REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
29-04-2020	Final Report	1-Feb-2019 - 31-Oct-2019

4. TITLE AND SUBTITLE
Final Report: Reactive Chemical for Environmental Mangagement

5a. CONTRACT NUMBER
W911NF-19-1-0064

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of Rhode Island
70 Lower College Road
Research Office
Kingston, RI 02881 -1967

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
74800-CH-II.1

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Jimmie Oxley
UU	UU	UU	UU		19b. TELEPHONE NUMBER 401-874-2103

RPPR Final Report
as of 29-Apr-2020

Agency Code:

Proposal Number: 74800CHII **Agreement Number: W911NF-19-1-0064**
INVESTIGATOR(S):

Name: Jimmie C. Oxley Ph.D.
Email: joxley@chm.uri.edu
Phone Number: 4018742103
Principal: Y

Organization: **University of Rhode Island**
Address: 70 Lower College Road, Kingston, RI 028811967
Country: USA
DUNS Number: 144017188 EIN: 223011455
Report Date: 31-Jan-2020 Date Received: 29-Apr-2020
Final Report for Period Beginning 01-Feb-2019 and Ending 31-Oct-2019
Title: Reactive Chemical for Environmental Mangagement
Begin Performance Period: 01-Feb-2019 **End Performance Period:** 31-Oct-2019
Report Term: 0-Other
Submitted By: Jimmie Oxley Email: joxley@chm.uri.edu
Phone: (401) 874-2103
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 0 **STEM Participants:** 0

Major Goals: Overall goal:
Develop a system in which a species can be embedded during manufacture which will sit inertly until triggered. Upon triggering the species will facilitate the safe and environmentally friendly destruction of unwanted or unneeded materials.
Steps to overall goal:
Determine reactive species which can gently degrade explosive material and/or determine such species which can enhance sensitivity of the material to ensure ease of destruction.
Determine a way to inert a reactive species until destruction is desired.
Determine a way to remotely active the inerted reactive species.

Accomplishments: Accomplishments
Several potential methods of sensitizing explosive material were explored.
A method of inerting reactive species was developed and assessment measures probed.

Training Opportunities: Several graduate students (2) and undergraduate students (3) worked on this project.

Results Dissemination: Report in preparation

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Gerald Kagan
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N

Other Collaborators:

Reactive Chemical Systems for Environmental Management

2020

University of Rhode Island

Executive Summary

Unwanted or broken articles overflow in U.S. dumps and landfills or are left to mar the countryside. On military training ranges or former war zones, where duds and partially functioned ordnance have been abandoned, they are a menace to personnel, military and civilian, and a source of environmental contamination. This short-term innovative research (STIR) investigated two ways to alleviate this problem. Both are based on the premise that it may be possible to embed species in the munitions at their inception that can be triggered upon demand to facilitate the destruction of the unwanted item. However, the questions inherent in such an approach are many: What would be the actual function of the active material? How would it achieve that function? How could a potentially active material be placed in an explosive article without affecting the normal operation and safe storage of the item? How could the active ingredient be temporarily inerted? How would the dormant active material be triggered into reactivity? How much of such an active material can the explosive tolerate without greatly altering its performance?

Due to the short duration of this research program we have attempted to explore each question to some extent in order to prepare the path for future studies. While this is cast as a study in terms of "what to do with unwanted or discarded munitions," answers could be morphed into a more general problem, such as "what to do with unwanted or discarded plastics." Munitions is perhaps the harder problem set due to the inherent dangers.

What would be the function of the active material? What material could achieve that function? How could it be temporarily made inert?

We envisioned two useful functions for the embedded active material. 1) Upon triggering it could gently degrade the explosive. This first idea was explored in the form of a small workshop Trigger-Release & Encapsulation for Product Alteration in April 2019. 2) The second idea was increasing the sensitivity of the explosive so that blow-in-place procedures would be effective. Use of such techniques on the new "insensitive" explosives tends to scatter chunks of explosive throughout the area rather than destroy the explosive. With either of these approaches, several thorny problems were identified: finding an active ingredient that exhibited catalytic activity; inactivating this ingredient for years while maintaining its potential; and ensuring that its successful activation would result in an environmentally neutral product.

Choice of Degradant

It was expected that the choice of degradant would be highly dependent on the material to be degraded. To be of military interest two explosives from two "families" of explosives were chosen: 2,4,6-trinitrotoluene (TNT), a nitroarene, and 1,3,5-trinitroperhydro-1,3,5, triazine (RDX), a nitramine. Initially we studied solutions of these. This proved to be an easier problem than the actual one. In solution the species have the mobility to mix and, thus, interact. In condensed form that is not the case.

