-up costs. Thus, finding new alternatives which eliminate environmentally harmful materials but maintain performance is of high importance.

This effort evaluates the synthesis, scalability and potential environmental impact of a series of compounds reported or known to have equivalent or better performance than RDX, as ingredients in a minimum smoke rocket propellant formulation. The successful candidate or candidates will exhibit reduced toxicity as compared to RDX, and, via formulation and/or motor design, allow the overall system to meet IM requirements. The research objective of the project is the identification, synthesis and scale-up of a viable, less or non-toxic replacement for RDX in a minimum smoke rocket propellant formulation.

RDX replacement candidates must meet multiple criteria in order to be successful. Candidates must provide good performance in minimum smoke propellants, reduced sensitivity to meet IM requirements, and must show improved toxicological and environmental characteristics. Fortunately, NSWC IHD and Aerojet have developed a high level of predictive capability which is directly applicable to this effort. This project utilizes predictive models, combined with small-scale synthesis and testing, to assess and anchor properties of targeted RDX candidates. The performance of an RDX replacement material in a minimum smoke propellant is dependent on multiple factors which include hydrogen content, heat of formation, and density. Estimation of heat of formation and density[1] from structure/property relations is shown in Figure 1 and will be applied to this project.

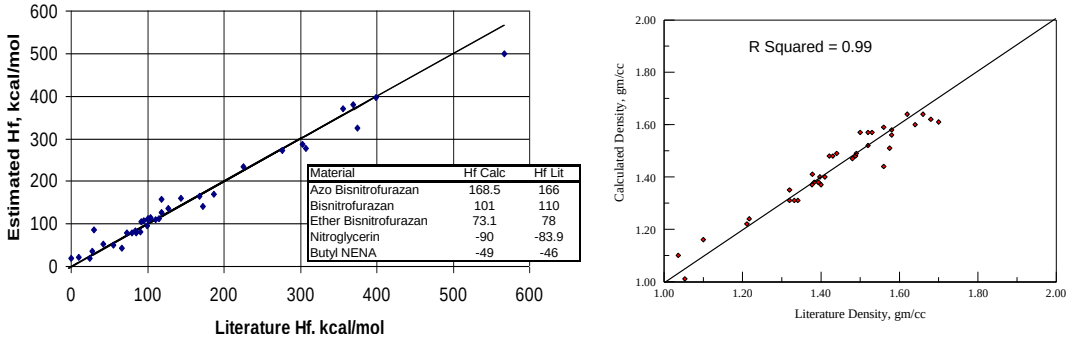

Figure 1. Predicted versus literature values for chemical structure properties: Heat of formation and Density

It is critical that targeted RDX replacement materials have lower shock sensitivity. Technology is available[2] to predict the shock sensitivity of energetic structures as shown in Figure 2. This figure shows the detonation shock sensitivity of various explosive ingredients (solid line) with predicted shock response (dotted lines). Structure property relationships from this predictive model were used to identify RDX replacement materials having reduced sensitivity.

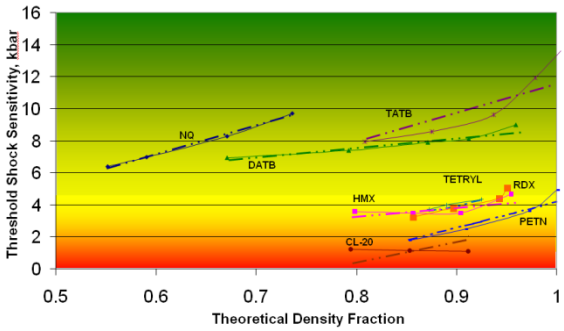

Figure 2. Measured and predicted threshold shock sensitivity as a function of theoretical density fraction

After assessment of performance characteristics and potential shock sensitivity, the toxicity and environmental effects were evaluated through QSAR methods. Follow on evaluation will be done experimentally[3] in a staged gate approach. This stage gate approach is shown in Figure 3 and is modeled after the model developed by the U.S. Army Public Health Command (USAPHC).

