

FINAL REPORT

Self-Remediating Energetic Fills Based on Cyclic Dinitroureas

SERDP Project WP-2147

DECEMBER 2016

Roxanne L. Quintana

Dr. Robert Chapman
Dr. Kenny Young
Dr. Lawrence Baldwin
Dr. Andrew Nelson
Dr. Hung Hoang
Dr. Anna Merritt
Dr. Joshua Carter

**Naval Air Warfare Center Weapons Division
China Lake
Naval Air Systems Command**

Distribution Statement A

This document has been cleared for public release



Page Intentionally Left Blank

This report was prepared under contract to the Department of Defense Strategic Environmental Research and Development Program (SERDP). The publication of this report does not indicate endorsement by the Department of Defense, nor should the contents be construed as reflecting the official policy or position of the Department of Defense. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the Department of Defense.

(This page intentionally left blank)

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 09 - 05 - 2017		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) March 2011 - September 2015	
4. TITLE AND SUBTITLE Self-Remediating energetic Fills Based on Cyclic Dinitroureas Final Report				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Quintana, Roxanne, L.; Chapman, Robert; Kenny Young; Baldwin, Lawrence; Nelson, Andrew; Hoang, Hung; Merritt, Anna; Carter, Joshua				5d. PROJECT NUMBER WP2147	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Air Warfare Center Weapons Division Chemistry Branch(Code4F0000D) 1900 N. Knox Rd. Stop 6303 China Lake, CA 93555				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) SERDP Program Office 901 N. Stuart Street, Suite 303 Arlington, VA 22203-1853				10. SPONSOR/MONITOR'S ACRONYM(S) SERDP	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT					
13. SUPPLEMENTARY NOTES: n/a n/a					
14. ABSTRACT Unexploded ordnance (UXO) resulting from munitions failures creates significant safety and environmental hazards. Smaller munitions, such as BLU-97 bomblets, are notorious for their tendency to dud (Pellerin, 2006). A typical submunition fill, such as PBXN-107, uses cyclotrimethylenetrinitramine (RDX) in an acrylate binder as the main explosive component. RDX is persistent in the environment and is prevalent on and near Department of Defense (DoD) training ranges (Pennington et al., 2006; Jenkins et al., 2006). The Environmental Protection Agency (EPA) has issued a drinking water guideline limit for RDX of 2 µg/L. As a potential solution to the persistent environmental problems of UXO, cyclic <i>N,N'</i>-dinitrourea derivatives may provide an attractive replacement for currently used energetics like RDX. Many cyclic <i>N,N'</i>-dinitrourea derivatives have similar explosive performance parameters to RDX but are more hydrolytically reactive. The objective of this project was to develop and characterize an energetic fill formulation incorporating cyclic <i>N,N'</i>-dinitrourea derivatives as a replacement for currently used energetics like cyclotrimethylenetrinitramine (RDX). This energetic fill would readily decompose into benign products when exposed to moisture (i.e., high humidity or precipitation). Three cyclic <i>N,N'</i>-dinitrourea derivatives were investigated for use in self-remediating energetic fills; tetranitroglycoluril (TNGU), hexanitrohexaazatricyclododecanedione (HHTDD), and 2,4,8,10-tetraazaspiro[5.5]undecane-3,9-dione (TNSUK). TNGU was chosen for scale-up because of its straightforward synthesis, rapid degradation under humid conditions, relative stability in dry conditions, and explosive performance greater than RDX (detonation pressure and detonation velocity; (Muthurajan et al., 2004 and Boileau et al., 1984) and). TNGU has been successfully scaled-up to the 400 gram per batch level. The physical properties (purity, density, morphology) and safety properties (impact, friction and electrostatic sensitivity) of TNGU have been characterized. As-synthesized, TNGU crystals have a small particle size and a needle-like crystal morphology that is typically undesirable for plastic bonded explosive (PBX) formulations. Recrystallization efforts examined a variety of conditions to produce larger, lower-aspect-ratio morphologies. Basic compatibility testing of TNGU with other explosive formulation ingredients has shown that TNGU is compatible with conventional acrylate binders such as lauryl methacrylate (LMA) and 2-ethylhexyl acrylate (EHA). The TNGU/EHA PBX has been scaled up to 50 g. The TNGU/LMA PBX has been scaled up to 250 g. A proton high-resolution magic-angle-spinning nuclear magnetic resonance (¹H HR-MAS NMR) technique has been developed to characterize the hydrolyzability of TNGU in PBX formulations. Safety properties, thermal stability, and detonation velocity have also been evaluated. The ability of the TNGU PBX to self-remediate, even in a hydrophobic binder system, was demonstrated. Ultimately, the TNGU PBX formulations were unable to pass Vacuum Thermal Stability (VTS) testing. We hypothesize that the characteristic that made it attractive as a self-remediating explosive, its rapid hydrolyzability, also made it susceptible to unacceptable degradation under VTS test conditions. Unfortunately, the TNGU PBX's inability to pass VTS testing indicates that it is unlikely to be developed as an energetic fill in confined ordnance items unless the gas generation at elevated temperatures can be mitigated. HHTDD degraded much faster than TNGU in water, so we believe that it would also perform poorly in VTS testing. HHTDD was also difficult to synthesize and purify, making it an unattractive candidate for scale-up. HHTDD was not pursued further. Current synthesis strategies for TNSUK are more complicated (a four step synthesis) than the TNGU synthesis with a low yield, but still acceptable. TNSUK was synthesized at the 5 gram scale. A small scale (5 gram) TNSUK PBX mix was prepared and preliminary characterization was completed. A preliminary hydrolysis experiment was performed using the techniques developed for the TNGU PBX, confirming that the method could be successfully adapted to monitor the progression of hydrolysis in a TNSUK PBX. Further development and characterization of TNSUK and a TNSUK PBX may result in a hydrolyzable PBX with acceptable properties. If TNSUK is pursued with a follow-on effort, its complex synthesis and low-yield will have to be mitigated. This project demonstrated the feasibility of a high performance self-remediating PBX using a conventional binder system. The development and ultimate implementation of a successful self-remediating PBX would prevent future contamination of military test and training ranges while allowing the continued use of live munitions. We were unable to develop an acceptable TNGU PBX, but the methods developed and lessons learned should facilitate the more efficient development of an acceptable self-remediating PBX.					
15. SUBJECT TERMS Hydrolyzable explosives, TNGU, RDX, environmental, cyclic dinitroureas					
16. SECURITY CLASSIFICATION OF: Public Release/Unlimited					
a. REPORT N/A			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 63	19a. NAME OF RESPONSIBLE PERSON Roxanne L. Quintana
	b. ABSTRACT n/a	c. THIS PAGE n/a			19b. TELEPHONE NUMBER (include area code) 760-939-1895

(This page intentionally left blank)

Table of Contents

Table of Contents	i
List of Tables.....	iii
List of Figures	iv
List of Acronyms and Abbreviations	v
Acknowledgements.....	vii
1.0 Abstract	1
2.0 Objective	2
3.0 Background.....	3
4.0 Materials and Methods.....	3
4.1 Synthesis of Energetic Compounds	3
4.1.1 TNGU	4
4.1.2 TNSUK	4
4.1.3 HHTDD.....	6
4.2 TNGU Crystallization.....	7
4.3 Compatibility	7
4.4 Differential Scanning Calorimetry (DSC)	8
4.5 Thermogravimetric Analysis (TGA)	8
4.6 Safety Testing	8
4.6.1 Electrostatic Discharge (ESD)	8
4.6.2 Friction.....	9
4.6.3 Impact	9
4.6.4 Vacuum Thermal Stability (VTS)	9
4.7 Hydrolysis Study	10
4.7.1 Energetic Material.....	10
4.7.2 TNGU PBX.....	10
4.8 Detonation Velocity	11
5.0 Results and Discussion	11
5.1 Energetic Materials.....	11
5.1.1 TNGU	14
5.1.2 TNSUK	21
5.1.3 HHTDD.....	23
5.2 PBX	23
5.2.1 TNGU PBX.....	25

5.2.2 TNSUK PBX	31
5.3 PBX Characterization and Performance.....	31
5.3.1 Thermal Stability	31
5.3.2 Hydrolysis	34
5.3.3 Detonation Velocity Measurements	43
6.0 Conclusions and Implications for Future Research/Implementation.....	44
Literature Cited	47
Appendix A – List of Scientific/Technical Publications	50
Appendix B –SERDP SEED Project WP1624 Report.....	51

List of Tables

Table 1. Comparison of relevant properties of several hydrolyzable explosives.	13
Table 2. Safety data for neat TNGU and Fluorinert TM -coated TNGU as compared to PETN and RDX.	15
Table 3. TNGU crystallographic data.	21
Table 4. TNSUK crystallographic data.	23
Table 5. Generalized TNGU PBX formulation.....	27
Table 6. Safety properties of TNGU PBXs.....	27
Table 7. TNGU PBX gas production rate.	32
Table 8. Explosive performance parameters of cyclic dinitroureas comparison with nitramines.	45

List of Figures

Figure 1. Synthesis of TNGU.	4
Figure 2. Synthesis of TNSUK.	5
Figure 3. Synthesis of HHTDD.	7
Figure 4. Preparation and suggested hydrolysis mechanism of TNGU (Zheng et al., 1988; Peng and Wan, 1980)	15
Figure 5. SEM images of as-synthesized TNGU. 50 g batch (left), 400 g batch (right).	17
Figure 6. TNGU recrystallization methods and solvent systems.....	18
Figure 7. Anti-solvent recrystallization of TNGU from tetrahydrofuran and dichloromethane mixtures.....	19
Figure 8. TNGU crystal morphology as a function of the initial TNGU concentration in tetrahydrofuran.....	20
Figure 9. ORTEP of TNGU – acetone.	21
Figure 10. SEMS of as-synthesized TNSUK crystals	22
Figure 11. ORTEP of TNSUK	23
Figure 12. Mixing Technologies evaluated to prepare the high solids loaded TNGU PBX. Left – Baker Perkins (BP) planetary style impeller mixer. Right – Laboratory Scale Resonant Acoustic Mixer (LabRAM®).....	25
Figure 13. Compatibility studies of TNGU with various binder prepolymers and curatives.	26
Figure 14. Photograph of LabRAM® mixer with stainless steel mix vessel.....	28
Figure 15. Effect of mixing intensity, mixing time, and mix vessel empty volume on the consolidation of TNGU PBXs in the LabRAM®	29
Figure 16. Consolidated TNGU PBX sphere (82% TNGU, 50 g scale).....	30
Figure 17. VTS analysis of TNGU PBX at 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, and 100 °C. The analysis at 90 °C was stopped early because the amount of pressure generated exceeded the capability of the pressure transducer. The analysis at 100 °C used a much smaller sample size to avoid this problem. The extrapolated quantity of gas generated at 90 °C at 48 h was 30.47 mL/g.	32
Figure 18. SBAT slow ramp (13 °C/h).....	33
Figure 19. Isothermal heating of TNGU/LMA PBX at 83°C for one week.	33
Figure 20. ¹ H HR-MAS NMR spectrum of LMA-TNGU PBX in CD ₃ CN-CD ₂ Cl ₂	35
Figure 21. (a) ¹ H HR-MAS NMR spectra of TNGU PBX formulation swollen in CD ₃ CN/CD ₂ Cl ₂ versus time; (b) quantitative analysis of TNGU and TNAE content in the PBX versus time.	36
Figure 22. TNGU concentration in unswollen PBXs exposed to liquid water and moist soil.	37
Figure 23. Hydrolysis of unswollen TNGU-LMA PBX with D ₂ O.....	38
Figure 24. ¹ H HR-MAS NMR of EHA–TNGU PBX in a single solvent vs. a mixed solvent.	39
Figure 25. Cure of TNGU-EHA PBX, after LabRam® mix	40
Figure 26. Hydrolysis of swollen TNGU-EHA PBX in D ₂ O.	40
Figure 27. TNGU-LMA PBX large scale hydrolysis test item (~100g).	41
Figure 28. TNGU-LMA PBX test item while being submerged in water for 1 min, 1 h, 12 h, and 24 h.....	42
Figure 29. Temperature vs. absolute time data collected from tank water.....	43
Figure 30. Pretest photographs of the TNGU PBX samples cut for detonation velocity measurements.....	44

List of Acronyms and Abbreviations

°C	degrees Celsius
µg/L	microgram per liter
¹ H NMR	proton nuclear magnetic resonance
ACN	acetonitrile
BLU-97	a combined effects submunition used in cluster bomb weapons
BP	Baker Perkins
CAPA7201A	trade name for a polycaprolactone polyol
CL-20	hexanitrohexaazaisowurtzitane
cm	centimeter
cm ³	cubic centimeter
Comp B	castable explosive consisting of 60:40 RDX–TNT
DC	direct current
D ₂ O	deuterium oxide
DCM	dichloromethane
DoD	Department of Defense
DSC	differential scanning calorimetry
EHA	2-ethylhexyl acrylate
EPA	Environmental Protection Agency
ESD	electrostatic discharge
FC-43	trade name (3M) of a specific of polyfluorocarbon-based fluid
Fluorinert™	trade name (3M) of a family of polyfluorocarbon-based fluids
g	gram
<i>g</i>	unit of acceleration; 1 <i>g</i> = 9.80665 m/s ²
g/cm ³	grams per cubic centimeter
GPa	Giga Pascal
h	hour(s)
HHTDD	hexanitrohexaazatricyclododecanedione
HMX	cyclotetramethylenetetranitramine
HR-MAS	high-resolution magic-angle-spinning
HTPB	hydroxy-terminated polybutadiene
J	joule
K-6	2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane
kHz	kilohertz
kg	kilogram
km/sec	kilometers/second
L	liter
LabRAM®	Laboratory Scale Resonant Acoustic® Mixer
lb	pound
lbf	pound force
LMA	lauryl methacrylate
LTI	lysine triisocyanate
m/s	meters per second
mg	milligram
MHz	megahertz

min	minute
mL	milliliter
mm	millimeter
MPEG 550	trade name (Dow) for methoxypolyethylene glycol
NATO	North Atlantic Treaty Organization
NAWCWD	Naval Air Warfare Center, Weapons Division
NF	no fire
NM	nitromethane
NMC	New Materials Committee
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge Thermal Ellipsoid Plot
PBX	plastic-bonded explosive
PBXN-105	a Navy qualified plastic-bonded explosive
PBXN-107	a Navy qualified plastic-bonded explosive
P _{CJ}	calculated detonation pressure
PEG	polyethylene glycol
PEGA	polyethylene glycol adipate
PETN	pentaerythrityl tetranitrate
ppm	parts per million
pH	measure of how acidic a water-based solution is
psia	pounds per square inch absolute
RDX	cyclotrimethylenetrinitramine
s	second
SEM	scanning electron microscope
SERDP	Strategic Environmental Research and Development Program
SON	statement of need
T _c	critical temperature
TEGDMA	triethylene glycol dimethacrylate
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMeoETP	trimethylolethane tripropiolate
TNAE	tetranitraminoethane
TNGU	tetranitroglycoluril
TNSUK	2,4,8,10-tetranitro-2,4,8,10-tetraazaspiro[5.5]undecane-3,9-dione
UXO	unexploded ordnance
VTs	vacuum thermal stability
wt%	percent by weight

Acknowledgements

This project is funded by the Strategic Environmental Research and Development Program.

All of the work for this project was performed at the Naval Air Warfare Center Weapons Division, China Lake, California.

The project team would like to acknowledge and thank the following for their contributions:

Mr. Brandon Ferguson, Formulations
Mr. Michael Mann, Safety Test Data
Ms. Stephanie Leach, Optical Images
Mr. Dan Kline, SEM Images
Mr. Michael Celestine, Formulations
Dr. Thomas Groshens, Crystallography
Ms. Aubrey Farmer, Large-Scale Hydrolysis Test

1.0 Abstract

Unexploded ordnance (UXO) resulting from munitions failures creates significant safety and environmental hazards. Smaller munitions, such as BLU-97 bomblets, are notorious for their tendency to dud (Pellerin, 2006). A typical submunition fill, such as PBXN-107, uses cyclotrimethylenetrinitramine (RDX) in an acrylate binder as the main explosive component. RDX is persistent in the environment and is prevalent on and near Department of Defense (DoD) training ranges (Pennington et al., 2006; Jenkins et al., 2006). The Environmental Protection Agency (EPA) has issued a drinking water guideline limit for RDX of 2 µg/L.

As a potential solution to the persistent environmental problems of UXO, cyclic *N,N'*-dinitrourea derivatives may provide an attractive replacement for currently used energetics like RDX. Many cyclic *N,N'*-dinitrourea derivatives have similar explosive performance parameters to RDX but are more hydrolytically reactive. The objective of this project was to develop and characterize an energetic fill formulation incorporating cyclic *N,N'*-dinitrourea derivatives as a replacement for currently used energetics like cyclotrimethylenetrinitramine (RDX). This energetic fill would readily decompose into benign products when exposed to moisture (i.e., high humidity or precipitation).

Three cyclic *N,N'*-dinitrourea derivatives were investigated for use in self-remediating energetic fills; tetranitroglycoluril (TNGU), hexanitrohexaazatricyclododecanedione (HHTDD), and 2,4,8,10-tetranitro-2,4,8,10-tetraazaspiro[5.5]undecane-3,9-dione (TNSUK). TNGU was chosen for scale-up because of its straightforward synthesis, rapid degradation under humid conditions, relative stability in dry conditions, and explosive performance greater than RDX (detonation pressure and detonation velocity; (Muthurajan et al., 2004 and Boileau et al., 1984) and). TNGU has been successfully scaled-up to the 400 gram per batch level. The physical properties (purity, density, morphology) and safety properties (impact, friction and electrostatic sensitivity) of TNGU have been characterized. As-synthesized, TNGU crystals have a small particle size and a needle-like crystal morphology that is typically undesirable for plastic bonded explosive (PBX) formulations. Recrystallization efforts examined a variety of conditions to produce larger, lower-aspect-ratio morphologies.

Basic compatibility testing of TNGU with other explosive formulation ingredients has shown that TNGU is compatible with conventional acrylate binders such as lauryl methacrylate (LMA) and 2-ethylhexyl acrylate (EHA). The TNGU/EHA PBX has been scaled up to 50 g. The TNGU/LMA PBX has been scaled up to 250 g. A proton high-resolution magic-angle-spinning nuclear magnetic resonance (¹H HR-MAS NMR) technique has been developed to characterize the hydrolyzability of TNGU in PBX formulations. Safety properties, thermal stability, and detonation velocity have also been evaluated.

The ability of the TNGU PBX to self-remediate, even in a hydrophobic binder system, was demonstrated. Ultimately, the TNGU PBX formulations were unable to pass Vacuum Thermal Stability (VTS) testing. We hypothesize that the characteristic that made it attractive as a self-remediating explosive, its rapid hydrolyzability, also made it susceptible to unacceptable degradation under VTS test conditions. Unfortunately, the TNGU PBX's inability to pass VTS

testing indicates that it is unlikely to be developed as an energetic fill in confined ordnance items unless the gas generation at elevated temperatures can be mitigated.

HHTDD degraded much faster than TNGU in water, so we believe that it would also perform poorly in VTS testing. HHTDD was also difficult to synthesize and purify, making it an unattractive candidate for scale-up. HHTDD was not pursued further.

Current synthesis strategies for TNSUK are more complicated (a four step synthesis) than the TNGU synthesis with a low yield, but still acceptable. TNSUK was synthesized at the 5 gram scale. A small scale (5 gram) TNSUK PBX mix was prepared and preliminary characterization was completed. A preliminary hydrolysis experiment was performed using the techniques developed for the TNGU PBX, confirming that the method could be successfully adapted to monitor the progression of hydrolysis in a TNSUK PBX. Further development and characterization of TNSUK and a TNSUK PBX may result in a hydrolyzable PBX with acceptable properties. If TNSUK is pursued with a follow-on effort, its complex synthesis and low-yield will have to be mitigated.

This project demonstrated the feasibility of a high performance self-remediating PBX using a conventional binder system. The development and ultimate implementation of a successful self-remediating PBX would prevent future contamination of military test and training ranges while allowing the continued use of live munitions. We were unable to develop an acceptable TNGU PBX, but the methods developed and lessons learned should facilitate the more efficient development of an acceptable self-remediating PBX.

2.0 Objective

The Strategic Environmental Research and Development Program (SERDP) Statement of Need (SON) WPSON-08-04 called for the development of approaches to reduce or mitigate the release of hazardous energetic materials into the environment when munitions do not perform as intended. The objective of this project was to develop and characterize an energetic fill formulation that would readily decompose into benign products when exposed to moisture (i.e., high humidity or precipitation). We proposed developing energetic formulations incorporating cyclic *N,N'*-dinitrourea derivatives as a replacement for currently used energetics like cyclotrimethylenetrinitramine (RDX). These compounds have similar explosive performance parameters to RDX, but are significantly more hydrolytically reactive. Our goal was that the new formulation would meet or exceed the performance of currently used formulations (e.g., PBXN-107 in the BLU-97) and readily decompose into benign products when exposed to moisture.