Choice of Degradant -Experimental Details

TNT was dissolved in water/methanol (1:1) to create a 250 ppm solution; and the solution was allowed to stand in the dark for 3 days monitoring the TNT NO_2 absorbance (227 nm) by ultraviolet-visible spectroscopy (UV-vis). Once the baseline was established, i.e. that TNT was stable under these conditions, aliquots of this solution were treated with a variety of potential digestion agents. Appendix A lists digestion agents considered.

Bases

Sodium hydroxide (NaOH)
Triethanol amine (TEA)
Calcium hydroxide ($Ca(OH)_2$)

Acids

Hydrochloric acid (HCl)
Sulfuric acid (H_2SO_4)

While bases appeared to decrease the concentration of TNT in 66 hours at room temperature (Figure 1), acids had no effect.

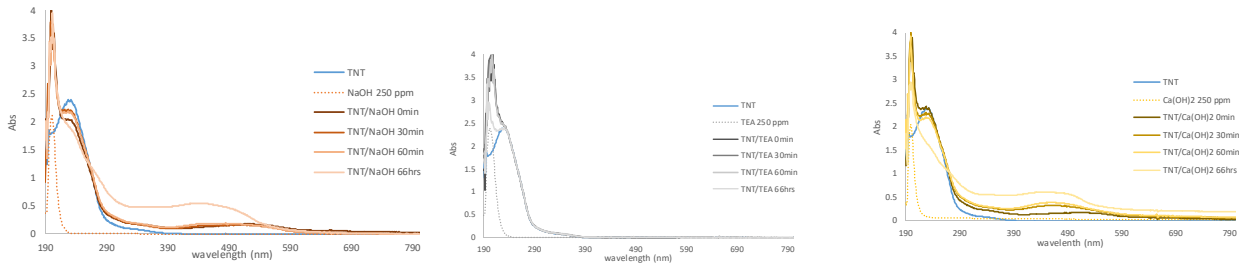


Figure 1: TNT in various basic solutions (left to right): NaOH; TEA; $Ca(OH)_2$

Since the material to be digested would likely be a solid, solid TNT or RDX were mixed with potential degradants (10 wt% of the explosive mass): NaOH; iron; aluminum; zinc. After one hour at 100 °C (TNT melt 81 °C) TNT showed decomposition only with NaOH. A new set of degradants was tested with TNT and RDX. Degradation within 2 hours at 100 °C was observed (Figure 2).

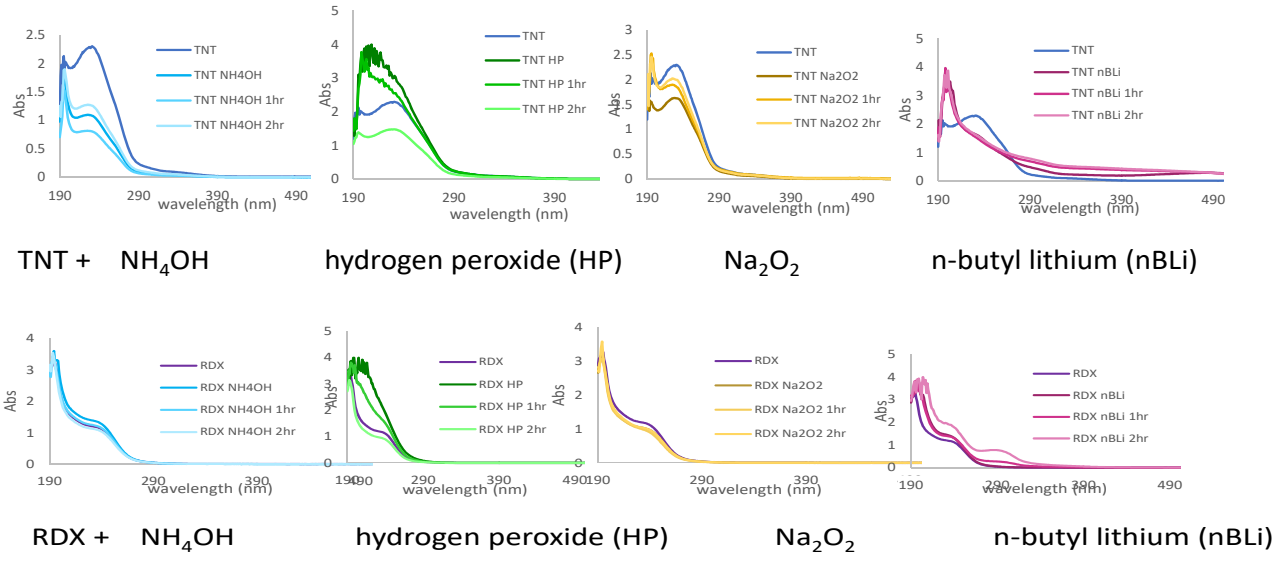


Figure 2: UV-vis traces monitoring potential degradation of explosives in solution