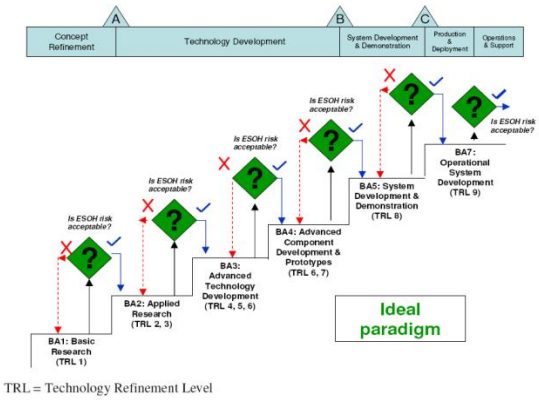

Figure 3. Stage-gate environmental testing for advanced energetic materials

RESULTS AND DISCUSSION

Chemical structures based on heterocyclic groups such as furazan, triazole, tetrazole oxides, compounds that contain azo or azoxy bridges between these moieties, as well as other structural groups were evaluated for their potential as RDX replacements in minimum smoke rocket propellant formulations. Examples of preliminary target compounds are shown in Figure 4.

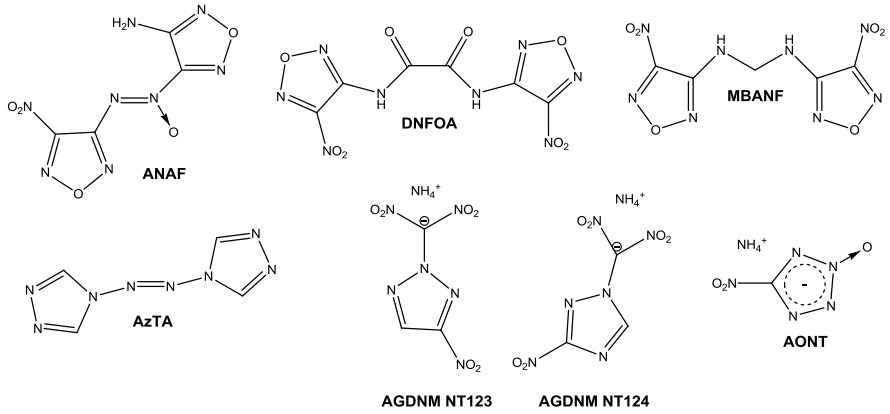

Figure 4. RDX replacement candidates

All these compounds have been synthesized either in the U.S. or abroad and thus are known compounds. In preliminary screening, these compounds were assessed for material properties (Figure 5). As the data show, reported and predicted properties match closely, thus providing a level of confidence.

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	$C_5H_4N_8O_6$	272.12	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

Figure 5. Thermo-chemical calculation inputs

These thermo-chemical 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 6, predicted formulation density ranges are given in Figure 7, and predicted volumetric I_{sp} (I_{vol}) ranges are given in Figure 8.