3.0 Background

Unexploded ordnance (UXO) resulting from munitions failures in the field (testing and training ranges as well as battlefields) create significant safety and environmental hazards. Smaller munitions, such as BLU-97 bomblets, are notorious for their tendency to dud, and their failure rate can be high. Both incomplete detonations and duds result in the release of energetic materials to the soil, water, and air.

A typical submunition fill, such as PBXN-107 in the BLU-97, uses RDX in an acrylate binder as the main explosive component. RDX exhibits significant deleterious environmental effects on water supplies and is prevalent near Department of Defense (DoD) domestic live fire training ranges (Pennington et al., 2006; Jenkins et al., 2006). The Environmental Protection Agency (EPA) has issued a drinking water guideline limit (lifetime) for RDX of 2 µg/L. RDX has high to moderate mobility in soil, and its natural (aerobic) biodegradation is very slow.

As a potential solution to the persistent environmental problems of UXO, we investigated energetic formulations incorporating cyclic *N,N'*-dinitrourea derivatives as a replacement for currently used energetics like RDX. These compounds have similar explosive performance parameters to RDX, but are significantly more hydrolytically reactive. These properties make them attractive candidates for explosive fillers in self-remediating munitions. Several of these types of compounds have received some development over the last couple of decades (predominantly in other countries). Specific examples include tetranitroglycoluril (TNGU or Sorguyl) and hexanitrohexaazatricyclododecanedione (HHTDD). During a recently completed SERDP SEED effort (WP-1624), we quantified these ingredients' susceptibility to environmental hydrolysis and demonstrated that they show acceptable stability for processing into munitions. These compounds also undergo sufficiently rapid degradation when exposed to environmental elements (e.g., high humidity or rain) to be characterized as "self-remediating." Thus the formulation of these hydrolyzable explosive ingredients into self-remediating plastic bonded explosives (PBX) should be feasible so long as the PBX binder system produces no hazardous degradation products and permits water permeation for the hydrolysis of the dinitrourea compounds.

4.0 Materials and Methods

4.1 Synthesis of Energetic Compounds

Three cyclic *N,N'*-dinitrourea derivatives were synthesized and investigated for use in self-remediating energetic fills; TNGU, 2,4,8,10-tetranitro-2,4,8,10-tetraazaspiro[5.5]undecane-3,9-dione (TNSUK), and HHTDD.

General methods and materials.

Glycoluril was purchased from AK Scientific, Inc. and used as is. All other reagents and solvents were purchased from Aldrich or VWR and used as is. The ethanol was 200 proof; all other solvents were reagent grade. ¹H NMR spectra were recorded on a 300 MHz Bruker NMR. Chemical shifts are referenced to residual solvent. These materials are energetic and must be handled with care. Proper safety equipment such as leather/Kevlar gloves, leather aprons, face

shields, blast shields, and/or remote operations should be used to reduce risk. The azide intermediate for the preparation of TNSUK should not be isolated.

4.1.1 TNGU

TNGU was synthesized at the 400 g scale (theoretical yield) as shown in Figure 1. TNGU was synthesized in one step from commercially available glycoluril using acetyl nitrate (nitric acid–acetic anhydride) nitrating reagent based on a literature procedure (Peng and Wan, 1980). It is important to dry the TNGU for at least two days immediately after washing to ensure all water, solvent and trace acid are removed. If TNGU is allowed to sit wet or partially dried, the TNGU will start to decompose.

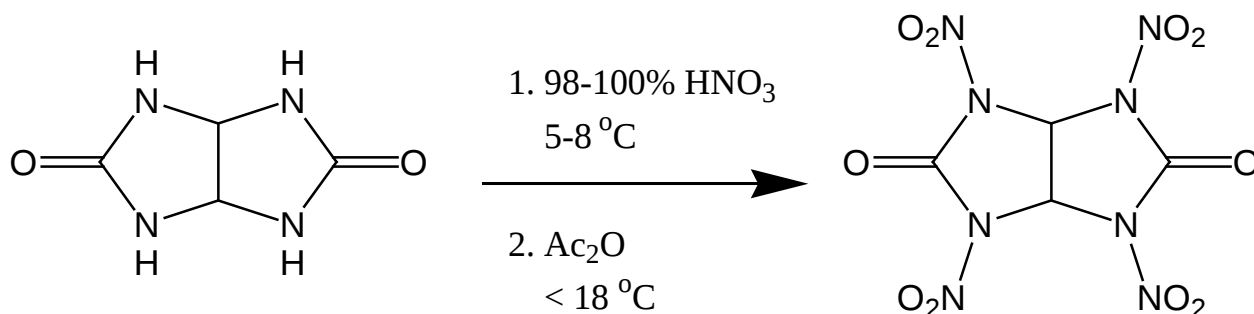


Figure 1. Synthesis of TNGU.

Synthesis of TNGU.

To a 10 L jacketed reactor, nitric acid (3.6 L, >99%) was added. The reactor was then chilled to 5 °C, and glycoluril (200 g, 1.41 mol) was slowly added to the reactor while keeping the temperature below 8 °C. The reaction was stirred for 1 h at 5 °C. Acetic anhydride (1.8 L, 19.04 mol) was slowly added at a rate to keep the temperature between 15 – 18 °C. The reaction was stirred overnight at 5 °C and then chilled to –5 °C while stirring for 30 min. The white suspension was drained and the solid collected in a Buchner funnel with filter paper. The white solid was washed with ice-cold water until the water was no longer acidic followed by 50:50 ethanol/chloroform (~1.5 L) and chloroform (~1 L). The solid was immediately transferred to a recrystallization dish and dried under vacuum in a desiccator at ambient temperature. While still damp the solid was occasionally carefully broken into smaller particles to prevent large chunks from forming. Vacuum drying for two days was required to remove all volatiles. Typical yields were in the range of 60 – 80%. The TNGU was >98% pure as measured by NMR. ¹H NMR (C₃D₆O) 7.77 (s).

4.1.2 TNSUK

TNSUK was synthesized at the 5 g scale. TNSUK was synthesized in four steps in approximately 40% overall yield as shown in Figure 2 from commercially available pentaerythritol based on literature procedure (Fleischer et al., 1971; Adil et al., 2004; Fu et al., 1992).



A modified procedure was used for the synthesis of the pentaerythritol tetratosylate. To a 2 L jacketed vessel with an overhead stirrer, dichloromethane (400 mL) and pyridine (240 mL) were added. While stirring at room temperature pentaerythritol (40.000g, 0.294moles) was added, then tosyl chloride (247.572g, 1.299 mol) was added in portions over 5 minutes. The reaction was stirred overnight holding the temperature at 25 °C. The reactor was cooled to 5 °C and an acidic aqueous methanol solution (200 mL HCl, 125 mL deionized water, and 250 mL of methanol) was added. The organic layer was collected, and the aqueous layer was washed with dichloromethane (2 x 250 mL). The organic fractions were combined and dried with magnesium sulfate. The solvent was removed under reduced pressure, and the solid was dried under vacuum over P₂O₅, yielding 183.21 g (82.8%). ¹H NMR (CDCl₃) 7.69 (d, ²J = 8.19 Hz, 2H), 7.37 (d, ²J = 7.98 Hz, 2H), 3.82 (s, 2H), 2.49 (s, 3H).

The pentaerythrityltetramine tetrahydrochloride was made with a modified procedure in which the tetra-bromopentaerythritol was replaced with pentaerythritol tetratosylate. Under nitrogen pentaerythritol tetratosylate (75.000 g, 0.100 mol) and sodium azide (77.713 g, 1.195 mol) were added to a 1 L Schlenck flask. Under a positive flow of nitrogen anhydrous dimethylformamide (575 mL) was added. The solution was stirred and heated at 100 °C for 20 h, cooled to room temperature and poured into 2.5 L of deionized water. The azide intermediate was extracted with di-ethyl ether (800 mL, then 4 x 300 mL). The ether was dried over MgSO₄, filtered and the solvent was reduced to ~ 600 mL. Then dioxane (400 mL) was added, and the solvent was reduced down to ~ 600 mL. While stirring triphenylphosphine (130.642 g, 0.498 mol) and 20% NH₃ (630 mL) were added. The milky solution was stirred at 20 °C overnight, during which gas evolved. The solvent was then removed and chloroform (1.8 L) was added. The solution was extracted with 2.5 M HCl (5 x 300 mL). The aqueous layers were reduced down to ~ 200 mL, and concentrated HCl (75 mL) was added. The white suspension was filtered, and washed with cold HCl (30 mL), then ethanol (3 x 50 mL), then ether (5 x 90 mL) and dried under vacuum over P₂O₅, yielding 24.95 g (90.1%). ¹H NMR (D₂O) 3.43 (bs)

Synthesis of 3,9-dinitroimino-2,4,8,10-tetraazospiro(5,5)undecane.

In a 250 mL flask pentaerythrityltetramine tetrahydrochloride (15 g, 0.0539 mol)) was dissolved in 5 wt% NaOH (90 mL). The pentaerythrityltetramine tetrahydrochloride solution was added to nitroguanidine (11.293 g, 0.108 mol) in deionized water (250 mL). The suspension was heated at 70 °C for 5 h, during which it became clear and a white solid precipitated. The suspension was cooled to room temperature, filtered, and washed with deionized water and ethanol then dried under vacuum over P₂O₅, yielding 8.42 g (57.4%). ¹H NMR (C₂D₆OS) 8.85 (bs, 4H), 3.17 (s, 8H)

Synthesis of TNSUK.

To a 250 mL 3-neck round bottom flask with an addition funnel and overhead stirrer acetic anhydride (42 mL) was added. While stirring, 3,9-dinitroimino-2,4,8,10-tetraazospiro(5,5)undecane (5 g, 18.3 mmol) was added. The flask was cooled to <10 °C, and 98% HNO₃ (63 mL) was added at a rate to keep the solution between 0 – 10 °C. The solution was slowly warmed to room temperature and stirred for 4 h. It should be noted that during the acid addition the 3,9-dinitroimino-2,4,8,10-tetraazospiro(5,5)undecane formed a gummy ball which slowly redissolved. A white solid eventually formed. The suspension was filtered, washed with ice-cold water, then 50/50 ethanol/chloroform, then chloroform. The solid was immediately dried under vacuum for at least 2 days, yielding 5.24 g (78.3%). ¹H NMR (C₃D₆O) 4.60 (s).

4.1.3 HHTDD

As shown in Figure 3, HHTDD was synthesized in three steps according to a literature procedure (Dagley and Flippen-Anderson, 1994). The first step involves the reaction between formamide and glyoxal in the presence of base (pH = 10) to form 1,4-diformyl-2,3,5,6-tetrahydropiperazine. This reaction is high-yielding and results in very pure intermediate compound. The subsequent reaction, which involves the formation of the imidazo rings, proved to be difficult. Two alternative paths may be used for a condensation reaction to form the imidazo rings. Both synthetic pathways were tried. Neither the urea nor the guanidine route yielded pure tricyclic intermediate. The results from either synthetic pathway yielded impure product that was difficult to purify. Attempts to conduct the final nitration step with impure tricyclic intermediate did not result in final product, and it was inconclusive what product was formed.

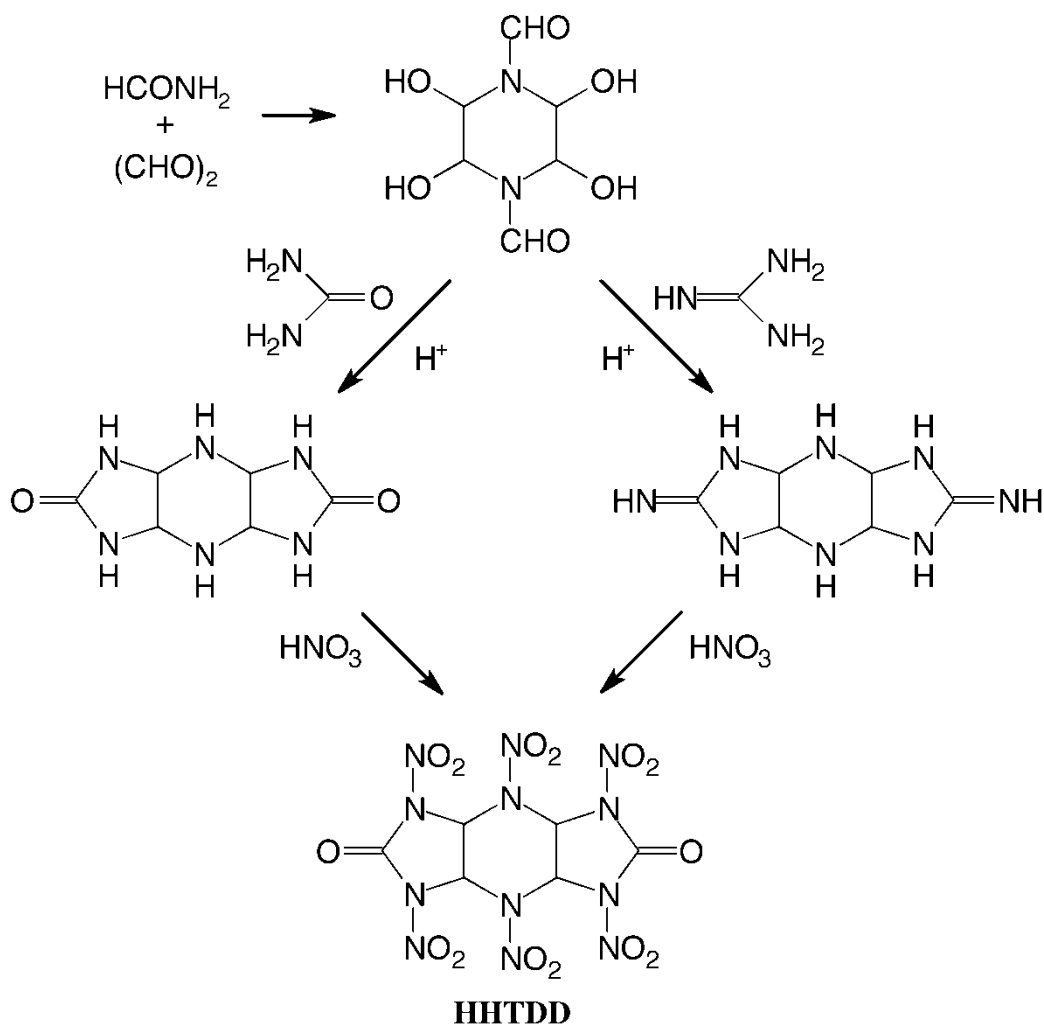


Figure 3. Synthesis of HHTDD.

4.2 TNGU Crystallization

TNGU was recrystallized by several techniques. In a typical slow evaporation experiment 10 – 25 milligrams (mg) of TNGU were dissolved in 1 mL of a suitable solvent (nitromethane, acetone, tetrahydrofuran) and allowed to evaporate. Crystals were also obtained by adding an anti-solvent. In a typical experiment 140 mg of TNGU was dissolved in tetrahydrofuran, then dichloromethane was slowly added, ranging from 0.35/1 up to 0.45/1 (tetrahydrofuran to dichloromethane). Crystals were also obtained by vapor diffusion of an anti-solvent. In a typical experiment 100 – 500 mg of TNGU was dissolved in a suitable solvent (nitromethane, acetone, tetrahydrofuran, acetonitrile) in a vial or beaker. That vial/beaker was then placed in a larger container with a lid that contained an anti-solvent such as dichloromethane. The anti-solvent was allowed to slowly diffuse into the beaker and crystals formed overnight.

4.3 Compatibility

Chemical compatibility tests were conducted based upon NATO's STANAG No. 4147 – Chemical Compatibility of Ammunition Components with Explosives (Non-nuclear Applications)

which gives specific procedural guidelines for analyzing the compatibility of materials to be used in explosive mixes/formulations via differential scanning calorimetry (DSC). A 50/50 mixture of the energetic with the candidate binder ingredient (e.g., prepolymer, catalyst, plasticizer) is heated at a ramp rate of 2 °C/min past ignition (300 °C). Individual components are also analyzed independently under the same conditions. Calculation of the difference between the mixture decomposition temperature and neat energetic decomposition temperature (both recorded as maximum peak heights) provides a measure of the mixture compatibility. Generally, negative shifts of greater than 20 °C indicate chemical incompatibility that would result in unstable PBX formulations. Shifts of 4 °C and under indicate full compatibility, whereas those between 4 and 20 °C require further investigation.

4.4 Differential Scanning Calorimetry (DSC)

All experiments were performed on a TA Instruments Q10 DSC. One to two mg of sample was placed into standard aluminum pan. Two holes were punched into an aluminum lid (~ 0.2 mm diameter each). The lid was inverted, placed above the sample, and crimped into place using a hermetic press. The samples were heated from 25 °C to 300 °C at a rate of 5 °C/min, under a nitrogen stream with a flow rate of 50 mL/min.

4.5 Thermogravimetric Analysis (TGA)

All experiments were performed on a TA Instruments Q5000 TGA. Two to five mg of sample was placed into a platinum pan. For the standard experiments, the samples were heated from 25 °C to 300 °C at a rate of 5 °C/min, under a nitrogen stream with a flow rate of 50 mL/min. For the isothermal experiments, the samples were placed into the TGA oven at room temperature. The temperature was equilibrated to either 80 °C or 100 °C within 1 to 2 min. The samples were then heated for a period of 48 hours.

4.6 Safety Testing

Safety test standards were performed quarterly.

4.6.1 Electrostatic Discharge (ESD)

ESD tests were conducted in accordance with AOP-7 Edition2, NAWC/NSWC Method ESD Category US/201.03.002/003. The ESD test is designed to simulate an electrostatically charged person or object discharging through a thin layer of sample to a grounded conductive surface. A sample is placed on a grounded steel button. A capacitor (0.02 microfarad) is charged to a select voltage by means of a high voltage power supply. The positive side of the capacitor is brought into contact with the sample by means of a steel phonograph needle on the end of a probe and discharges through the sample to the steel button, which is grounded to the other side of the capacitor. Voltages over 5000 volts DC are not normally tested because it is estimated that a human body can deliver a maximum discharge of 0.001 joules (J). The test is begun at 0.25 J (0.02 microfarad) level. If results are negative, i.e., no reaction, the test is continued until 20 consecutive failures are reported. If the test sample has a positive result, i.e., flash, spark, burn, odor, or noise other than instrument noise, the testing is performed at the next lower level until 20 consecutive

failures are reported. A sample is considered to be electrostatically sensitive if it ignites at 0.25 J or lower and extreme caution should be used when dealing with these samples.

4.6.2 Friction

Frictions tests were conducted in accordance with AOP-7 Edition 2 ABL sliding Friction Category US/201.02.005. The Alleghany Ballistics Laboratory Design (ABL) Sliding Friction Sensitivity Test is used to determine the relative sensitivity of an energetic sample to initiation by friction. The test is conducted using a pendulum drop angle of 90 degrees. This imparts an initial velocity of 8 feet per second to the sliding steel plate. A sample is placed on the plate and the edge of a 1/8 inch wide steel disc is pressed down on the sample with a selected force obtained by means of a hydraulic ram. The plate is free to slide exactly 1 inch after being struck by the pendulum and the sample is arranged on the plate so that it is carried between the sliding metal surfaces. The test is performed at a maximum load of 1000 pound (lb). If the sample shows a negative response 20 tests are performed at this level yielding 20/20 no fires (NF) @ 1000 lb. A 20 shot modified Bruceton method is used defining the 50% point if a positive test is detected by visible sparks, visible flame, audible explosion, loud crackling, or the detection of reaction products by a gas analyzer. Low Fire is the lowest level at which a fire is obtained and approximates the level at which the sample will fire 10% of the time. This data is compared to standards of RDX and pentaerythryl tetranitrate (PETN). Extreme caution should be used if the data is below 50 lb.

4.6.3 Impact

Impact tests were conducted in accordance with AOP-7 Edition 2 ERL/Bruceton impact test category US/201.01.001. The Impact Sensitivity Test (ERL Model Design) is used to determine the sensitivity to impact of energetics, when not under confinement. The machine uses a 2.5 kilogram (kg) drop weight, a 2.5 kg modified Type 12 tool striker, and a Type 12 tool anvil. A sample of energetic material is placed onto garnet sandpaper and placed together in the center of the anvil and the striker is lowered to rest on top of the sample. The drop weight is raised to the desired height, dropped and results observed. A positive test is detected by an observance of smoke, odor or sound. After each drop the test sample is removed and a fresh sample is used for the next drop. The modified Bruceton method is used, defining the 50% point at which the sample would fire 50% of the time. The Low Fire is the lowest level at which a fire is obtained, approximates the level at which the sample will fire 10% of the time. This data is compared to standards of RDX, and PETN.