Inerting the Degradant

At this point we asked whether we had the ability to encapsulate a caustic or reactive solution. With little added equipment, the encapsulation method available to us was the solvent evaporation method (Figure 3). This method stirs together two immiscible layers; over time the volatile organic solvent, in which the polymer is dissolved, evaporates leaving microspheres behind. These are thoroughly washed with water and dried.

Inerting the Degradant Experimental Details

In the case of a basic encapsulant, e.g. NaOH, the microspheres are water washed until the water-stream is neutral. This removes non-encapsulated and excess NaOH.

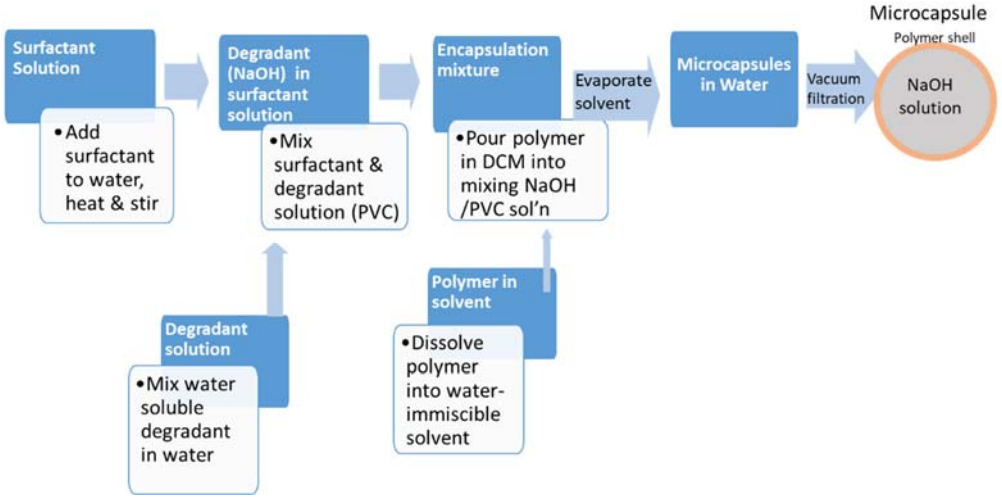


Figure 3: Solvent evaporation method flowchart

An unforeseen issue using NaOH, or any basic degradant, was that it was not only reactive to the target compounds, but it was also reactive during the encapsulation process. The process involves dissolving the reactant in water and mixing in a water/surfactant solution. Although high concentrations of NaOH solution would have been ideal, as this would have delivered more degradant per microsphere; at high pH the surfactant, polyvinyl alcohol (PVA), underwent hydrolysis and congealed forming a semisolid mass. To avoid this, various molecular weight PVAs were tested with different surfactants. The surfactants tested are listed in Table 1.

Not all surfactants were compatible with solutions of sodium hydroxide. The heavier molecular weight PVAs would very readily congeal with the addition of dilute NaOH. Intermediate weights (20-50 KDa) showed some crosslinking as the pH increased, making it difficult to stir the solution. In addition to testing various surfactants, four polymers were investigated as potential encapsulating material: poly(methyl methacrylate) (PMMA); polystyrene (PS); polyvinyl chloride (PVC); and polyethylene terephthalate (PET) (Figure 4). Only the surfactant appeared sensitive to strong alkaline solutions.