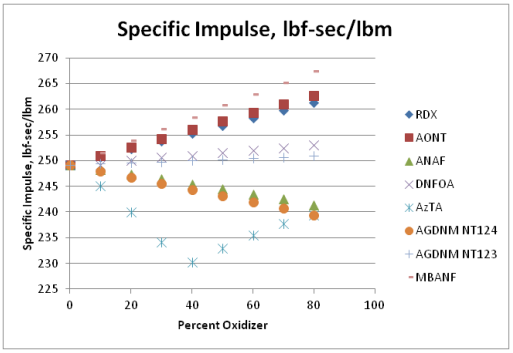

Figure 6. I_{sp} of baseline formulation

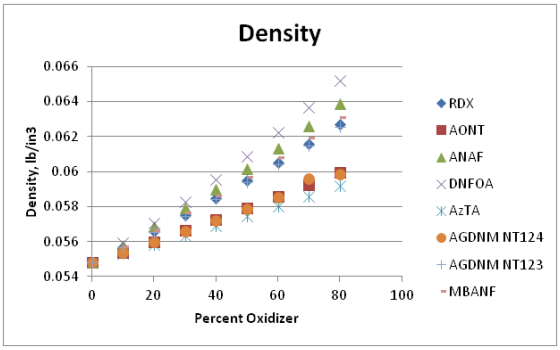

Figure 7. Density of baseline formulation

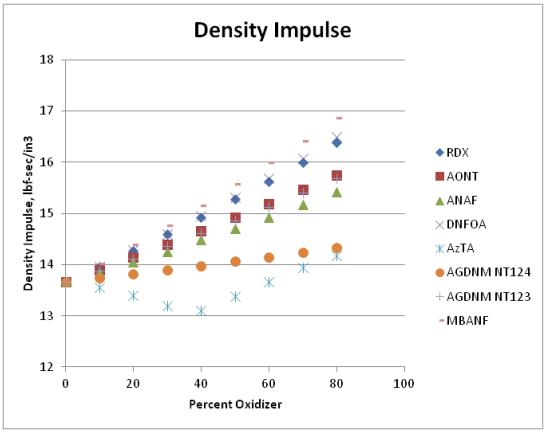

Figure 8. I_{vol} of baseline formulation

As seen in Figure 8, DNFOA and MBANF exhibit clear advantages in volumetric I_{vol} over the other compounds under consideration.

Another important consideration in selecting viable RDX replacement is the relative ease of synthesis and scale-up, and the associated costs. Several of the compounds (ANAF, ADNM NT123, ADNM NT124) have multi-step, low yielding syntheses, and the physical properties are not well characterized. Additionally, sensitivity data for them has not been reported and is 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 Command. 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 (Accelrys Inc.). (EPI Suite™ and ECOSAR™ are trademarks of the USEPA.) The banding criteria for eco-tox assessment are shown in Figure 9.

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 9. 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 10. Modeling projections should only be regarded as tentative because energetics of these types are generally not 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 10).

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

Figure 10. Selection criteria matrix for RDX replacements

DNFOA and MBANF were selected for further evaluation based upon the ranking in the selection criteria matrix. Figure 11 shows the available small scale sensitivity data for DNFOA and MBANF, as compared to RDX.

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**

Figure 11. Comparison of small scale sensitivity data for down-selected candidates with RDX

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, coupled with the somewhat lower EcoTox ranking and some unexpected difficulties in the synthesis of DNFOA, led to the down-selection of MBANF as the RDX replacement candidate.

MBANF was originally synthesized in 1992 by Willer, et al.[4] and was later synthesized by Fluorochem in 100 gram batches. It is synthesized in two high yielding steps from 3,4-diaminofurazan (DAF) as shown in Figure 12. It has been prepared at NSWC IHD at the 400 gram scale, and scale-up to kilogram levels is anticipated by 1QFY14.

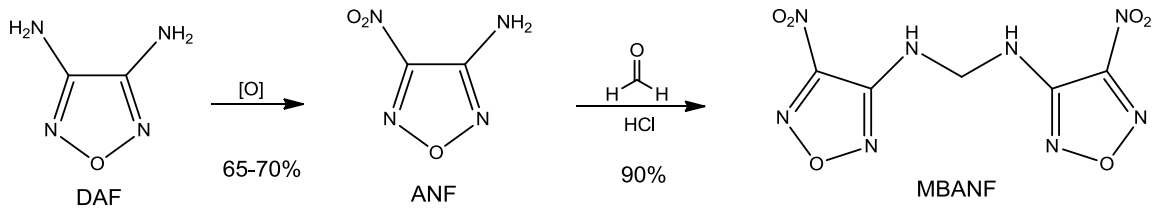

Figure 12. Two step synthesis of MBANF

MBANF has also been evaluated in propellants. The material was first evaluated under IHPRPT funding in 2006[5], but was not beneficial for composite aluminized propellants. In 2007, Aerojet 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 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.

SUMMARY AND CONCLUSIONS

Seven compounds were initially evaluated as RDX replacements in minimum smoke rocket propellant formulations using thermo-chemical calculations. Six selection criteria were used to down-select to one final candidate; density, heat of formation, relative EcoTox ranking, insensitivity (if known), ease of synthesis and scale-up, and performance. Methylene-bis-aminonitrofurazan (MBANF) was found to be the most viable RDX replacement and has been prepared at NSWC IHD at the 400 gram scale. It is anticipated that kilogram-scale batches will be manufactured in 1QFY14.

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