4.6.4 Vacuum Thermal Stability (VTS)

Two methods were used to measure the VTS of the oxidizers and formulations; the manometer method and the transducer method.

The manometer method involves loading a 14 mL glass culture tube (Fisher catalog # 14-961-29) with 0.500 – 1.000 g of material. Typically 2 – 3 tubes are loaded. The septa (Fisher catalog # 03-225-5) were greased (vacuum grease) and placed on the top of the tube. The tube is evacuated to approximately 0.08 pounds per square inch absolute (psia) and the pressure and temperature were recorded. Parafilm was used to secure the septa and vacuum grease was applied

to the hole. Typically a blank is also run with the samples. The tubes are loaded into an aluminum heating block and heated at either 80 or 100 °C (± 0.5 °C) for 48 h. After the 48 h the block is turned off and the samples are allowed to cool to room temperature. The temperature and final pressure are recorded. The blank is used to subtract from the sample.

The transducer method is similar to the manometer method and followed STANAG 4556. The septa are replaced with a pressure transducer to allow real time measuring of the pressure. Typically 2 – 3 replicates are run per sample, and a blank is also run. A 1.00 g sample is used.

4.7 Hydrolysis Study

4.7.1 Energetic Material

The hydrolytic decomposition of neat energetic in a variety of environments (dry air, humid air, dry soil, or moist soil) can be monitored by ^1H -NMR analysis, and a detailed description of the experimental method is provided in Appendix B (Chapman et al., 2009). Briefly, to carry out a degradation study, a measured quantity of energetic crystals is placed in a vial and exposed to the environment of interest for a controlled period of time. A measured amount of acetonitrile D3 (CD_3CN) is then added to the vial, and the dissolved energetic and decomposition products are measured by ^1H NMR analysis. The observed decrease in area under the energetic peak(s) versus that of the solvent's residual protons (CHD_3CN used as an internal integration standard) was used to determine the extent of hydrolysis at a given exposure time.

4.7.2 TNGU PBX

A method has been developed for this project using proton high-resolution magic-angle-spinning nuclear magnetic resonance (^1H HR-MAS NMR) spectroscopy to quantify the degradation of TNGU in a 2-ethylhexyl acrylate (EHA) or a lauryl methacrylate (LMA) based PBX formulation. During this project this method was also shown to work for TNSUK PBX (appropriately modifying the peaks monitored). The binder in the PBX is made gel-like by placing the sample in a 50/50 mixture of CD_3CN – CD_2Cl_2 . The samples are analyzed via ^1H HR-MAS NMR spectra.

For the solvent assisted method, a 40 mg sample of the PBX formulation was cut into pieces (~ 1 millimeter [mm] square). Roughly 2 drops of a 50/50 mixture of CD_3CN – CD_2Cl_2 was added to a 4 mm MAS rotor, followed by addition of the PBX formulation. Then, 14.0 mg of deuterium oxide (D_2O) was syringed into the rotor. The rotor was then filled to just below its top (approximately 1 mm) with the 50/50 solvent mixture. The rotor was sealed with a cap that contained a 0.3 mm hole pre-drilled into its center in order to allow any evolved gases to escape. ^1H HR-MAS NMR spectra were taken hourly, with a 5 s recycle delay time between scans and a sample spinning rate of 5 kilohertz (kHz). The relative peak heights for TNGU (7.70 ppm) and its initial decomposition product, tetranitraminoethane (TNAE) (6.57 ppm), were then obtained.

Non-solvent assisted data was generated by placing 40 mg (single piece) samples of the PBX into 20 mL vials containing approximately 3 mL of D_2O each. Prior to analysis, each sample was blotted dry and placed into a 4 mm rotor. A 50/50 mixture of CD_3CN – CD_2Cl_2 was added to

fill the rotor. The rotor was then capped and the sample was left to soak for 15 min. Each sample-containing rotor was inserted into the HR-MAS NMR probe and spun at 5 kHz. Three samples were analyzed per day and the results were averaged to generate one data point. Percent loss of TNGU due to hydrolysis was determined by calculating the ratio of the area under the TNGU peak (~7.70 ppm) to that of the internal standard methyl peak of LMA (~1.80 ppm).

4.8 Detonation Velocity

Failure Diameter/Unconfined Detonation Velocity testing was completed on two samples of TNGU PBX. The samples were made up of three billets cut from a single 250 g piece. The billets were stacked one on top of the other and taped together. The samples were initiated using an RP-501 Exploding Bridge Wire detonator and one PBXN-5 booster pellet, 0.3 inch by 0.5 inch diameter. Six piezoelectric pins were used to determine the detonation velocity. The pins were held in place using a 2 inch long piece of plastic. Holes were drilled through the plastic and the pins pushed through the holes and against the side of the explosive charge. Pin distances were measured and recorded prior to testing.

Detonation velocity was determined by comparing time versus distance data received from the piezoelectric pins. Measured distances are accurate to ± 0.001 inch and timing accuracy is ± 200 picoseconds.

5.0 Results and Discussion

5.1 Energetic Materials

TNGU, HHTDD, and TNSUK were all considered as candidate hydrolyzable explosive components at the beginning of this project. A summary of the hydrolyzable explosive components considered and their relevant properties is summarized in

Table 1. The properties listed in Table 1 were either determined experimentally, or reported in literature and therefore the reporting is sometimes not consistent from compound to compound.

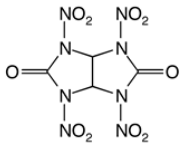
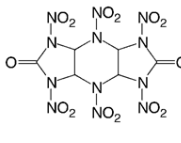
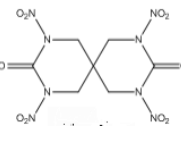
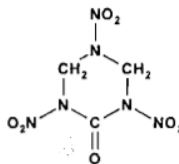
Initially, TNGU, TNSUK, and HHTDD were all synthesized at the 5 g scale. TNGU was chosen to move forward because of its straightforward synthesis, rapid degradation under humid conditions, relative stability in dry conditions, and explosive performance. It was scaled up to 400 g batches and a PBX formulation was developed and characterized. Ultimately, the TNGU PBX formulation was unable to pass VTS testing. In consultation with the SERDP Weapons Systems and Platforms technical committee, it was decided to continue with the TNGU PBX formulation and characterization rather than start over with a different hydrolyzable explosive component. We believe that the characteristic that made it attractive as a self-remediating explosive, its rapid hydrolyzability, also made it susceptible to degradation under VTS test conditions. In light of our inability to pass VTS test with the TNGU PBX, we briefly reexamined TNSUK and HHTDD as possible candidates for hydrolyzable explosives and also considered 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (K-6).

TNSUK hydrolyzed much slower than TNGU in water, and had a higher degradation temperature via DSC, indicating that it might perform better during VTS testing. Near the end of the project, a small TNSUK PBX mix was prepared and preliminary characterization was completed to determine if our lessons learned from developing a TNGU PBX could be applied to a TNSUK PBX.

HHTDD degraded much faster than TNGU in water, so we believe that it would also perform poorly in VTS testing. HHTDD was also difficult to synthesize and purify, making it an unattractive candidate for scale-up. HHTDD was not pursued further.

A literature search revealed that initial screening experiments on K-6 indicate that it is more toxic than RDX (Krikštopaitis, K., 2013). Even if it degrades relatively quickly in water, a substance more toxic than RDX is not consistent with the goals of this project, so K-6 was not investigated during this project. If a follow-on effort is pursued, a more rigorous toxicity test should be performed before completely ruling out K-6.

Table 1. Comparison of relevant properties of several hydrolyzable explosives.

	TNGU 	HHTDD 	TNSUK 	K-6 
Hydrolysis in water at room temperature	100% in 14 h ^a	100% in 3 h ^a	31% in 16 days (measured; the degradation was not monitored past 16 days)	~ 11% weight loss in 11 days ^c , (reported in the literature; we were unable to find any reports beyond 11 days)
Stability in dry air	$t_{50} \sim 357$ days ^a	$t_{50} \sim 388$ days ^a	"...put aside in atmosphere for 5 months: ... hydrolysis stability was relatively good." ^b	
Thermal stability	DSC: exotherm onset ~ 190 °C (measured)	DSC: exotherm onset ~ 205 °C ^a	DSC: exotherm onset ~ 234 °C ^b	TGA: weight loss begins in the range $144\sim 159$ °C (sample-dependent) ^{c,e}
Detonation pressure P_{CJ} (GPa)	38.7 ^h	46.2 ⁱ	-	37.98 ^g
Detonation velocity D (km/sec)	9.07 ^j	~ 9.75 ^{k,l}	8.67 ^b	8.81 ^g
Toxicity	Benign hydrolysis products (glyoxal, nitrous oxide, and water) ^{m,n}	Because of its similarity to TNGU, it is believed to have similar hydrolysis products	Unknown, but similar model compounds appear benign ^d	Cytotoxicity (mice splenocytes) indicates more toxic than RDX ^f
Synthesis	One-step synthesis, 80% yield	Difficult with low yield	Several methods reported. We used a four-step synthesis: $\sim 40\%$ yield overall	Various methods reported ^{c,e,g}

^a Chapman, R.D., Quintana, R.L., Baldwin, L.C., and Hollins, R.A., "Cyclic Dinitroureas as Self-Remediating Munition Charges", Project WP-1624 Final Report, SERDP, Arlington, VA (Feb 2009); *Fifth Primary Explosives Workshop* (Scottsdale, AZ), 5 May 2009.

- ^b Fu, Q. *Binggong Xuebao [Acta Armamentarii]* **1992**(1), 28.
- ^c Boniuk, H. *International Annual Conference of ICT 2000*, 31st(Energetic Materials), 46/1.
- ^d Leasure, J.K. *U.S. Patent* 3356483 (1967).
- ^e Ritter, H. *International Annual Conference of ICT 2001*, 32nd(Energetic Materials), 91/1.
- ^f Krikštopaitis, K. *New Trends in Research of Energetic Materials, Proceedings of the Seminar, 16th*, Pardubice, Czech Republic, Apr. 10 – 12, 2013 (Part 2), 735.
- ^g Mitchell, A.R. *Propellants, Explosives, Pyrotechnics* **1994**, 19(5), 232.
- ^h Muthurajan, H., Sivabalan, R., Talawar, M.B., Asthana, S.N. *J. Hazard. Mater.* **2004**, A112, 17.
- ⁱ Ju, X.-H., Xiao, J.-J., Xiao, H.-M., *Chinese J. Struct. Chem.* **2003**, 22m 223,
- ^j Boileau, J.; Emeury, J.-M.L.; Kehren, J.-P. *U.S. Patent* 4487938 (1984).
- ^k Hu, R.; Lu, X.; Fang, Y. *J. Energ. Mater.* **1993**, 11, 219.
- ^l Zhilin, V.F.; Rudakov, G.F.; Ladonin, A.V.; Sinditskii, V.P.; Egorshhev, V.Yu.; Berezin, M.V. *International Annual Conference of ICT [Proc.]* **2003**, 34, 141/1.
- ^m Zheng, Y.; Zhou, J.; Zhou, D.; Zhang, M. The Synthesis of 1,1,2,2-Tetrakis(Difluoroaminomethylenenitroamino)ethane and its Related Compounds. *Binggong Xuebao*. **1988**(1), 59.
- ⁿ Peng, Z. and Wan, D. Synthetic Study of Tetranitroglycoluril and Its Hydrolyzed Product. *Binggong Xuebao [Acta Armamentarii]* **1980**, 3(3), 23–27.

5.1.1 TNGU

TNGU was first prepared at Picatinny Arsenal in the 1950s (publicly revealed in 1974) (Minskey et al., 1952; Fedoroff and Sheffield, 1974), and was independently developed and patented by French researchers starting in the 1970s (Boileau et al., 1984). TNGU was reported to have a density of 2.02 g/cm³ (Boileau et al., 1984), which is greater than those of RDX (1.816 g/cm³) and HMX (1.902 g/cm³). It was also reported to be more sensitive than both RDX (*H*₅₀ of 40 cm) and HMX (*H*₅₀ of 42–51 cm) with an impact sensitivity *H*₅₀ of 10 cm (Vaullerlin et al., 1998) and a detonation velocity of 9073 meters per second (m/s) (Boileau et al., 1984), which is greater than that of RDX (8741 m/s). Until recently, very few studies of the hydrolysis of TNGU had been reported and only under relatively harsh laboratory conditions, usually intended to determine the mechanism (Peng and Wan, 1980; Hu et al., 1996) rather than the degradation rate under common environmental conditions. One exception is recent work by Chapman et al. (2009), which demonstrated that TNGU is quickly hydrolyzable under humid conditions, providing for possibly fast remediation/demilitarization, but is stable under dry ambient conditions, allowing for its production and processing. Zheng et al. (1988) and Peng and Wan (1980) indicated that TNGU decomposes to glyoxal, nitrous oxide, and water (Figure 4). We have confirmed the presence of glyoxal as one of the early decomposition products via NMR. Boyer et al. (2007) states that "glyoxal will rapidly break down to form carbon dioxide in moist soil and aqueous environments". An extensive study on the breakdown of glyoxal was also reported by Hawari (2006).

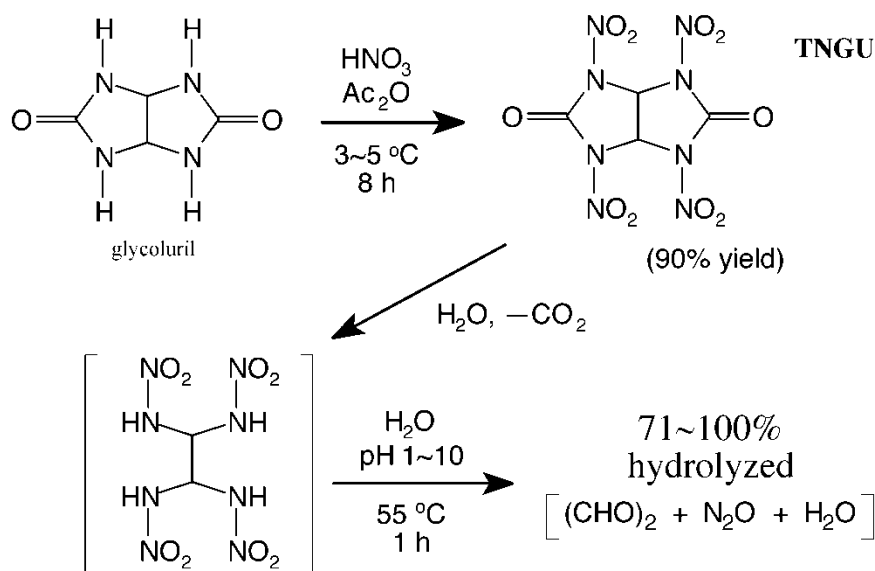


Figure 4. Preparation and suggested hydrolysis mechanism of TNGU (Zheng et al., 1988; Peng and Wan, 1980)

During this project, the TNGU synthesis has been successfully scaled in 5 g, 25 g, 100 g, and 400 g batches with no change in TNGU purity or yield. ^1H NMR (300 MHz, $\text{C}_3\text{D}_6\text{O}$) analysis of TNGU shows a single peak at 7.76 ppm. NMR analysis consistently indicates that a small impurity (<2%) is present, a doublet at 7.62 and 6.65 ppm and a singlet at 9.13 ppm was observed. The splitting pattern suggests a trisubstituted diglycouril. Ross et al. (1978) has reported that the NMR solvent must be scrupulously dry, since any moisture present almost instantaneously gives rise to extraneous NMR peaks attributable, that have inconclusively assigned, to tri- and dinitroglycoluril isomers. We did not attempt to dry the NMR solvents to determine if this minor second species was due to trace water in the solvent.

Helium pycnometry yields a density value of 2.03 g/cm^3 , which is in good agreement with the literature value of 2.02 g/cm^3 (Boileau et al., 1984). A DSC thermogram of TNGU up to $300\text{ }^{\circ}\text{C}$ (at $5\text{ }^{\circ}\text{C/min}$) yields a single, exothermic peak at $215\text{ }^{\circ}\text{C}$ that corresponds to its decomposition.

The safety properties of neat TNGU crystals from different size batches are shown in Table 2. Although TNGU displays no sensitivity to ESD initiation at 0.25 J and only moderate sensitivity to friction initiation, when synthesized in smaller batches, especially the 5 g and 25 g batches, it displayed a significant sensitivity to impact initiation. The impact sensitivity is consistent with other literature reports (Vaullerin et al., 1998) where neat TNGU crystals display impact sensitivity similar to that of PETN (Table 2). High sensitivity to impact initiation presents safe handling concerns, so coatings to mitigate this high sensitivity were evaluated. FluorinertTM FC-43, an inert, non-volatile, polyfluorocarbon-based fluid with low water solubility, was coated onto the TNGU by preparing a slurry of FC-43, pentane, and TNGU followed by evaporation of pentane. As little as 5 wt% FC-43 significantly reduces the impact sensitivity of TNGU (Table 2).

Table 2. Safety data for neat TNGU and FluorinertTM-coated TNGU as compared to PETN and RDX.

Sample	Impact Height (cm)	Friction (lbf)	Electrostatic
TNGU (synthesized in 5 g, 25 g, and 100 g scales)	50% Point: 10 Low Fire: 8	50% Point: 427 Low Fire: 251	10/10 NF at 0.25 J
TNGU (100g scale retested, without clumps)	50% Point: 22 Low Fire: 20	—	—
TNGU (400g Scale)	50% Point: 31 Low Fire: 25	50% Point: 309 Low Fire: 251	10/10 NF at 0.25 J
TNGU coated with 5 wt% Fluorinert™ FC-43	50% Point: 21 Low Fire: 16	50% Point: 427 Low Fire: 398	10/10 NF at 0.25 J
TNGU coated with 10 wt% Fluorinert™ FC-43	50% Point: 26 Low Fire: 25	—	—
PETN	50% Point: 12	50% Point: 262	10/10 NF at 0.25 J
RDX Type II, Class 2	50% Point: 20	50% Point: 537	10/10 NF at 0.25 J

Since the safety data on the initial 5 g batches of TNGU indicated that neat TNGU crystals have impact sensitivity similar to PETN, appropriate care was taken in scaling up the reaction. TNGU crystals were kept solvent-wet until the final vacuum-drying step and were kept from contacting ground glass fittings and fritted glass.

At the 400 g scale we observed a lowering in impact sensitivity from 10 cm to 31 cm. Scanning electron microscope (SEM) images of a 400 g batch and a 50 g batches showed significant differences in the TNGU particles (Figure 5). The 400 g batch particles appear to be somewhat smoother, almost polished, when compared with the particles from the smaller batches. We believe that either the different stirring mechanisms for the different sized batches, or the mechanical action of the particles hitting each other (like a tumbler) made the TNGU in the larger batch smoother, and therefore less sensitive to impact. The materials from the smaller batches had slightly more clumps. The smaller batches were retested after the clumps were broken up, and lower sensitivity was observed (50% point, 22 cm).

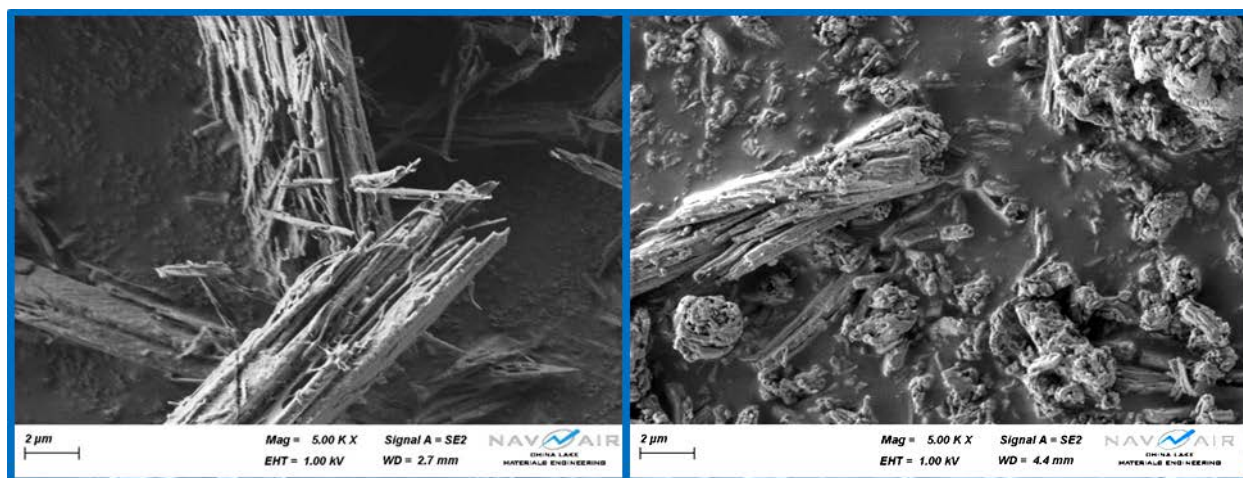


Figure 5. SEM images of as-synthesized TNGU. 50 g batch (left), 400 g batch (right).