Table 1: List of surfactants tested

Surfactant	MW (Da)	[NaOH] solution	Polymer	Microsphere size
PVA (98% hydrolyzed)	13,000-23,000	3 M	PMMA	12-62 μm
PVA (98% hydrolyzed)	13,000-23,000	3 M	PS	23-73 μm
PVA (98% hydrolyzed)	13,000-23,000	3 M	PVC	45-150 μm
PVA (98% hydrolyzed)	13,000-23,000	3 M	PET	No spheres
PVA (88% hydrolyzed)	20,000-30,000	1-2 M	PMMA	No spheres
PVA (98-99% hydrolyzed)	31,000-50,000	1-2 M	PMMA	No spheres
PVA (100% hydrolyzed)	70,000-79,000	incompatible	-	-
PVA (99-100% hydrolyzed)	~86,000	incompatible	-	-
DOW GR-7M Triton	-	5 M	PMMA	20-220 μm

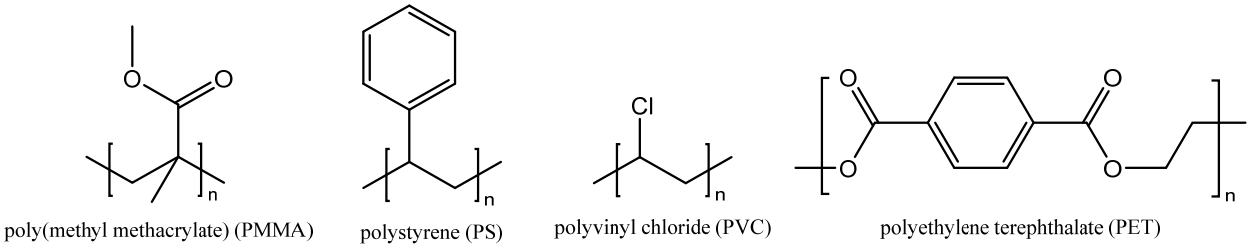


Figure 4: Polymers tested

Empty microspheres are clear and colorless; they become opaque white when encapsulating NaOH solutions (Figure 5). Forming PVC microspheres required a slight modification to the method used to make PMMA and PS microspheres. Due to the poor solubility of PVC in dichloromethane (DCM), additional solvent and mild heating were necessary to fully dissolve the PVC. After dissolving PVC into DCM, the procedure was the same as for the other plastics. A few attempts to use PET for an encapsulating plastic produced no observable microspheres. PET is sparingly soluble in DCM and other water-immiscible organic solvents. This makes it difficult to use in the solvent evaporation method, as the organic solvent, in which the plastic is dissolved, must be immiscible in water. PET was dissolved in a mixture of organic solvents and added to the stirring water/PVA solution. A solid formed after the organic solvents had evaporated; however, the solid proved to be one massive ~2 g clump of PETN.

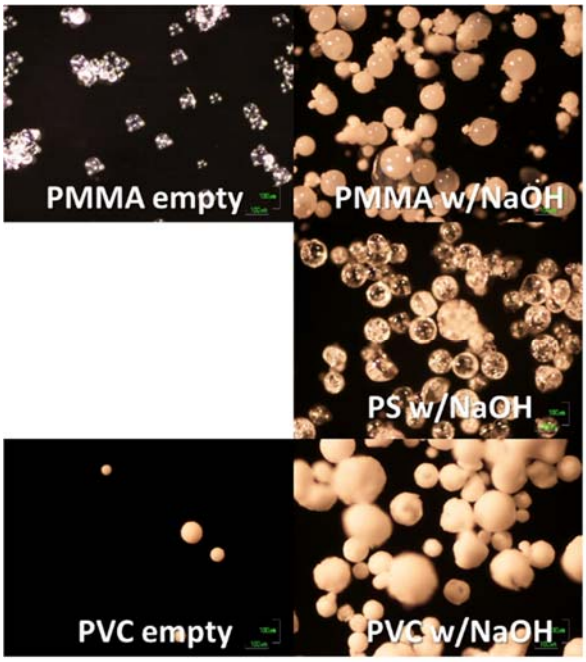


Figure 5: Microspheres a. PMMA empty; b. PMMA w/NaOH; c. PS w/NaOH; d. PVC empty; e. PVC w/NaOH

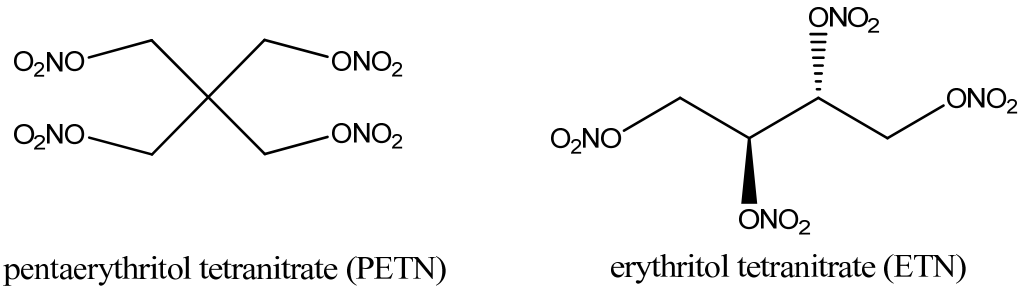
The integrity of the microspheres during each of the stages of formulation was investigated. After the microspheres were washed and dried, a sample of the batch was placed in water; and after an hour the pH was tested to check for leaking capsules. If the solution remains neutral, the microspheres were dissolved in DCM, and the pH of the aqueous layer was again checked to confirm that the spheres contained NaOH. This procedure was repeated for the microspheres after addition into an inert silica gel/PE wax formulation to check for potential leakage.