The thermal stability of TNGU was examined by VTS at 80 °C and 100 °C for 48 h. A value of less than 2 mL of gases generated per g of materials is considered a “pass”. Analysis of our TNGU at 80 °C has ranged from 2.0 mL/g to 8.8 mL/g. Analysis at 100 °C has ranged from 9.0 mL/g to 21.6 mL/g. The literature reports (Ross et al., 1978) a value of < 1 cc/g at 80 °C for 22 h by a different method, Chemical Reactivity Test (CRT). Since an exact number was not given it is difficult to determine if it would pass at 48 h, but it appears to be a lower value than what we observed. Numerous methods of purifying and drying TNGU were tried to improve VTS values, but the results have been similar. Recrystallized TNGU yielded a sharper peak in the DSC, but still did not pass VTS. VTS was performed back to back on the same sample and evacuated in between runs, and both runs failed. TNGU is very reactive with water or acidic protons at elevated temperatures, and the VTS experiment is a closed system so any water, trace acid, or reactive trace impurities will react with TNGU and cause it to degrade. Isothermal thermogravimetric analysis (TGA) analysis was performed on TNGU for 160 h at 80 °C. The first 80 h (the length of the VTS test) the sample lost 0.6% weight. The sample lost an additional 0.2% weight between 80 h and 160 h. In this test nitrogen gas is passed over the sample, therefore any water or reactive species present is carried away. These results indicate that there might be a contaminant present that either volatilizes or causes the TNGU to degrade until the contaminant is depleted, causing the relatively high VTS results. A calculation was done to estimate the amount of weight loss from TNGU that would generate enough gas to fail the VTS. A weight loss of ~0.4% could generate enough gas to fail the VTS. This calculation provides a guideline for comparing weight loss during TGA analysis to VTS.

TNGU crystals produced directly from the synthesis are small needle-like crystals (Figure 5). The small size and needle-like shape of the TNGU crystals result in large surface areas and limits filler loading in PBX binders. Spherical particles, with mono-disperse size distributions, are preferred for energetic formulations. Therefore, efforts to recrystallize the needle-like TNGU crystals into lower-aspect-ratio morphologies were undertaken.

Crystallization is a complex phenomenon governed by kinetic and thermodynamic parameters that control crystal nucleation and growth processes; hence it remains one of the lesser understood chemical operations (Tung et al., 2009). Crystallization of a solute is brought about by decreasing compounds’ solubility in the mother liquor, which causes saturation and spontaneous

crystal nucleation and growth. For large-scale crystallization unit operations, there are four common methods to adjust the solubility of the solute in the mother liquor (Boileau et al., 1975):

- Anti-solvent crystallization – the solute’s solubility in the mother liquor is decreased by addition of a non-solvent
- Solvent evaporation crystallization – the amount of dissolved solute in the mother liquor is decreased by the removal of solvent
- Temperature-induced crystallization – the solute’s solubility is decreased by cooling the mother liquor
- Reactive crystallization – the solute’s solubility is adjusted by chemical reaction (e.g., as in the precipitation of TNGU from the reaction medium described in the synthesis section)

Methods for recrystallizing TNGU into non-needle-like morphologies have not been previously reported, although Boileau et al. (1975) did describe the preparation of >1 cm-sized TNGU crystals from slow recrystallization in nitromethane and recrystallization of TNGU with unspecified morphology from a 50/50 mixture of nitromethane/dichloromethane (Boileau et al., 1984). Therefore, a number of recrystallization experiments using anti-solvent, solvent evaporation, and temperature-induced crystallization methods with various solvent systems were evaluated, as shown in Figure 6.

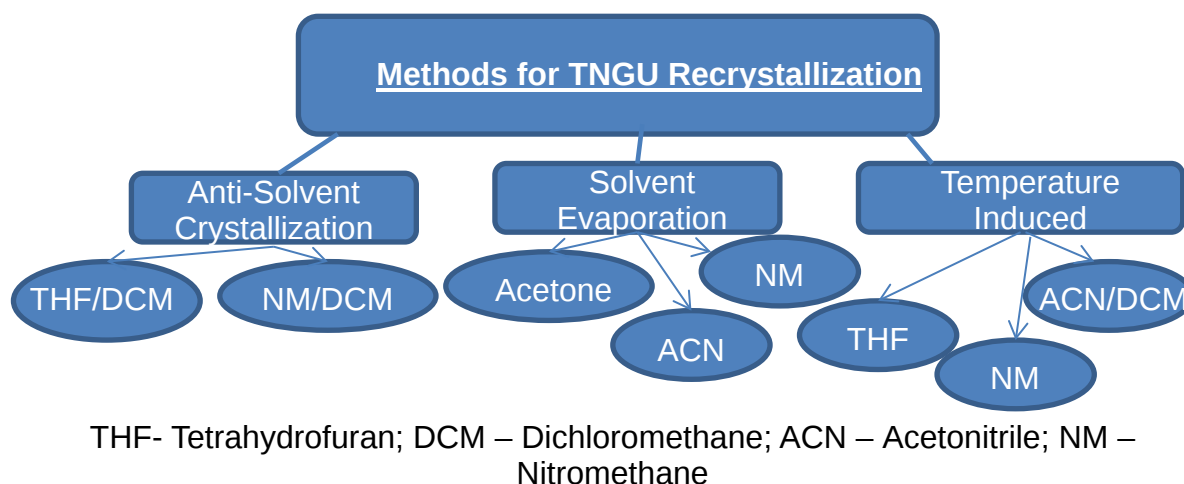


Figure 6. TNGU recrystallization methods and solvent systems.

Solvent evaporation crystallization studies evaluated the evaporation of known solvents (nitromethane, acetone, acetonitrile) from TNGU/solvent solutions at room temperature. All three solvents—over initial concentration ranges of 10–25 mg TNGU per 1 g solvent—yielded long, fragile needles of TNGU within 12 h of evaporation.

Temperature-induced crystallization studies yielded only needle-like TNGU crystals. For temperature-induced crystallization from tetrahydrofuran, TNGU was added to boiling tetrahydrofuran until saturation was achieved. The mother liquor was then allowed to cool to room temperature. Long TNGU needles formed after several minutes at room temperature. Temperature-induced recrystallization of TNGU from nitromethane and acetonitrile/dichloromethane solutions (40/60, 50/50, 60/40 by wt) was attempted at two different temperatures (–3 °C and –18 °C). TNGU concentrations were kept relatively low (10–25 mg TNGU per g of solvent/non-solvent

mixture) to encourage slow growth. However, no TNGU crystals formed after several days at low temperature, indicating that the solutions may never have reached saturation conditions.

Anti-solvent crystallization studies examined the crystallization of TNGU from known solvents such as tetrahydrofuran, acetone, and nitromethane by the addition of a chlorinated non-solvent (dichloromethane). Initial anti-solvent crystallization experiments involved room-temperature dissolution of the TNGU in tetrahydrofuran at saturation conditions (140 mg TNGU per 1 g tetrahydrofuran) followed by the addition of a controlled amount of dichloromethane non-solvent. The molar ratio of tetrahydrofuran to dichloromethane was adjusted from 0.35:1 up to 0.45:1 (tetrahydrofuran to dichloromethane). For the 0.35:1 condition, which corresponds to the highest relative volume of non-solvent, a mixture of crash-precipitated micro-needles and large needle-like TNGU crystals was obtained (see first image in Figure 7). As the crystallization process is slowed down through the reduction of non-solvent volume, large needle-like crystals were obtained (second and third images in Figure 7).

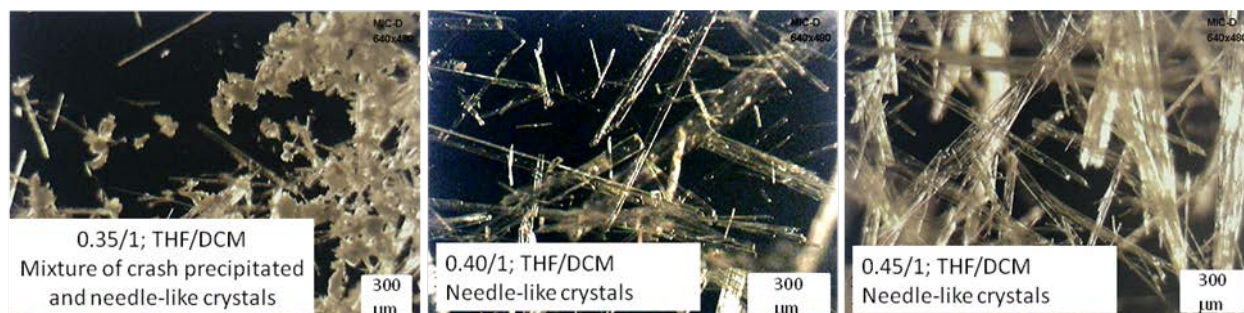


Figure 7. Anti-solvent recrystallization of TNGU from tetrahydrofuran and dichloromethane mixtures.

In an attempt to additionally slow the crystallization process and grow larger crystals, which could later be fluid-energy-milled or ground to non-needle-like shapes, dichloromethane non-solvent vapor was allowed to slowly diffuse into the TNGU–solvent mixture. To begin a diffusion anti-solvent crystallization experiment, TNGU was first dissolved in either tetrahydrofuran or nitromethane. A vial of the TNGU solution was then placed in a closed vessel with dichloromethane. The dichloromethane was allowed to diffuse into the TNGU solution and the solvent was allowed to diffuse out of the mother liquor. After a three-day growth period, the vessels from the tetrahydrofuran–dichloromethane and nitromethane–dichloromethane experiments were inspected. nitromethane–dichloromethane experiments yielded no TNGU crystals, but tetrahydrofuran–dichloromethane experiments yielded several types of recoverable TNGU crystals. Interestingly, as shown in Figure 8, the morphology of the crystals can be adjusted from film-like to cube-like to needle-like by controlling the starting TNGU/tetrahydrofuran concentration. An initial TNGU concentration of 50 mg/g of tetrahydrofuran yielded well-formed cubic crystals which would likely formulate very well in PBX mixtures. Concentrations higher than 50 mg/g TNGU in tetrahydrofuran led to mixtures of needles and cubes (e.g., 63 mg/g in tetrahydrofuran), and saturation concentrations resulted in long needle-like crystals (e.g., 140 mg/g in tetrahydrofuran).

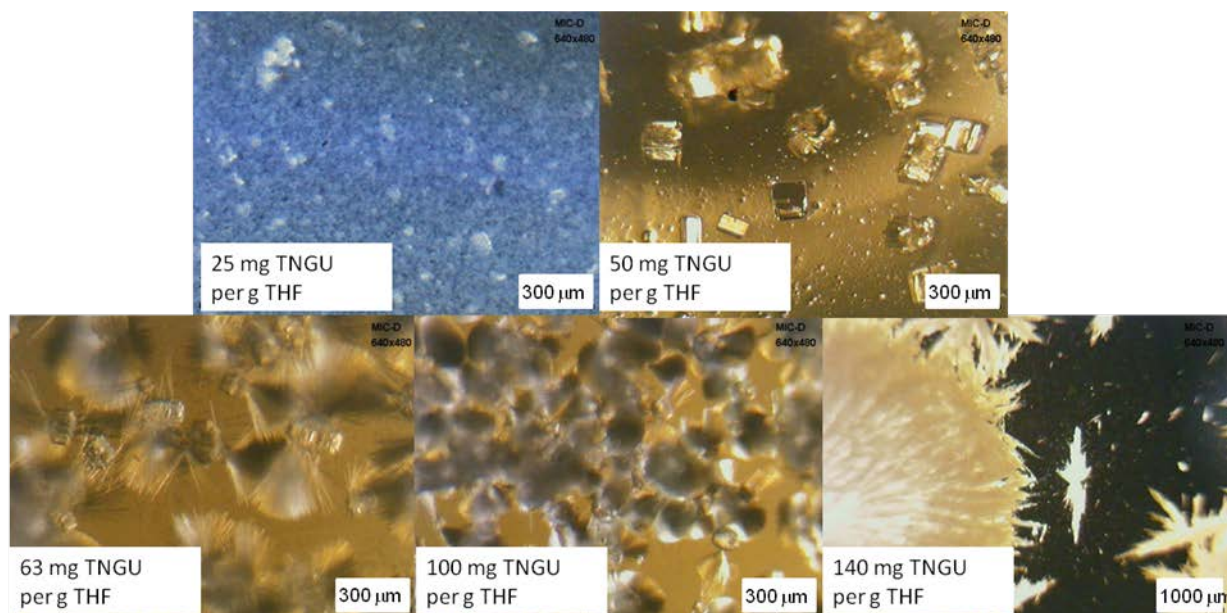


Figure 8. TNGU crystal morphology as a function of the initial TNGU concentration in tetrahydrofuran.

Although the anti-solvent method was able to produce TNGU crystals with a desirable cube-like morphology, the low concentration of TNGU in the mother liquor coupled with the long growth times (~ 3 days) makes the production of pound-scale quantities of TNGU cubes by this method impractical. Therefore, the production of TNGU cubes by a secondary crystal nucleation or seeding process was evaluated. A solution of tetrahydrofuran saturated with TNGU solute was prepared at room temperature (140 mg TNGU/1 g tetrahydrofuran). A small amount of cube-like TNGU seed crystals were then added to the TNGU/tetrahydrofuran solution followed by a volume of dichloromethane. Since the dichloromethane non-solvent induces saturation of TNGU in the mother liquor, TNGU is driven out of solution. Molar ratios of 0.35:1 and 0.40:1 tetrahydrofuran-to-dichloromethane were selected because previous anti-solvent recrystallization studies indicated that these ratios cause prompt crystallization of TNGU. Both seeding conditions resulted in the rapid growth of small needle-like crystals within 10 min of non-solvent addition; unfortunately, no cube-like crystals were produced. Recrystallization from acetone/dichloromethane yields needles. Single crystal x-ray analysis showed that an acetone adduct was formed. Figure 9 shows the ORTEP of TNGU and Table 3 shows some of the crystallographic data.

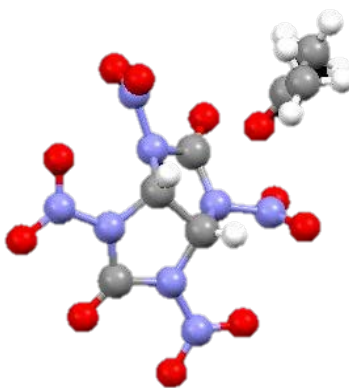


Figure 9. ORTEP of TNGU – acetone.

Table 3. TNGU crystallographic data.

Space Group	Pca2 ₁
Cell Length	a 24.713 b 6.4360 c 18.899
Cell Angles	α 90 β 90 γ 90
Cell Volume	3005.94
Z	8
Rf	4.82%

Recently Sherrill et al. (2015) has reported a method for forming spherical TNGU. The spherical particles were formed by dissolving the TNGU in 100% nitric acid then adding drop wise below the surface into dichloromethane. They were able to recover ~73–74% of the material. However the method is solvent intensive 823 mL of acid for 2.3 g of TNGU. The thermal stability by DSC or VTS wasn't reported.

5.1.2 TNSUK

TNSUK is also a cyclic *N,N'*-dinitrourea that can be decomposed by water. The synthesis of TNSUK from pentaerythrityl tetrabromide was reported by Chinese researchers in 1992 (Fu and Fu et al., 1992). TNSUK was reported to have a density of 1.91 g/cm³, which is greater than those of RDX (1.816 g/cm³) and HMX (1.902 g/cm³). It was also reported to be less sensitive than both RDX (*H*₅₀ of 40 cm) and HMX (*H*₅₀ of 42–51 cm) with an impact sensitivity *H*₅₀ of 63 cm and a detonation velocity of 8670 meters per second (m/s), which is slightly lower than that of RDX (8741 m/s).

The synthesis of TNSUK was successfully performed on the 5 g scale. The Chinese literature reported a 50% impact value of 63 cm however we observed a 50% impact value of 17 cm (RDX Type II, Class 5: 16 cm). This difference may be due to a different crystal polymorph. There is some moderate friction sensitivity, a 50% value of 513 lb (RDX Type II, Class 5) was observed. The product is however ESD sensitive, 20/20 NF @ 0.06 J (RDX Type II, Class 5: 20/20 NF @ 0.25 J) was observed. The density of 1.8472 g/mL was measured by helium pycnometry. This value is lower than the density reported by Chinese researchers (1.91 g/cm³) and that obtained from the x-ray diffraction (1.913 g/cm³), suggesting that the material formed in the reaction may not be the highest density polymorph.

The thermal stability of TNSUK was determined by DSC, TGA, and VTS. The DSC showed an exotherm at 239 °C with an onset temperature of ~229 °C. TGA analysis of TNSUK exhibited a ~15% weight loss at 181 °C and a 65% weight loss at ~222 °C. Long term isothermal TGA at 100 °C for 48 h showed a 1.6% weight loss. VTS of two 1 g samples of TNSUK at 100 °C for 48 h produced 1.2 mL/g of gas. Although the values are moderately high compared to most PBX's it is still a "pass".

The TNSUK recovered from the reaction was a white powder which is not optimal for processing in a formulation. Therefore we explored if we could recrystallize TNSUK in a different crystal morphology that was better suited for formulations. TNSUK is readily soluble in acetone and is insoluble in dichloromethane. Large cubes were obtained by the slow vapor diffusion of dichloromethane into a solution of TNSUK in acetone. Fast diffusion of dichloromethane into acetone or acetonitrile results in needles. Diffusion of dichloromethane into a solution of TNSUK in acetonitrile yielded crystals of suitable size for single crystal x-ray analysis.

Select crystallographic data, collected at 223 K, is shown in Table 4. There was significant disorder in the crystal at one nitro- group oxygen site. The disorder was modeled by splitting the oxygen atoms. An R factor of 5.76% was obtained for the orthorhombic crystal system, with a calculated density of 1.854 g/cm³. The TNSUK crystals exhibited sharp, smooth facets, and were mostly octahedral, but many had additional twinned growth (Figure 10). Figure 11 shows the ORTEP of TNSUK.

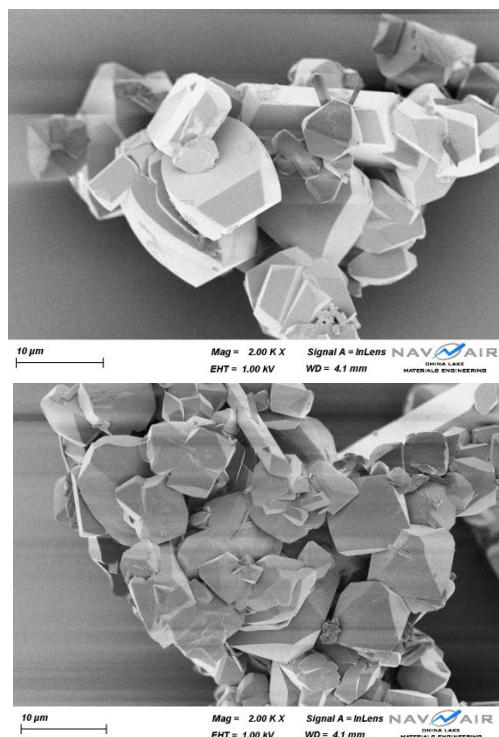


Figure 10. SEMS of as-synthesized TNSUK crystals

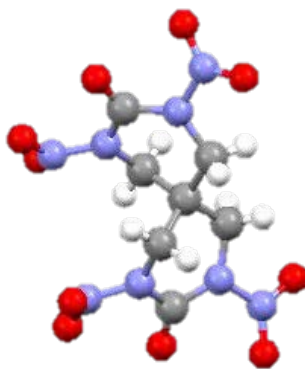


Figure 11. ORTEP of TNSUK

Table 4. TNSUK crystallographic data.

Space Group	Pccn
Cell Length	a 8.1127 b 10.1376 c 15.8632
Cell Angles	α 90 β 90 γ 90
Cell Volume	1304.64
Z, Z'	4, 0
Rf	5.76%

5.1.3 HHTDD

HHTDD was another possible explosive candidate that may potentially exhibit hydrolyzable characteristics. HHTDD first appeared in Chinese literature in the early 1980s (Ma and Lu, 1980; Hu et al., 1981), though it was not reported in Western literature until 1991 (Vedachalam et al., 1991). HHTDD was reported to have a density of 2.07 g/cm³ (Hu et al., 1993), which is greater than that of ϵ -CL-20 (hexanitrohexaazaisowurtzitane) (2.04 g/cm³). It was also reported to have a detonation velocity of about 9750 meters per second (m/s) (Hu et al., 1993), which is greater than that of RDX (8741 m/s). DSC of HHTDD shows decomposition at 215 °C. HHTDD was synthesized at a 5 g scale. Overall, HHTDD was difficult to synthesize and purify. In addition it hydrolyzed faster than TNGU raising concern about how it would perform during the VTS testing. HHTDD was not investigated further.

5.2 PBX

TNGU was selected as the energetic ingredient to be incorporated into a PBX formulation. The TNGU PBX was scaled up to a 250 g batch. Ultimately we were unable to pass VTS testing with TNGU PBX formulations. Late in the project we performed a small 5 g PBX mix with TNSUK to determine if the lessons learned from developing a TNGU PBX would apply to a different hydrolyzable PBX. Preliminary hydrolysis data for TNSUK PBX was obtained. HHTDD was not incorporated into a PBX primarily because it exhibited faster hydrolysis than TNGU, and we believed that it would exhibit the similar problems during VTS testing. In addition, purification of HHTDD was difficult and obtaining enough pure HHTDD for a small mix was problematic.

The formulation of self-remediating PBXs, in principle, follows a similar mixing procedure as for conventional PBXs: the solid energetic filler is mixed into the liquid binder prepolymers, curatives, and plasticizers, followed by casting and curing the formulation into the desired end-use article. However, because self-remediating PBXs must readily hydrolyze upon exposure to small amounts of moisture, the selection of formulation ingredients, namely, binder prepolymers and curatives, was afforded some special consideration. Initially, it was thought that an ideal binder system for a self-remediating PBX must facilitate fast transport of water throughout the explosive charge in order to quickly neutralize the energetic fill. Previous research had examined polyethylene glycol adipate (PEGA) binders for explosive and propellant formulations that hydrolyze upon exposure to liquid water (Lee, 1992; Chan et al., 2000). Although the primary focus of those efforts was the recovery of the non-hydrolyzable energetic fillers (e.g., RDX, ammonium perchlorate, aluminum) for demilitarization of aged energetic formulations, the hydrolysis properties of the PEGA binder were extensively characterized. The hydrophilicity of the PEGA binder and the presence of electron-withdrawing groups in the vicinity of the ester linkage facilitate binder decomposition upon exposure to water (Adil et al., 2004).

In addition to PEGA, other common PBX binders such as hydroxy-terminated polybutadiene (HTPB), LMA and EHA were also evaluated. Initial chemical compatibility testing of the TNGU explosive with each of the proposed binder systems, was conducted before picking the most suitable binder with which to proceed.

The processing of the PBX formulations were conducted using either a planetary style Baker Perkins (BP) mixer or a newer mixing technology, Laboratory Scale Resonant Acoustic™ Mixer (LabRAM®) (Figure 12). The planetary BP mixers are high sheer bladed mixers that are the industry standard for processing highly solids filled energetic composite material. The newer LabRAM® technology utilizes vibration waves in the place of impeller blades to rapidly homogenize high viscosity composites. While the BP mixers have a long history of successful processing with PBX materials the new LabRAM® technology offers some advantages such as reduced mixing time and the ability to process materials with higher viscosities than what are currently processed using the BP mixers. We have evaluated both technologies for the production of the TNGU based PBX. The LabRAM® was ultimately used for most of the processing. It was more efficient and enabled us to achieve the desired high solids loading.



Figure 12. Mixing Technologies evaluated to prepare the high solids loaded TNGU PBX. Left – Baker Perkins (BP) planetary style impeller mixer. Right – Laboratory Scale Resonant Acoustic Mixer (LabRAM®).

5.2.1 TNGU PBX

Chemical compatibility testing of the TNGU explosive with each of the proposed binder prepolymers and curatives was conducted before picking the most suitable binder system. Generally, negative shifts of greater than 20 °C indicate chemical incompatibility that would result in unstable PBX formulations. As shown in Figure 13, the mixture of TNGU and PEGA has a very large shift in decomposition temperature (−82 °C) which prohibits the use of the well-known PEGA binder system in TNGU PBX formulations. The compatibility of TNGU with a second well-known explosive binder, HTPB, was also evaluated, and a large shift in mixture decomposition temperature was also obtained. Lysine triisocyanate (LTI), a curative for the hydroxy-terminated prepolymers, is seen to be incompatible with TNGU as well. It is possible that hydroxyl and isocyanate groups promote rapid hydrolysis of TNGU at elevated temperatures.

Due to the suspected reactivity of the hydroxyl and isocyanate end groups, binder systems that utilize alternative cure chemistries—and hence possess different end groups—were evaluated in compatibility tests with TNGU. The triazole cure, which is achieved by a 1,3-dipolar cycloaddition of azide and acetylene functional groups, has been evaluated as a novel cure chemistry for propellants and explosives (Katritzky et al., 2006). Although the acetylenic curative trimethylolethane tripropiolate (TMEoETP) shows relatively good compatibility with TNGU, the polyethylene glycol (PEG) and polycaprolactone (CAPA7201A) diazide polymers have poor compatibility with TNGU.

LMA and EHA, two very commonly used acrylate binders in current state-of-the-art PBXs, were compatibility-tested with TNGU. Both LMA and EHA were found to have suitable chemical compatibility with TNGU. A hydrophilic methacrylate, methoxypolyethylene glycol (MPEG 550) methacrylate, was evaluated since it was hypothesized that the hydrophilicity of the binder backbone might help facilitate water transport, but its poor compatibility with TNGU does not permit its use in formulations.

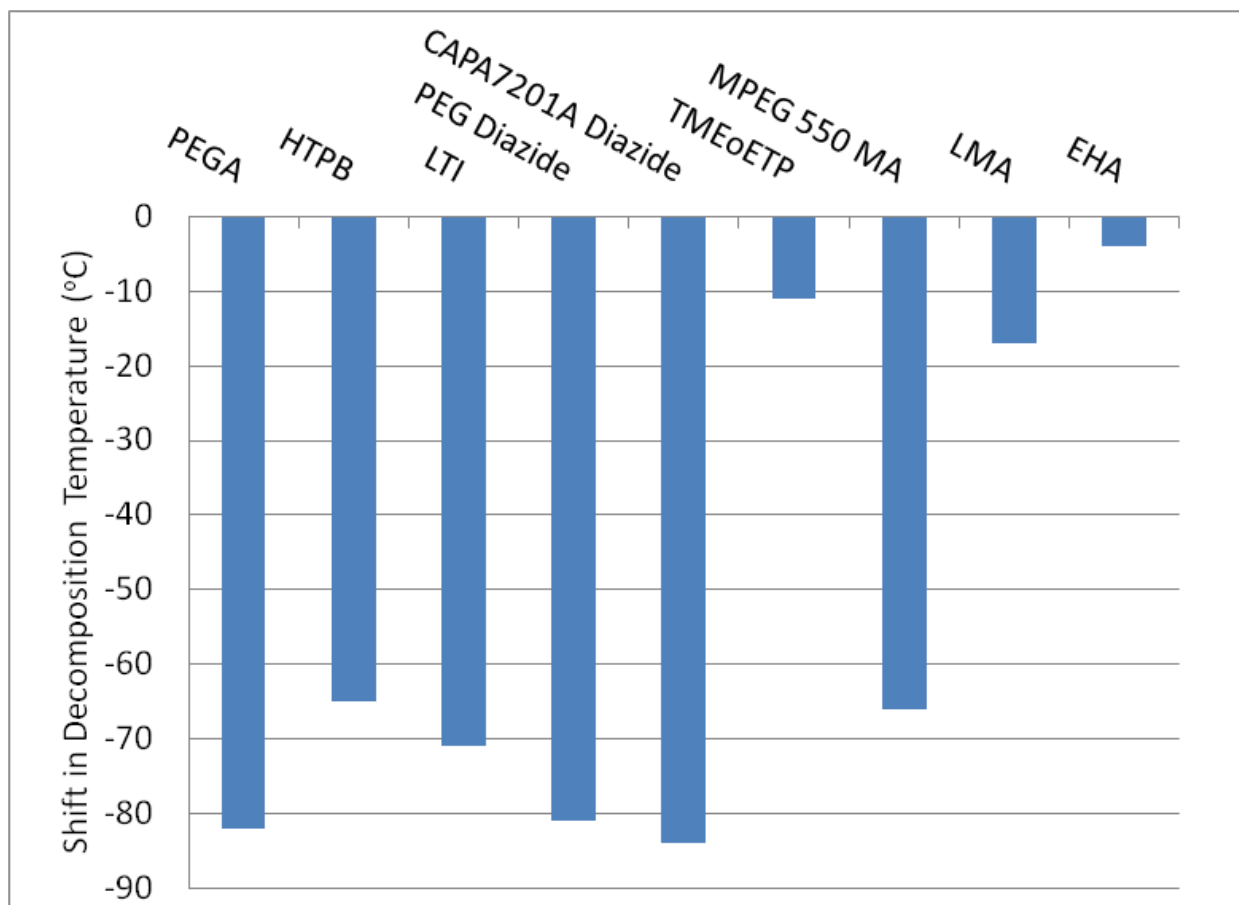


Figure 13. Compatibility studies of TNGU with various binder prepolymers and curatives.

Hand-mixes of TNGU PBXs (5 g scale) were formulated with both the LMA and EHA binder systems. To initiate curing in acrylate binder systems, a very small amount of organic peroxide combined with a very small amount of cobalt catalyst is added to the acrylate binder. Crosslinking of the PBX is achieved through the addition of a small amount of triethylene glycol dimethacrylate (TEGDMA). The ingredients and weight percentages of a generic TNGU PBX formulation are shown in Table 5.

As-synthesized TNGU crystals (as shown in Figure 5) were used in initial hand-mixes. Due to the high surface area of the needle-like TNGU crystals, a maximum of 75 wt% filler could be incorporated using hand-mixing techniques. At 75 wt% TNGU the PBXs were cured into hard but flexible rubbers over 16 h at 43 °C.

The safety properties of cured TNGU PBXs compared to the explosive PBXN-107 are shown in Table 6. Incorporation of TNGU into the PBX formulation is seen effectively to mitigate the high impact sensitivity observed for neat TNGU crystals. The impact sensitivity of both PBXs is less than that of PBXN-107.

Table 5. Generalized TNGU PBX formulation.

Ingredient	% by Weight
TNGU	68–82
Acrylate Binder (LMA or EHA)	17.8–31.8
TEGDMA, Initiators/Catalysts	0.2

Table 6. Safety properties of TNGU PBXs.

Sample	Impact Height (cm)	Friction (lb)	Electrostatic
TNGU(75 wt%), LMA(25 wt%) PBX	50% Point: 42 Low Fire: 40	10/10 NF at 1000 lb	10/10 NF at 0.25 J
TNGU(68 wt%), EHA(32 wt%) PBX	50% Point: 40 Low Fire: 40	10/10 NF at 1000 lb	10/10 NF at 0.25 J
PBXN-107	50% Point: 32 Low Fire: 32	20/20 NF at 1000 lb	20/20 NF at 0.25 J

DSC analysis of the TNGU PBX formulations showed a single, narrow exothermic peak. The peak decomposition temperatures of the LMA–TNGU and EHA–TNGU formulations were 194 °C and 199 °C, respectively.

The performance target for TNGU self-remediating PBXs is a detonation velocity equivalent to PBXN-107 since self-remediating explosives could potentially replace the current PBXN-107 bomblet fill for the BLU-97 submunition. Provatas (2003) reports that the formulation PBXN-107 contains 86% RDX with 14% binder ingredients and has a Cheetah-calculated detonation velocity of 7690 m/s. Cheetah calculations for the TNGU PBX indicate that an 82 wt% loading of TNGU is required to match the detonation velocity of PBXN-107. Notably, the density of TNGU PBXs is higher than that of PBXN-107 due to the higher crystal density of TNGU (2.03 g/cm³) relative to RDX (1.81 g/cm³). Therefore, the detonation pressure of TNGU PBXs will be higher than that of PBXN-107 at the same detonation velocity.

Since 82 wt% TNGU is necessary to match PBXN-107's performance the use of the planetary style BP mixers was abandoned due to the viscosity at this solids loading. In place of the BP mixers, a relatively new technology, LabRAM[®], was evaluated. The LabRAM[®] is rapidly gaining popularity in as an alternative mixing technique in the energetics community. LabRAM[®] is capable of dispersing high weight-fractions of high-surface-area particles into small amounts of

liquid (Howe et al., 2007; Cross et al., 2012), without the use of impeller blades. LabRAM[®] facilitates the mixing of high solids loaded composites through application of high-intensity, low-frequency acoustic waves. The localized shear fields that result from the application of the acoustic waves result in bulk flow and mixing. Previous programs at the Naval Air Warfare Center, Weapons Division (NAWCWD) have shown that LabRAM[®] can quickly and effectively process and mix viscous propellant and explosive formulations even when the formulation viscosity would prohibit successful mixing with conventional mechanical mixing technologies. An initial hazards analysis to gauge the response of TNGU PBXs to resonant acoustic energy input was conducted by preparing 1 g and 5 g mixtures of TNGU and acrylate binder (1:1). The TNGU–binder mixture was processed on a LabRAM[®] at 100% mix intensity (acceleration of ~100 g) for 10 min. No unusual temperature rises or physical changes in the mixtures' appearances were noted.

After completion of the hazards analysis, a 25 g quantity of the TNGU formulation (as shown in Table 5) with 82 wt% TNGU and 17.8% EHA was prepared in the LabRAM[®]. A photograph of the LabRAM[®] with a stainless steel mix vessel assembly is shown in Figure 14.



Figure 14. Photograph of LabRAM[®] mixer with stainless steel mix vessel.

As previously reported (Katritzky et al., 2006), the LabRAM[®] mix vessel assembly is fabricated from a stainless steel beaker that is compressively sealed against a gasketed aluminum lid. The first step of the mixing process involves weighing the liquid ingredients (acrylate binder, TEGDMA, initiator, and catalyst) into the mix vessel. The TNGU powder is then incrementally added to the mix vessel in three addition steps to facilitate fast and homogenous wetting of the

TNGU crystals by the liquid binder ingredients. After each addition of TNGU powder, any residue on the bottom or walls of the mix vessel is recombined into the bulk mix with a spatula. The far left image in Figure 15 shows a 25 g 82 wt% TNGU mix after several LabRAM[®] mix cycles. The TNGU powder has been completely wetted by the liquid binder and has been formed into small spherical particles. After curing, these small particles of TNGU PBX were cross-sectioned and visually inspected. The TNGU crystals appeared to be uniformly distributed throughout the binder matrix; the TNGU crystals were also strongly bound into the binder matrix. Although the TNGU crystals appeared to be homogeneously distributed throughout the binder system, the development of a fully dense, consolidated PBX (rather than small PBX particles) is necessary for the end-use application of the hydrolyzable explosive formulation.

Mixing intensity, mixing time and the empty volume of the mixing vessel have been cited as important parameters that strongly influence the processing of viscous materials in the LabRAM[®] unit. Hence, the consolidation of TNGU PBX particles was evaluated over a series of several mixes that varied the mix intensity (90 *g* – 40 *g*), the mix time (110 – 170 min), and the empty volume inside the mix vessel (72% – 95% void volume). It was found that the application of lower-intensity acceleration (60 *g* or less) over long periods of time with less mixing-vessel-void-volume improved the consolidation of the TNGU formulation as shown in Figure 15. At higher mixing intensity, the large vibrational amplitude causes the PBX formulation to decouple (or break away) from the mix vessel walls and results in poor energy transfer between the LabRAM[®] and the PBX formulation. Mixing at lower intensity allows the PBX formulation to couple with the mix vessel walls and enables efficient transfer and good bulk flow of the formulation ingredients. The empty or void volume of the mix vessel also affects the energy coupling of the PBX formulation with the mix vessel walls. Smaller void volumes maximize the interaction of the PBX with the mix vessel walls and result in more efficient energy coupling than large mix vessels. Within the efforts to formulate consolidated PBXs with 82% by weight TNGU at the 50 g scale using LabRAM[®], new mix vessels that contain only 50% void volume when filled with 50 g of TNGU PBX that can be inserted into the LabRAM[®] jacked mixing vessel were fabricated by Resodyn Acoustic Mixers Inc. and provided to NAWCWD. These new vessels allow for better control of the temperature within the LabRAM[®] mix container independent of the mix acceleration or mix duration. In the end the development of a fully dense, consolidated PBX formulation with 82% TNGU was accomplished at the 50 g scale (Figure 16).

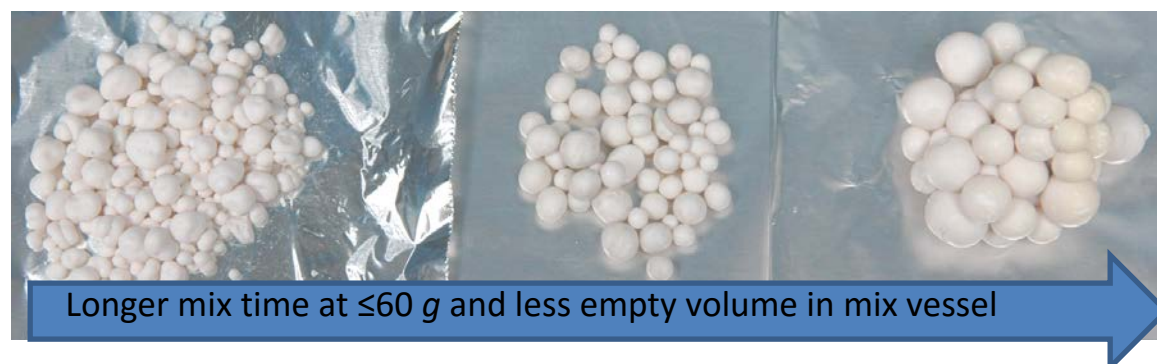


Figure 15. Effect of mixing intensity, mixing time, and mix vessel empty volume on the consolidation of TNGU PBXs in the LabRAM[®].



Figure 16. Consolidated TNGU PBX sphere (82% TNGU, 50 g scale).

As mentioned above, numerous binder system ingredients were tested with TNGU for compatibility. LMA and EHA binder systems were both found to have suitable chemical compatibility with TNGU. Further compatibility testing using VTS testing indicated the EHA formulations to be more stable than those with LMA. Furthermore samples evaluated qualitatively for elasticity and mechanical strength indicated that the EHA formulations were superior to the LMA formulations. For these reasons EHA was originally selected for scale-up as the TNGU based PBX binder.

Processing the TNGU PBX under reduced pressure

Because of the novelty of the LabRAM[®] technology, the ability to mix under reduced pressure — a key LabRAM[®] process parameter — was not available during the early stages of the TNGU PBX formulation. Reducing the pressure in the mixing container promotes better energy coupling between the composite formulation and the resonant mixer which induces better mixing of the formulation. Furthermore the reduced pressure helps to remove voids caused by air entrapped during the mixing process. The ability to mix under reduced pressure was integrated into the TNGU PBX LabRAM[®] process at the same time the efforts to scale up the EHA based TNGU PBX began. It was discovered is that under reduced pressure the EHA binder would condense on the lid of the mixing vessel as well as in the vacuum lines leading to the vacuum pump. Under these conditions the EHA would not be homogenously incorporated in to the TNGU composite which lead to poor mixing and poor PBX production. The relatively high vapor pressure of EHA led to poor mixing under reduced pressure. To overcome the limitations of the EHA binder at reduced pressure, the formulation switched to the LMA based binder. One additional change that was made to the binder system was to eliminate the use of the crosslinking agent. Because of the high solids loading and the irregular shape of the TNGU crystals, it was not necessary to use a cross linking agent such as TEGDMA in order to form a firm cured composite rubber. Instead the removal of the crosslinking agent resulted in the composite PBX that was firm but still soft enough to trim without cracking and flaking.

Like the EHA based PBX, the LMA based TNGU PBX suffered from poor VTS results which are detailed elsewhere in this report. Despite these repeated failing of the VTS test, scale up of the LMA based PBX was granted by the NAWCWD New Materials Committee (NMC) up to the 250 g scale. This scale allowed us to prepare the samples necessary to evaluate the detonation

performance of the new PBX as well as the hydrolytic decomposition of a larger bulk sample of the PBX. The detonation performance of the new PBX was demonstrated with unconfined detonation velocity measurements. For both the detonation velocity measurements and the bulk hydrolytic decomposition tests, the samples had to be cut from a cured 250 g batch of the PBX.