A critical determination is the moles of NaOH per mass of microspheres. This value provides encapsulation efficiency and informs as to how much material can be degraded by a given amount of added microspheres. To determine moles NaOH per mass microcapsules, the microspheres were dissolved in DCM; the base, extracted by washing with water; and the extract, titrated with dilute HCl. To neutralize the solution between 6.9 - $9.3 \cdot 10^{-5}$ mol HCl was needed which calculates to 3.45-$8.30 \cdot 10^{-5}$ mole NaCl per gram microspheres. Whether this is sufficient to digest the target material in a reasonable amount of time and what is a "reasonable" amount of time are questions yet to be answered.

Choice of Sensitizer

Two types of explosive sensitizers were considered; a small fraction of a sensitive explosives or a species that would create voids on-demand. By encapsulating sensitive explosives and adding them to a less sensitive explosive formulation, we hope to reduce the sensitivity of the dopant while increasing the shock initiation of the bulk explosive. The hypothesis is that the sensitive explosive will support the initiation of the insensitive explosive if field disposal is necessary. By adding in a sensitive, but fully encapsulated, explosives the mechanical initiation of the munition would

remain the same but would be easier to initiate by shock, rendering unexploded ordnance easier to dispose of by field-expedient blow-in-place method. The choice in sensitive explosives was pentaerythritol tetranitrate (PETN), used in detonating cord and many initiating systems, and erythritol tetranitrate (ETN), an explosive considered for initiating systems, but found to be too sensitive for military use but used by terrorist (Figure 6).



pentaerythritol tetranitrate (PETN) erythritol tetranitrate (ETN)

Figure 6: Structures of PETN and ETN

Gas-generating agents and shape-memory polymers would both operate on the idea of generating hot spots within the explosive. The dichotomy in working with explosives is that high density is good for optimal performance, but some porosity is required for initiation. In fact, an explosive is "dead-pressed" if all the hot spots have been pressed out of it and detonation is almost impossible to initiation. Gas-generating agents or agents which changed shape sufficiently to create cracks or voids would sensitize explosives otherwise difficult to initiate (see Future Directions)

With gas-generating agents we encountered the same problem encountered with the degradants. We needed agents which were catalytic in their activity, that is a small volume of the agent would affect a large volume of explosive. In both cases, degradants and sensitizing agents, we are still searching for the appropriate materials through literature searches. Examination of a shape-memory polymer is an actively underway (see Future Directions).

Making the Explosive Sensitizers Inert-Experimental Details

As reported above, we used a solvent evaporation slurry method to encapsulate the agents. The method stirred together two immiscible liquid layers, one organic and the other aqueous. Over time the volatile organic solvent, in which the polymer and agent were dissolved, evaporated leaving microcapsules behind. The resulting solid was filtered and thoroughly washed with water to remove excess surfactant. The microcapsules were imaged using a polarized light microscope (PLM) at 10X to assess morphology and estimate encapsulation efficiency. The opacity of the microspheres was used as a quick initial evaluation of whether the polymer had successfully encapsulated the energetic. Empty microspheres appeared clear and colorless compared to filled microcapsules. (Figure 7)

Solvents for each compound were chosen based on the solubility of the energetic. For example, dichloromethane (DCM) was used only for ETN; PETN was only sparingly soluble in it. All liquids were mixed using a mechanical fixed-stand mixer set to 1000 rpm. For solvents which were

miscible in water, sodium chloride was added to the aqueous layer to prevent the solvent from mixing with the water. With some solvents, the temperature of the mixture was raised to enhance the evaporation rate of the organic layer. For solvents, such as toluene with vapor pressure 2.5 kPa at 20 °C, complete evaporation took as long as 2 hours. Two surfactants were used, a 10% polyvinyl alcohol (PVA) solution and Triton GR-7M from Dow. Triton is a sulfosuccinate-based surfactant.