The performance target for TNGU self-remediating PBXs is a detonation velocity equivalent to PBXN-107. A Cheetah-calculation for the detonation velocity of PBXN-107 is 7690 m/s (Provatas, 2003). The reported detonation velocity of PBXN-107 at 1.64 g/cm³ is 8120 m/s. The 6% discrepancy between the predicted and actual values for detonation velocity is due to the non-ideal nature of the composition PBX and is common to most cast cured composite PBXs. As stated previously, Cheetah calculations for the TNGU PBX indicate that an 82 wt% ($d = 1.67$ g/cm³) loading of TNGU is required to match the detonation velocity of PBXN-107.

5.2.2 TNSUK PBX

A 5 g mix of TNSUK was accomplished on the LabRAM[®] to verify that the lessons learned during development of a TNGU PBX could be applied to other hydrolyzable PBXs. The same binder (LMA 17.889%) and curative (CoAcAc2 0.008%, Luperox 0.096%) as the TNGU formulation was used. The liquids were loaded first then the solids. The solid slowly came together to form a solid mass. We were able to achieve a solid loading of 82% TNSUK. The sample was then cured at 43 °C for 7 days. After 7 days the sample was examined to verify that it cured. The solid was dry and chalky; it appeared that that oxygen poisoning had occurred. A preliminary hydrolysis experiment was performed (Section 5.3.2.2) to verify that hydrolysis can be monitored for a TNSUK PBX.

5.3 PBX Characterization and Performance

5.3.1 Thermal Stability

The thermal stability of TNGU PBX was examined by VTS at 50 °C, 60 °C, 70 °C, 80 °C, 90 °C and 100 °C for 48 h. A value of less than 2 mL of gases generated per g of materials at 100 °C is considered a “pass”. Analysis of TNGU PBX ranged from 1.8 mL/g to 74.9 mL/g (Figure 17). The gas generated by the TNGU PBX at 100 °C (74.92 mL/g) is considerably higher than that seen for neat TNGU at 100 °C (9.0 mL/g to 21.6 mL/g) indicating that the PBX is much less thermally stable than the neat TNGU. The rapid generation of gases during the first few hours is most likely due to impurities generated during the TNGU PBX mixing process, including TNGU degradation products. However, the steady linear production of gases after about 5 h is probably due to a thermal instability, with the rate of gas production approximately doubling every 10 °C (Table 7). Table 7

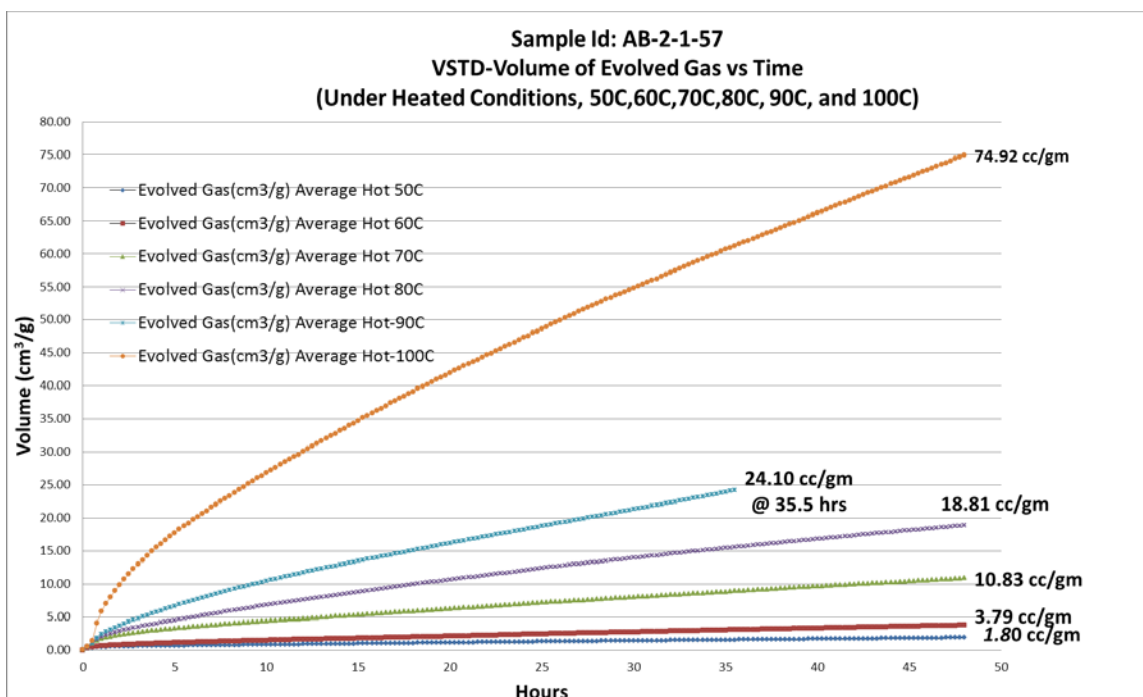


Figure 17. VTS analysis of TNGU PBX at 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, and 100 °C. The analysis at 90 °C was stopped early because the amount of pressure generated exceeded the capability of the pressure transducer. The analysis at 100 °C used a much smaller sample size to avoid this problem. The extrapolated quantity of gas generated at 90 °C at 48 h was 30.47 mL/g.

Table 7. TNGU PBX gas production rate.

Sample	Gas Production rate (mL/h, 20 h to end of run)
50 °C	0.03
60 °C	0.06
70 °C	0.17
80 °C	0.29
90 °C	0.51
100 °C	1.16

Simulated Bulk Auto-ignition Temperature (SBAT) testing was performed with TNGU PBX using a slow ramp (13 °C/h) to provide an indication of the bulk auto-ignition temperature (critical temperature, T_c). As shown in Figure 18, the temperature began to rise slightly below 100 °C, and the onset temperature was reported as 109 °C. SW010-AG-ORD-010 reports that the T_c of PBXN-107 is 108 °C and the “pass” criterion is greater than 82.2 °C. SBAT testing at 83 °C

(isothermal) was conducted on the TNGU PBX for seven days. The sample temperature remained constant, indicating that the T_c is above 83 °C (Figure 19).

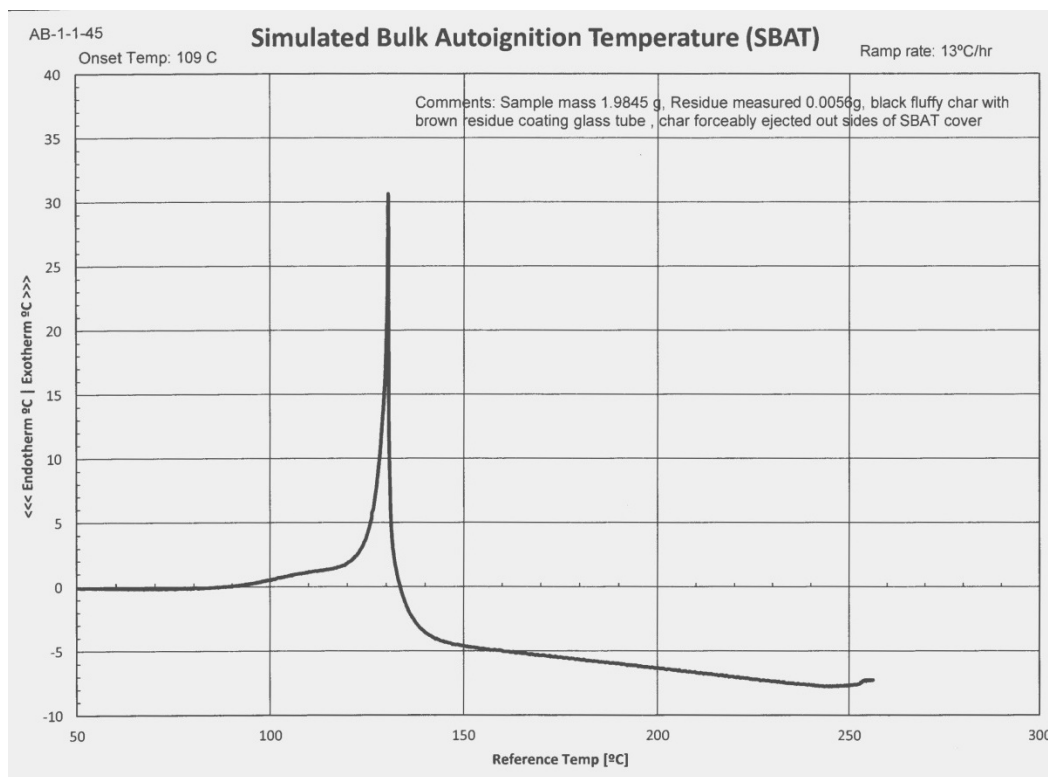


Figure 18. SBAT slow ramp (13 °C/h).

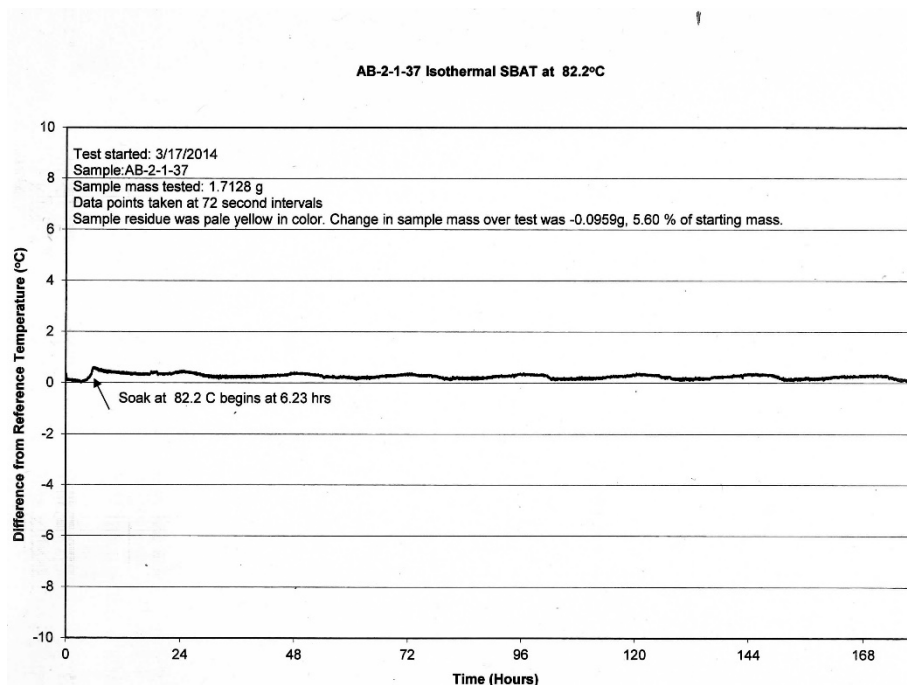


Figure 19. Isothermal heating of TNGU/LMA PBX at 83°C for one week.

5.3.2 Hydrolysis

5.3.2.1 TNGU PBX

5.3.2.1.1 Small Scale Hydrolysis

In preliminary experiments, approximately 90% of the TNGU content was hydrolyzed after 12 days of exposure to D₂O. Degradation of the PBX in moist soil also displayed a similar degradation profile as a function of time. These preliminary hydrolyzability results are encouraging and indicate that the TNGU PBXs will quickly degrade to environmentally benign products upon exposure to liquid water and thereby eliminate the health and environmental hazards of UXO.

Determination of the rate of hydrolysis of TNGU inside a PBX formulation requires a variation of the aforementioned method since the PBX binder system is insoluble in NMR solvents. Insoluble materials cannot be observed via solution-state NMR spectroscopy previously used. Commonly used solid-state NMR spectroscopy typically generates spectra with broad and less resolved peaks that are, in addition, often difficult to quantify. The less commonly used HR-MAS NMR spectroscopy is known for its ability to provide liquid-like resolution spectra of semi-solid/gel-like materials (Schnell, 2005; Power, 2011; Krikštopaitis, 2013) in addition to dissolved substances. Solids or materials having very slow segmental or chain motion cannot be observed via HR-MAS NMR. Generally when an organic material is in a gel-like state, its molecular motion is faster than that of a solid and slower than that of liquids. When the entire molecule is in a gel-like state, quantification is possible.

Preliminary attempts were made to obtain gel-like samples of a TNGU PBX formulation that was prepared by hand-mixing 68 wt% TNGU with 31.8% LMA and 0.2% initiators/crosslinkers. The LMA binder was found to gel in the presence of CD₂Cl₂ or CDCl₃, but the TNGU remained insoluble. TNGU is soluble in CD₃CN, but the binder would not gel fully. The TNGU PBX formulation became gel-like in the presence of a 50/50 mixture of CD₃CN–CD₂Cl₂. The ¹H HR-MAS NMR spectrum is shown in Figure 20. In the spectrum can be seen the cured LMA binder and the TNGU. The area under each peak is a representation of the amount of substance found in the formulation; therefore, the amount of TNGU in the binder can be determined/verified by ¹H HR-MAS NMR spectrometry. This can be done as long as the binder is fully in a gel-like state. It is interesting to note that ¹H HR-MAS NMR spectroscopy can also be used to determine if the binder system has completely or incompletely cured. Slightly incomplete cure in this spectrum can be recognized by the presence of the peaks near 6.3 ppm.

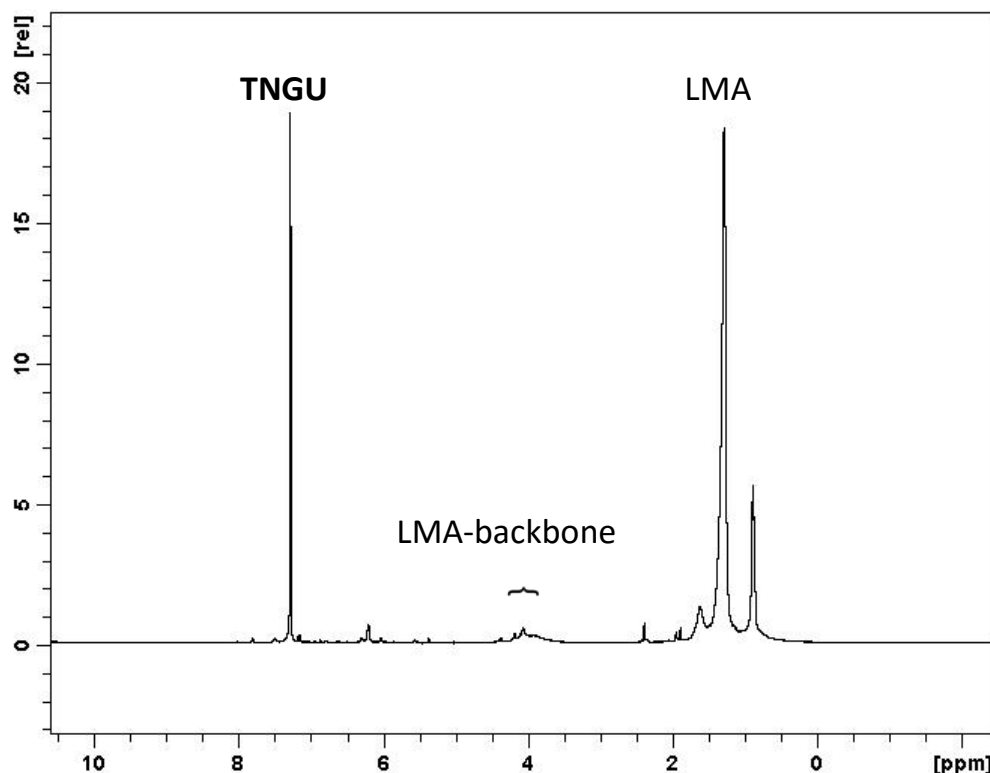


Figure 20. ^1H HR-MAS NMR spectrum of LMA-TNGU PBX in $\text{CD}_3\text{CN-CD}_2\text{Cl}_2$.

An initial ^1H HR-MAS NMR experiment was conducted to confirm that it is feasible to determine the degradation rate of a TNGU PBX. A stack plot of the NMR spectra of the tube containing the swollen TNGU PBX exposed to D_2O is shown in Figure 21 as a function of time. At time zero, the PBX sample contains predominantly TNGU. After two hours of exposing the swollen PBX to D_2O , the TNGU concentration decreases and a sizable TNAE peak appears. After ~ 7 h, TNGU is completely hydrolyzed. The peak areas associated with TNGU and TNAE can be quantitatively analyzed, and the plot in Figure 21 (b) shows the relative mole percentages of TNGU and TNAE as a function of time exposed to D_2O . Hence, it is seen that the ^1H HR-MAS NMR methodology *can* be used to quantitatively analyze the relative concentration of TNGU and TNAE in PBX formulations. TNAE in the formulation was stable enough to readily be observed during this study of the formulation, but not in the initial hydrolytic decomposition studies with TNGU alone.

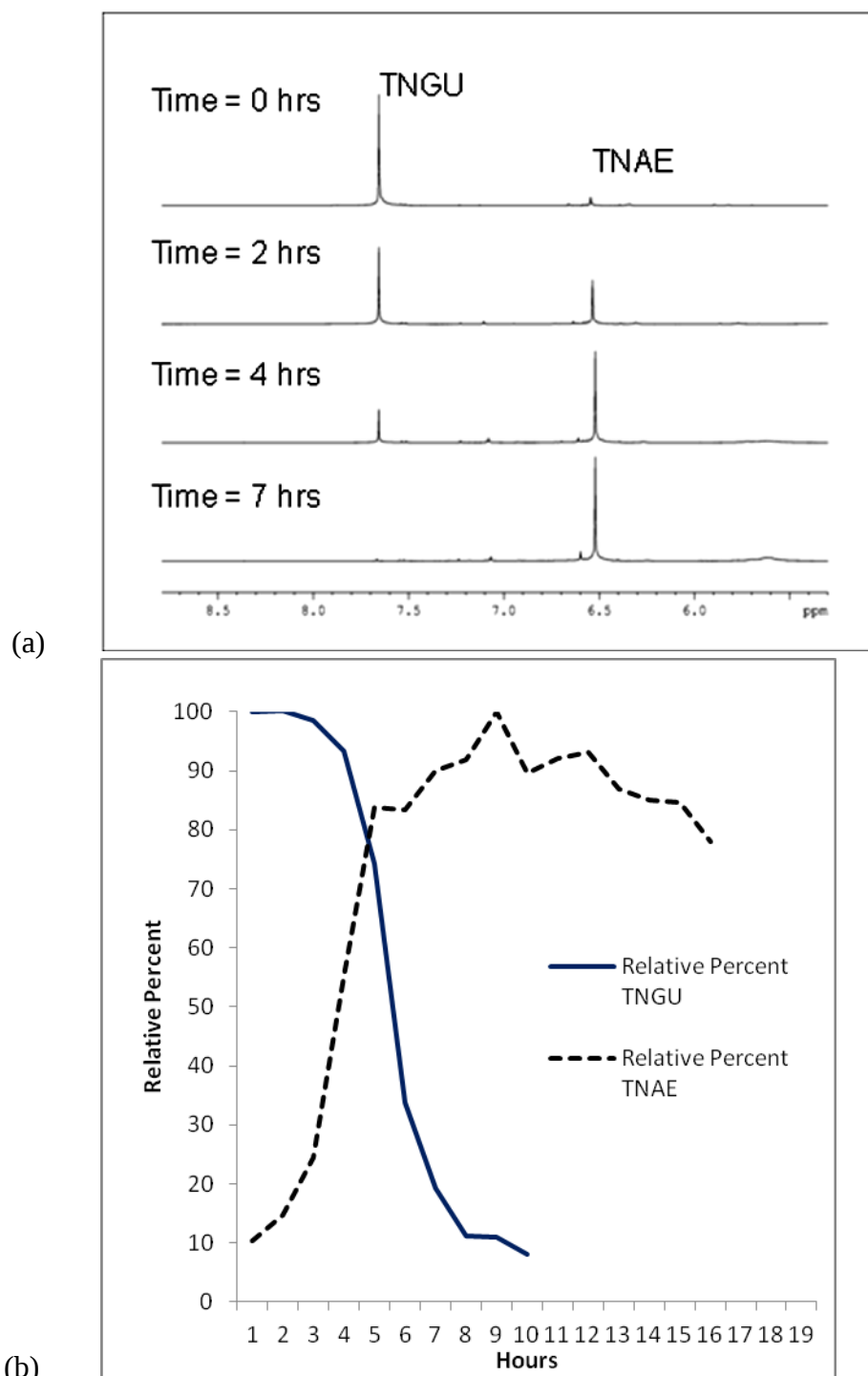


Figure 21. (a) ^1H HR-MAS NMR spectra of TNGU PBX formulation swollen in $\text{CD}_3\text{CN}/\text{CD}_2\text{Cl}_2$ versus time; (b) quantitative analysis of TNGU and TNAE content in the PBX versus time.

The data in Figure 21, although instructive for initial validation of the ^1H HR-MAS NMR quantification technique, represent an unrealistic scenario for TNGU PBX hydrolysis in a UXO scenario since the NMR solvents first extract the TNGU from PBX binder followed by D_2O

hydrolysis of the TNGU in free solution (solvent-assisted). Therefore, a second ^1H HR-MAS NMR analysis of the TNGU PBX was conducted in which samples of the PBX (unswollen) were exposed to environments of neat D_2O and of moist soil. The soil (Horizon A top soil, procured from Ward's Natural Science, pH 7.0, passed through #35 mesh screen) used for this study and its preparation were consistent with previous efforts (Chapman et al., 2009). A 40 mg sample of the formulation was cut into pieces (~1 mm square) and placed into vials containing either D_2O (1 mL) alone or D_2O (0.3 mL) with soil (0.3 g). The formulation was mixed briefly with a spatula and then allowed to sit at room temperature in the corresponding vial sealed by a cap. Prior to analysis, samples were taken out of the vials using tweezers and were patted dry with a Kimwipe®. Roughly two drops of a 50/50 mixture of CD_3CN – CD_2Cl_2 was added to a 4 mm rotor, followed by the PBX formulation. Then the rotor was filled with the solvent mixture and the rotor was capped. The total mixture was then allowed to sit for 25 min in order for the solvent to penetrate the LMA binder and form a gel. The samples, spun at 5kHz, were analyzed via ^1H HR-MAS NMR with a 5 s time delay between scans. The areas beneath the most upfield peak (lauryl methyl group of LMA used as an internal reference) and the single TNGU peak were used in the analysis. As can be seen in Figure 22, significant degradation of TNGU was observed for PBXs exposed both to water and to moist soil. After 12 days, ~90% of the TNGU in the PBX had been degraded. Notably, the binder's hydrophobicity did not prevent the hydrolysis of TNGU occluded in the binder matrix. Presumably, the interconnectivity of the TNGU crystals within the binder matrix provides sufficient porosity for water transport, and hence, the data suggest that the binder's hydrophilicity is less important than originally suspected.

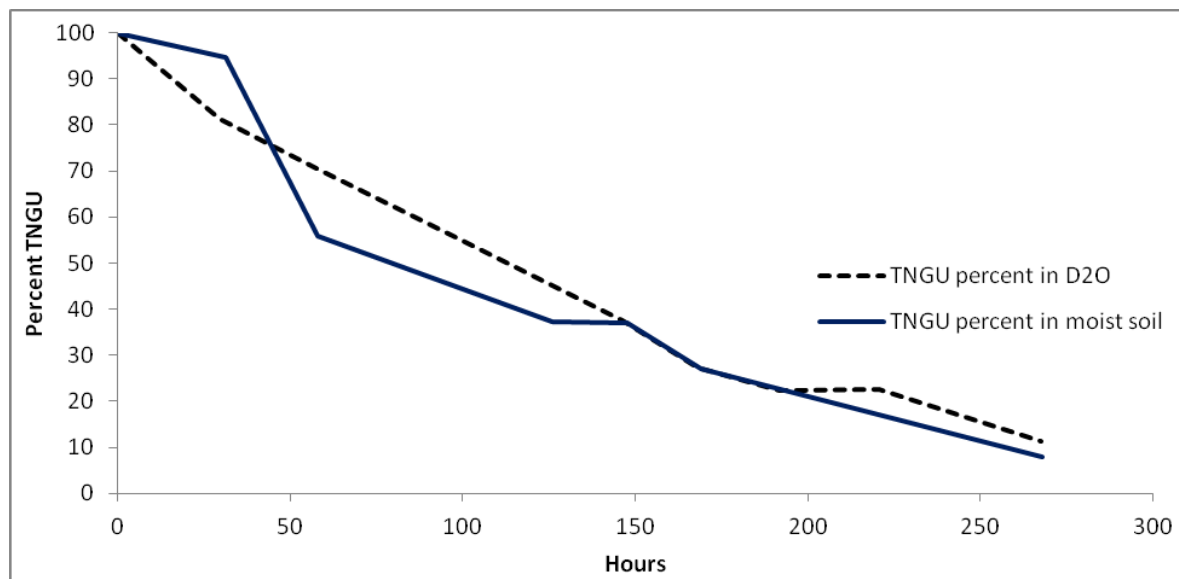


Figure 22. TNGU concentration in unswollen PBXs exposed to liquid water and moist soil.

A more thorough investigation of the hydrolyzability of the TNGU PBX formulation was conducted based upon the non-solvent assisted procedure described in section 4.6.2. Three samples were analyzed each day of sampling and those results were averaged to provide each data point shown on the graph in Figure 23. Percent loss of TNGU due to hydrolysis was determined by examining the ratio of the area under the TNGU peak (~7.7 ppm) to that of the internal standard methyl peak of LMA (~1.8 ppm). Standard error bars are indicated at each point. Non-linear degradation behavior was observed. This was likely due to an increased difficulty of water to pass

though the layers of LMA, although full penetration did occur. Total loss of TNGU transpired within 21 days of exposure to D₂O.

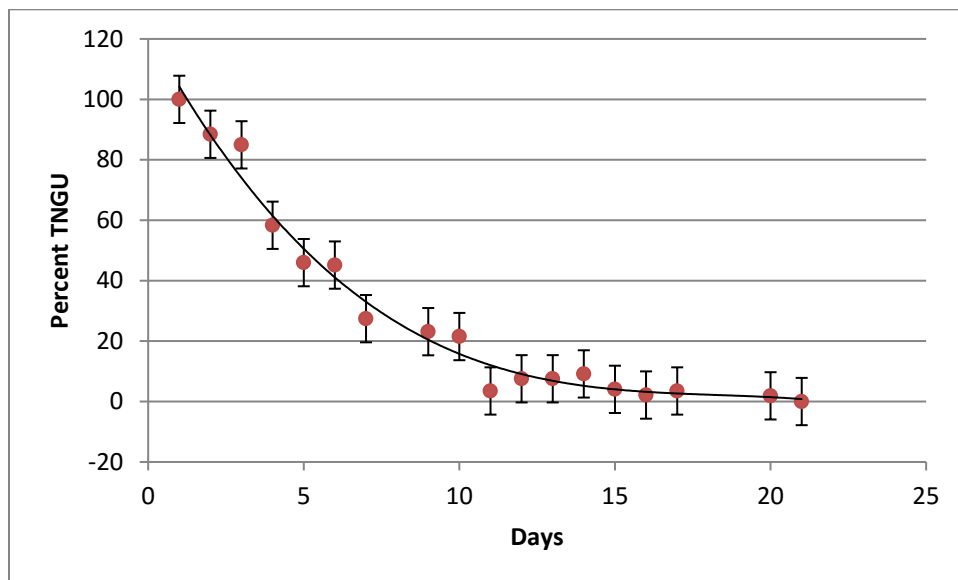


Figure 23. Hydrolysis of unswollen TNGU-LMA PBX with D₂O.

The initial samples of EHA-TNGU PBX formulations were also analyzed via ¹H HR-MAS NMR spectroscopy. It was found that the EHA binder could be made (visibly) gel-like by placing the system in CD₃CN. Upon further investigation, it was discovered that although the PBX visually appeared to be in a gel-like state, all of the EHA peaks were broad (Figure 24) by ¹H HR-MAS NMR spectroscopy. It was subsequently determined that a 50/50 mixture of CD₃CN–CD₂Cl₂ made the entire binder system have higher mobility, as indicated by the sharpening of the peaks. Higher mobility allows for more reliable quantification.

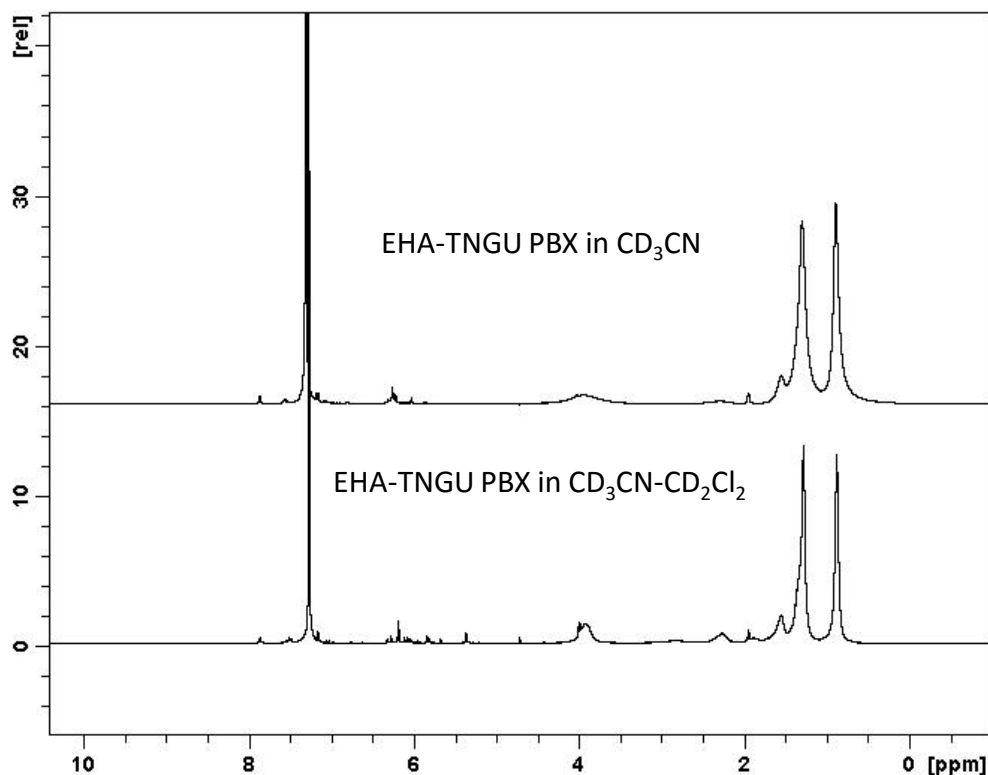


Figure 24. ^1H HR-MAS NMR of EHA-TNGU PBX in a single solvent vs. a mixed solvent.

Initial EHA-LMA PBX systems were analyzed for their hydrolytic stability, but the results were not consistent, likely due to inhomogeneity of the samples. Use of the LabRAM[®] for mixing has provided what appears to be a uniform EHA-TNGU PBX. A completeness of cure study was conducted on EHA-TNGU PBX after mixing with the LabRAM[®] (Figure 25). Curing of EHA can be observed via ^1H HR-MAS NMR spectroscopy by the decrease in intensity of peaks located at 4.95, 5.8, 6.05 and 6.15 ppm. It appears that it takes 5 – 6 days to completely cure the sample.

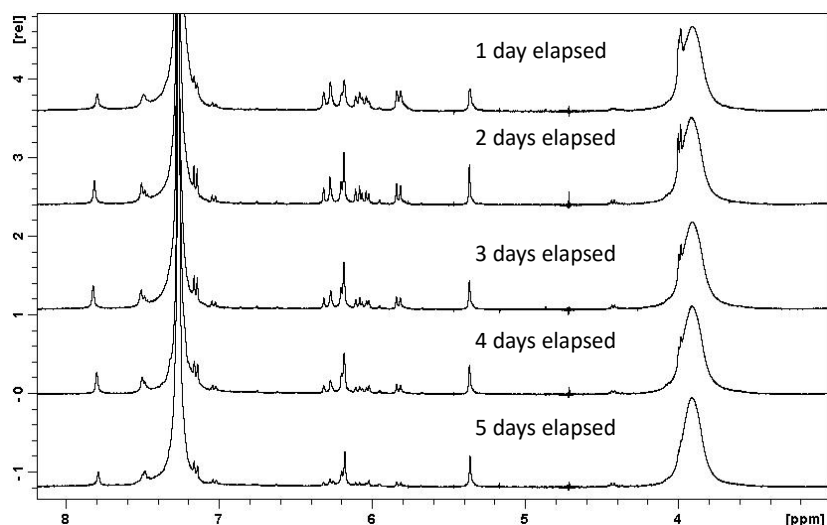


Figure 25. Cure of TNGU-EHA PBX, after LabRam® mix

The solvent-assisted hydrolysis of TNGU shown in Figure 21(b) was conducted for the TNGU-EHA PBX. TNGU is completely hydrolyzed within 9 h.

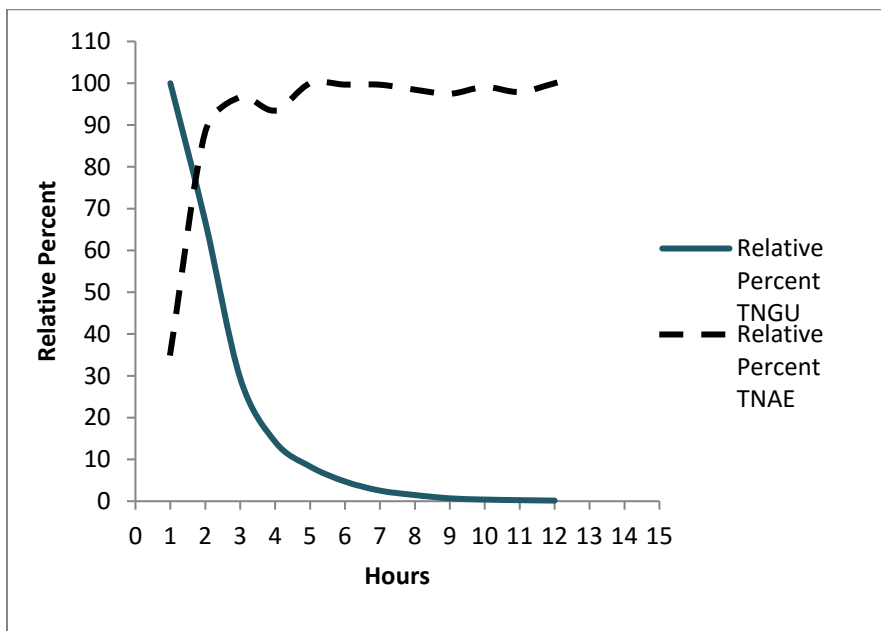


Figure 26. Hydrolysis of swollen TNGU-EHA PBX in D₂O.

In a separate study, within 4 days of the unswollen TNGU-EHA PBX (~40 mg) being placed into direct contact with D₂O (1 mL), 11% of the TNGU is hydrolyzed and by day 5, 20% of TNGU is lost to hydrolysis. Unswollen TNGU-LMA PBX loses roughly 40% in 4 days and 50% TNGU within 5 days of contact with D₂O. Swollen TNGU-LMA PBX is completely hydrolyzed within 7 h whereas swollen TNGU-EHA PBX is completely hydrolyzed within 9 h.

Thus, compared to TNGU-LMA PBX, TNGU in the TNGU-EHA PBX, hydrolyzes slower both swollen with solvent and unswollen.

5.3.2.1.2 Large Scale Hydrolysis Experiment

A larger scale qualitative hydrolysis experiment was designed and performed during this project to determine if the sample would be able to adequately dissipate the heat generated during hydrolysis of the TNGU. Approximately 100 g of TNGU-LMA PBX was submerged in 10 L of water for 30 days and 29 nights. Figure 27 shows the test item before being submerged in water. Figure 28 shows the test item after being submerged in water for 1 min, 1 h, 12 h, and 24 h. The appearance of the test item stayed about the same as the 24 h for the remainder of the test. The water temperature was recorded using a thermocouple, and the sample was monitored via time lapse and web cameras.

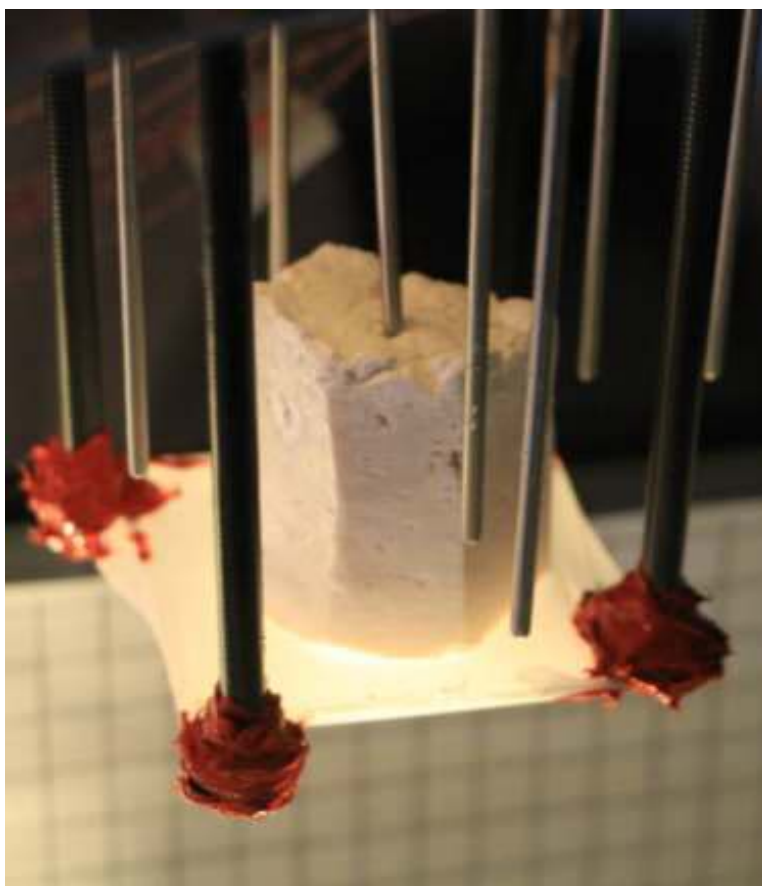


Figure 27. TNGU-LMA PBX large scale hydrolysis test item (~100g).



Figure 28. TNGU-LMA PBX test item while being submerged in water for 1 min, 1 h, 12 h, and 24 h.

An oscillatory trend in water temperature was observed due to the temperature changes of the environment (Figure 29), however there was no indication from the temperature of the surrounding water that the test item was reacting. Bubbles were produced on the surface of the test item almost immediately upon sample immersion, and appeared to continue to be formed for the duration of the test. The sample was destroyed at the conclusion of the test.

The test supported our theory that a safe self-remediation of a hydrolyzable explosive is likely feasible. The heat generated by hydrolysis reaction of the relatively large test item appeared

to be easily dissipated into the surrounding environment (water), and a benign degradation occurred. However, it must be noted that this test sample was completely unconfined, which may not be the case with UXO on a range.

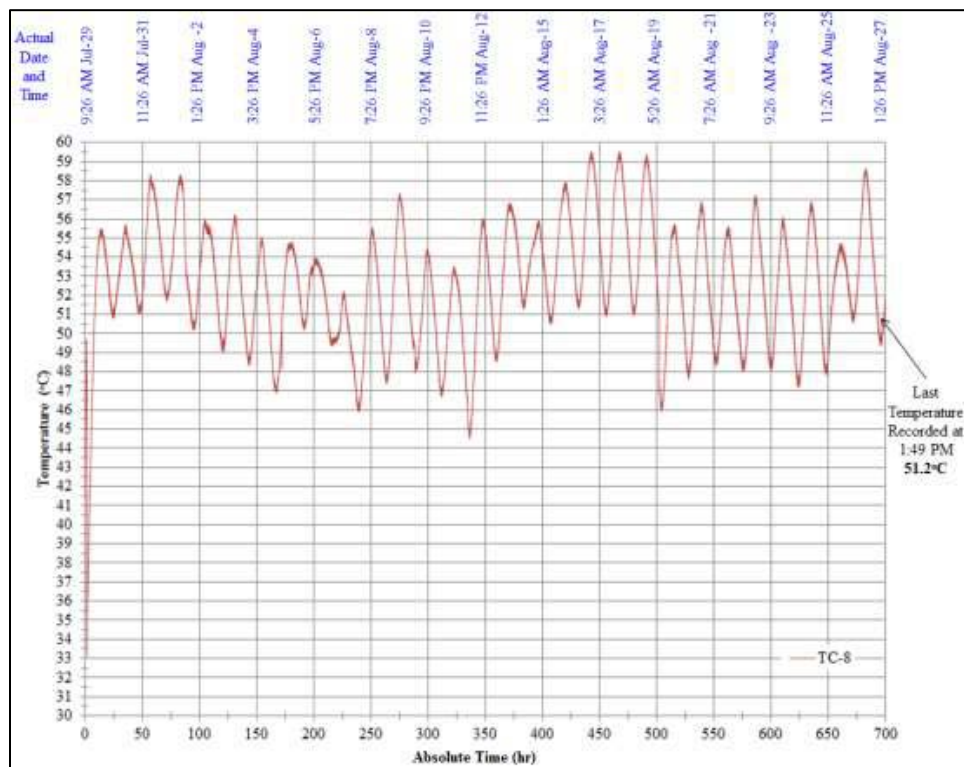


Figure 29. Temperature vs. absolute time data collected from tank water.

5.3.2.2 TNSUK PBX

A preliminary experiment based on the method developed for quantifying the hydrolysis of TNGU PBX (Section 4.7.2) was performed to verify that hydrolysis could be monitored for the TNSUK PBX. After 9 days in direct contact with water, no decomposition of TNSUK was observed. By day 16, there was a loss of approximately 10 – 20% TNSUK due to hydrolysis. Hydrolysis of the TNSUK PBX was much slower than the TNGU PBX, but still easily monitored. Hydrolysis of the TNSUK PBX was not monitored past 16 days.

5.3.3 Detonation Velocity Measurements

TNGU PBX was the only PBX scaled in a large enough quantity to perform detonation velocity measurements. The 250 g batch of TNGU PBX was cast into a single mass and used to perform two Failure Diameter/Unconfined Detonation Velocity Tests. The samples were made up of three billets cut from the 250 g mass of TNGU PBX. The billets were stacked one on top of the other and taped together. The density of the billets was not accurate due to the fact that the samples were full of voids and the standard water immersion method could not be used. The average density of the billets used for each test was 1.34 and 1.40 g/mL respectively. Photographs of the test sample voids and the alignment mismatch are included in Figure 30. The samples were initiated using an RP-501 Exploding Bridge Wire detonator and one PBXN-5 booster pellet, 0.3 inch by 0.5 inch

diameter. Six piezoelectric pins were used to determine the detonation velocity. The pins were held in place using a 2 inch long piece of plastic. Holes were drilled through the plastic and the pins pushed through the holes and against the side of the explosive charge. Pin distances were measured and recorded prior to testing.

Detonation velocity was determined by comparing time versus distance data received from the piezoelectric pins. Measured distances are accurate to ± 0.001 inch and timing accuracy is ± 200 picoseconds. Problems with instrumentation set-up resulted in us only getting data from pin 5 to pin 6 for both tests. The average detonation velocity was 7670 m/s.

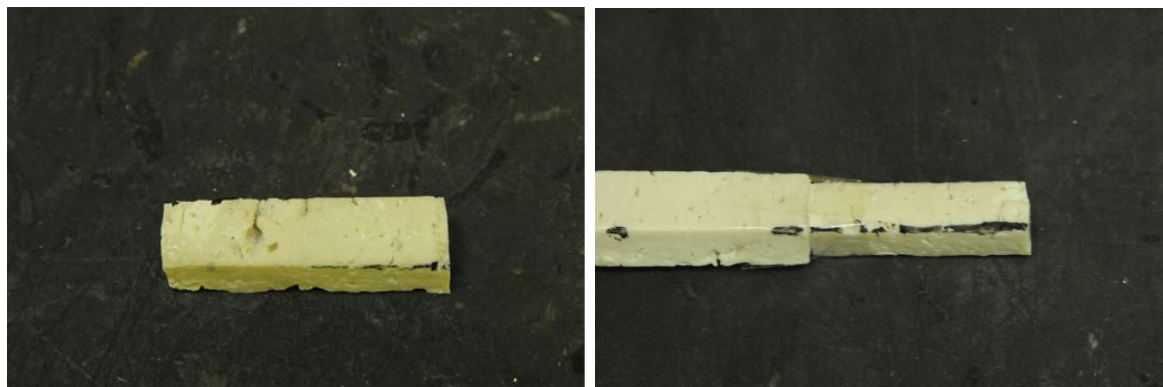


Figure 30. Pretest photographs of the TNGU PBX samples cut for detonation velocity measurements.

It is important to note that while the unconfined detonation velocity measured for the TNGU PBX (7670 m/s) matches well with the Cheetah predictions for the 82% solids TNGU PBX (7690 m/s), Cheetah underestimates the performance of the target material PBXN-107 by almost 6%. A similar under prediction of the TNGU PBX can be assumed based on the non-ideality of the TNGU composite. Therefore the target of 8120 m/s is a more accurate goal for the final TNGU formulation. However, the low detonation velocity is undoubtedly due to the large porosity and low density of the test samples. The Cheetah prediction for the detonation velocity of the TNGU PBX at a density of 1.37 g/cm^3 is 7209 m/s. If the 6% under prediction of performance is assumed then the detonation velocity of 7670 m/s measured for the current batch of TNGU PBX should extrapolate to meet the 8120 m/s goal for a high quality void free sample of the TNGU PBX with a density of 1.67 g/cm^3 .

6.0 Conclusions and Implications for Future Research/Implementation

As a potential solution to the persistent environmental problems of UXO, cyclic *N,N'*-dinitrourea derivatives may provide an attractive replacement for currently used energetics like RDX. Many of these cyclic *N,N'*-dinitrourea derivatives have similar explosive performance parameters to RDX and other nitramines (Table 8), but are typically more hydrolytically reactive.

TNGU, TNSUK, and HHTDD were considered as candidate hydrolyzable explosive components at the beginning of this project and were all synthesized at the 5 g scale.

Table 8. Explosive performance parameters of cyclic dinitroureas comparison with nitramines.

Compound	Density ρ (g/cm ³)	Detonation pressure PCJ (GPa)	Detonation velocity D (km/s)
RDX	1.81	33.8	8.74
HMX	1.90	39.0	9.11
CL-20	2.04	~46.6	~9.7
TNGU	1.98 – 2.01 ^a	~38.7 ^b	~9.20 ^c
HHTDD	2.07 ^d	~46.2 ^e	~9.75 ^{d,f}
TNSUK	1.91 ^g	-	8.67 ^g

^aBoileau, J.; Wimmer, E.; Carail, M.; Gallo, R. *Bull. Soc. Chim. France* **1986**, 465.

^bMuthurajan, H.; Sivabalan, R.; Talawar, M.B.; Asthana, S.N. *J. Hazard. Mater.* **2004**, A112, 17.

^cBoileau, J.; Emeury, J.-M.L.; Kehren, J.-P. *U.S. Patent* 4487938 (1984).

^dHu, R.; Lu, X.; Fang, Y. *J. Energ. Mater.* **1993**, 11, 219.

^eJu, X.-H.; Xiao, J.-J.; Xiao, H.-M. *Chinese J. Struct. Chem.* **2003**, 22, 223.

^fZhilin, V.F.; Rudakov, G.F.; Ladonin, A.V.; Sinditskii, V.P.; Egorshv, V.Yu.; Berezin, M.V. *International Annual Conference of ICT [Proc.]* **2003**, 34, 141/1.

^gHu, R.-Z.; Zhao, F.-Q.; Wanf, B.-Z.; Gao, S.-L.; Zhu, C.-H.; Ning, B.-K.; Chen, P.; Luo, Y.; Song, J.-R.; Shi, Q.-Z. *Chin. J. Chem.* **2004**, 22, 1075.

TNGU was chosen to move forward because of its straightforward synthesis, rapid degradation under humid conditions, relative stability in dry conditions, and explosive performance greater than RDX (detonation pressure and detonation velocity). TNGU was scaled up to 400 g batches and a PBX formulation was developed and scaled up to 250 g.

The ability of the TNGU PBX to self-remediate, even in a hydrophobic binder system, was demonstrated. An NMR method was developed to monitor the progression of the hydrolysis in a PBX. A simple larger scale (100 g) experiment was conducted demonstrating that the TNGU PBX would be able to adequately dissipate the heat generated during extreme conditions for TNGU hydrolysis (i.e., being submerged in water).

Detonation velocity was predicted with Cheetah and experimentally determined. The experimental value (7670 m/s) matched well with the Cheetah prediction (7690 m/s). Cheetah underestimates the performance of the target material PBXN-107 by almost 6%. A similar under prediction of the TNGU PBX can be assumed based on the non-ideality of the TNGU composite. If the 6% under prediction of performance is assumed then the detonation velocity of 7670 m/s measured for the current batch of TNGU PBX should extrapolate to meet the 8120 m/s goal for a high quality void free sample of the TNGU PBX with a density of 1.67 g/cm³.

Ultimately, the TNGU PBX formulation was unable to pass VTS testing. Though we did not have a large enough sampling of different hydrolyzable PBXs to make a definitive conclusion, we hypothesize that the characteristic that made it attractive as a self-remediating explosive, its rapid hydrolyzability, also made it susceptible to unacceptable degradation under VTS test conditions. Unfortunately, the TNGU PBX's inability to pass VTS testing indicates that it is unlikely to be developed as an energetic fill in confined ordnance items unless the gas generation at elevated temperatures can be mitigated.

Current synthesis strategies for TNSUK are more complicated (a four step synthesis) than the TNGU synthesis, but still acceptable. TNSUK degrades much slower than TNGU under humid conditions but it does eventually hydrolyze. The explosive performance is about the same as RDX. Most importantly, initial testing indicates that it produces significantly less gas than TNGU during VTS tests. In light of our inability to pass VTS tests with the TNGU PBX, near the end of the project a small scale (5 g) TNSUK PBX mix was prepared and preliminary characterization was completed to determine if our lessons learned from developing a TNGU PBX could be applied to a TNSUK PBX. The same LMA binder system and percent solid loading (82%) as the TNGU PBX was used for the TNSUK PBX formulation. The mix successfully formed a solid mass, however upon curing the solid was dry and chalky, indicating that oxygen poisoning had occurred. A preliminary hydrolysis experiment was performed using the techniques developed for the TNGU PBX, confirming that the method could be successfully adapted to monitor the progression of hydrolysis in a TNSUK PBX. Further development and characterization of TNSUK and a TNSUK PBX may result in a hydrolyzable PBX with acceptable properties. If TNSUK is pursued with a follow-on effort, its complex synthesis and low-yield will have to be mitigated.

HHTDD degraded much faster than TNGU in water, so we believe that it would also perform poorly in VTS testing. HHTDD was also difficult to synthesize and purify, making it an unattractive candidate for scale-up. HHTDD was not pursued further and is likely not a viable candidate for future efforts.

This project demonstrated the feasibility of a high performance self-remediating PBX using a conventional binder system. The development and ultimate implementation of a successful self-remediating PBX would prevent future contamination of military test and training ranges while allowing the continued use of live munitions. We were unable to develop an acceptable TNGU PBX, but the methods developed and lessons learned should facilitate the more efficient development of an acceptable self-remediating PBX. Based on this project, TNSUK is the most likely candidate. Future efforts should determine the VTS test performance of the energetic compound first to increase the likelihood of developing a successful self-remediating explosive.

Literature Cited

Adil, K.; Goreshnik, E.; Courant, S.; Dujardin, G.; Leblanc, M.; and Maisonneuve, V. Synthesis and structures of new hybrid fluorides template by tetraprotonated pentaerythrityl tetramine. *Solid State Sciences* **2004**, 6, 1229–1235.

Boileau, J.; Emeury, J.M.; and Kehren, J.P. Tetranitroglycoluril, Herstellungsverfahren dafür und Verwendung als Explosivstoff. Patent DE 2435651, 1975.

Boileau, J.; Emeury, J.M.; and Kehren, J.P. Tetranitroglycoluril and Method of Preparation Thereof. US Patent 4487938, 1984.

Boyer, I.; Miller, J. K.; Watson, R.E.; DeSesso, J. II; Vogel, C. M. Comparison of the Relative Risks of CL-20 and RDX. Noblis Technical Report, July 2007; <http://www.serdp-estcp.org/content/download/11915/144989/>

Chan, M.L.; Reed, R.; and Ciaramitaro, D.A. Advances in Solid Propellant Formulations. In *Solid Propellant Chemistry, Combustion, and Motor Interior Ballistics*; Yang, V., Brill, T.B., and Ren, W.-Z., Eds.; American Institute of Aeronautics and Astronautics, Reston, VA, 2000; Chapter 1.7.

Chapman, R.D.; Quintana R.L.; Baldwin, L.C.; and Hollins, R.A. Cyclic Dinitroureas As Self-Remediating Munition Charges, Project WP-1624 Final Report. SERDP, Arlington, VA, Feb 2009; <http://www.serdp.org/content/download/6571/86619/file/WP-1624-FR.pdf>; and references therein.

Cross, T.A.; Nelson, A.P.; and Ferguson, B.P. Processing Benefits of Resonance Acoustic Mixing on High Performance Propellants and Explosives. 38th International Pyrotechnics Seminar, Denver, CO, June 10–15, 2012.

Dagley, I. J. and Flippen-Anderson, J. L. *Aust. J. Chem.* **1994**, 47, 2033–2045.

Fleischer, E. B.; Gebala, A. E.; Levey, A.; and Tasker, P. A. Conversion of Aliphatic and Alicyclic Polyalcohols to the Corresponding Primary Polyamines. *J. Org.Chem.* **1971**, 36(20), 3042–3044.

Fu, Q.; Zhu, C.; and Fu, X. On the Synthesis, Structure and Properties of Spiro-Nitramines and Spiro-Nitrosamines. *Binggong Xuebao [Acta Armamentarii]* **1992(1)**, 28–35.

Hawari, J. Environmental Fate and Transport of a New Energetic Material, CL-20, Project ER-1256 Final Report. ESTCP, Arlington, VA, March 2006.

Howe, H.W.; Warriner, J.J.; Cook, A.M.; Coguille, S.L.; and Farrar, L.C. Apparatus and Method For Resonant-Vibratory Mixing. US Patent 7188993, 2007.

Hu, R.; Fang, Y.; and Lu, X. *Huozhayao* **1981**, 4, 1–11.

Hu, R.; Lu, X.; Fang, Y. *J. Energ. Mater.* **1993**, *11*, 219.

Hu, R.; Liang, Y.; Fang, Y.; Wang, J.; and Xie, Y. The Hydrolytic Stability of Some Cyclourea Compounds. *J. Therm. Anal.* **1996**, *46*, 1283–1289.

Jenkins, T.F.; Hewitt, A.D.; Grant, C.L.; Thiboutot, S.; Ampleman, G.; Walsh, M.E.; Ranney, T.A.; Ramsey, C.A.; Palazzo, A.J.; and Pennington, J.C. Identity and Distribution of Residues of Energetic Compounds at Army Live-Fire Training Ranges. *Chemosphere* **2006**, *63*, 1280–1290.

Katritzky, A.R.; Singh, S.K.; Meher, N.K.; Doskocz, J.; Suzuki, K.; Jiang, R.; Sommen, G.L.; Ciaramitaro, D.A.; and Steel, P.J. Triazole-oligomers by 1,3-dipolar cycloaddition. *ARKIVOC* **2006**(5), 43–62; <http://www.arkat-usa.org/get-file/23234/>.

Krikštopaitis, K. *New Trends in Research of Energetic Materials*, Proceedings of the Seminar, 16th, Pardubice, Czech Republic, Apr. 10-12, 2013 (Part 2), 735.

Lee, B.Y.S. Degradable and Hydrolyzable Binder Explosives. Minutes of the Twenty-Fifth Explosives Safety Seminar, Anaheim, CA, August 18–20, 1992, Volume 1, pp. 495–506.

Ma, M.-Y. and Lu, M.-J. Synthesis and Properties of Hexanitrohexaazatricyclododecanedione. *Bingong Xuebao [Acta Armamentarii]* **1980**, *3*(2), 27–38.

Minsky, I.; Adam, H.W.; Stroup, L.T.; and Hess, J.W. Oxidizers for Solid Propellants, Memorandum Report MR-16. Picatinny Arsenal, Dover, NJ, Jun 1952; cited in Fedoroff, B.T. and Sheffield, O.E., *Encyclopedia of Explosives and Related Items*, 1974, Vol. 6, p. G-117.

Muthurajan, H.; Sivabalan, R.; Talawar, M.B.; Asthana, S.N. *J. Hazard. Mater.* **2004**, *A112*, 17.

Pellerin C.J. Self-Remediating Munitions, SERDP Statement of Need WPSON-08-04, November 9, 2006. <http://www.serd-estcp.org/content/download/7680/96727/version/1/file/WPSON-08-04-Self%2BRemediating%2BMunitions.pdf>

Peng, Z. and Wan, D. Synthetic Study of Tetranitroglycoluril and Its Hydrolyzed Product. *Bingong Xuebao [Acta Armamentarii]* **1980**, *3*(3), 23–27.

Pennington, J.C.; Jenkins, T.F.; Ampleman, G.; Thiboutot, S.; Brannon, J.M.; Hewitt, A.D.; Lewis, J.; Brochu, S.; Diaz, E.; Walsh, M.R. et al. Distribution and Fate of Energetics on DoD Test and Training Ranges: Final Report, ERDC TR-06-13. U.S. Army Corps of Engineers, Vicksburg, MS, Nov 2006; ADA458391; <http://el.erd.usace.army.mil/elpubs/pdf/tr06-13.pdf>

Power, W.P. High-Resolution Magic Angle Spinning—Enabling Applications of NMR Spectroscopy to Semi-Solid Phases, *Annual Reports on NMR Spectroscopy* **2011**, *72*, 111–156.

Provatas, A. Formulation and Performance Studies of Polymer Bonded Explosives (PBX) Containing Energetic Binder Systems. Part I, DSTO-TR-1397, DSTO Systems Sciences

Laboratory, Edinburgh, S. Australia, Mar 2003.

<http://dspace.dsto.defence.gov.au/dspace/bitstream/1947/4241/1/DSTO-TR-1397%20PR.pdf>

Ross, D. L.; Coon, C. L.; McGuire, R. R. Tetranitroglycoluril: Preparation and Properties. JANNAF Paper, February 16, 1978.

Schnell, I. Merging Concepts from Liquid-State and Solid-State NMR Spectroscopy for the Investigation of Supra- and Biomolecular Systems. *Curr. Anal. Chem.* **2005**, *1*, 3–27.

Sherrill, W. M.; Johnson, E. C.; Banning, J. E. A Method for the Synthesis of Tertanitroglycoluril fom Imiazo-[4,5=d]-imidazoles with loss of Dinitrogen Oxide. *Propellants Explos. Pyrotech.* **2015**, *35*, 1-7.

Tung, H.-H.; Paul, E.L.; Midler, M.; and McCauley, J.A. *Crystallization of Organic Compounds – An Industrial Perspective*; John Wiley & Sons, Hoboken, NJ, 2009.

Vaullerin, M.; Espagnacq, A.; and Morin-Allory, L. Prediction of Explosives Impact Sensitivity. *Propellants, Explos., Pyrotech.* **1998**, *23*, 237–239.

Vedachalam, M.; Ramakrishnan, V.T.; and Boyer, J.H. Dense Compounds of C, H, N, and O Atoms: Nitramine Derivatives of Diimino- and Dioxodecahydro-1H,5H-diimidazo[4,5-b:4',5'-e]pyrazine. *Heteroat.Chem.* **1991**, *2*, 313–318.

Vedachalam, M.; Ramakrishnan, V.T.; Boyer, J.H.; Dagley, I.J.; Nelson, K.A.; Adolph, H.G.; Provatas, A. Formulation and Performance Studies of Polymer Bonded Explosives (PBX) Containing Energetic Binder Systems. Part I, DSTO-TR-1397, DSTO Systems Sciences Laboratory, Edinburgh, S. Australia. Mar 2003;
<http://dspace.dsto.defence.gov.au/dspace/bitstream/1947/4241/1/DSTO-TR-1397%20PR.pdf>.

Zheng, Y.; Zhou, J.; Zhou, D.; Zhang, M. The Synthesis of 1,1,2,2,-Tetrakis(Difluoroaminomethylenenitroamino)ethane and its Related Compounds. *Binggong Xuebao.* **1988**(1), 59.

Appendix A – List of Scientific/Technical Publications

“Self-Remediating Explosives Based on Tetranitroglycoluril (TNGU)” A. Merritt, H. Hoang, K. Young, L. Baldwin, B. Ferguson, R. Chapman, and R. Quintana, JANNAF 37th Propellant and Explosives Development and Characterization Subcommittee Meeting (San Antonio, TX), 2 May 2012; Eighth Primary Explosives Workshop (Chandler, AZ), 8 May 2012

“Processing Novel Energetic Formulations with Resonance Acoustic Mixing”, B. Ferguson, A. Nelson, T. Cross, and A. Merritt, JANNAF 37th Propellant and Explosives Development and Characterization Subcommittee Meeting (San Antonio, TX), 2 May 2012; Eighth Primary Explosives Workshop (Chandler, AZ), 8 May 2012

“Energetic Potpourri IV” (invited presentation) Robert D. Chapman, Gordon Research Conference on Energetic Materials (Mount Snow, VT), 18 June 2012

“Self-Remediating Energetic Fills Based on Cyclic Dinitroureas”, R. Quintana, R. Chapman, H. Hoang, K. Young, A. Merritt, L. Baldwin, SERDP Interim Report, 31 October 2012

“A Hydrolysable Explosive Formulation”, A. Merritt, H. Hoang, K. Young, L. Baldwin, R. Quintana, R. Chapman, and B. Ferguson, Invention Disclosure, Navy Case number 102518

Appendix B –SERDP SEED Project WP1624 Report