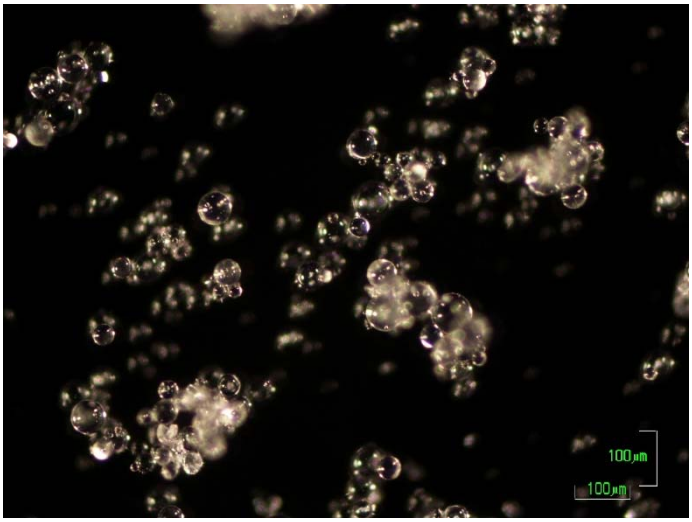


Figure 7: Empty PMMA microspheres

PETN encapsulation had a wide range of outcomes; depending on the solvent and temperature employed different morphologies were produced. The best solvent for PETN proved to be ethyl acetate (EtOAc). Under all conditions tested, EtOAc produced some microspheres (Table 2), and in the heated test, produced almost exclusively opaque spheres (Figure 8 b). The opacity of the microspheres is a good indication that PMMA encapsulated the energetic. When visually compared, empty microspheres (Figure 7) are clear and colorless compared to filled microcapsules. When mixed at room temperature in toluene PMMA formed plastic sheets with some spheres but opaque spheres when heated to 44 °C (Figure 9 c & d). Acetonitrile (ACN) created microspheres only when stirred over an hour (Figure 9 e & f).

Table 2: PETN/PMMA microspheres

Solvent	Temperature (°C)	Mix time (hrs)	Surfactant	Results
EtOAc	25	2	PVA	Figure 8 a
EtOAc	44	2	PVA	Figure 8 b
EtOAc	25	12	PVA	Figure 8 c
EtOAc	25	2	Triton	Figure 8 d
Toluene	25	2	PVA	Figure 9 a
Toluene	44	2	PVA	Figure 9 b
Acetone	25	1	PVA+NaCl	Figure 9 c
Acetone	25	2	PVA+NaCl	Figure 9 d
Acetonitrile	25	1	PVA+NaCl	Figure 9 e
Acetonitrile	25	2	PVA+NaCl	Figure 9 f

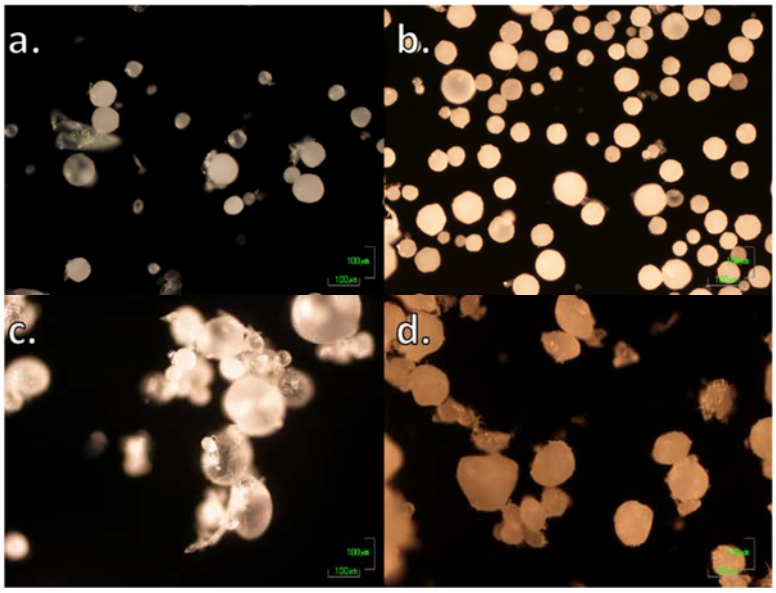


Figure 8: PETN in PMMA using EtOAc: a. rt 2hrs; b. hot, 2hrs; c. rt, overnight; d. w/Triton

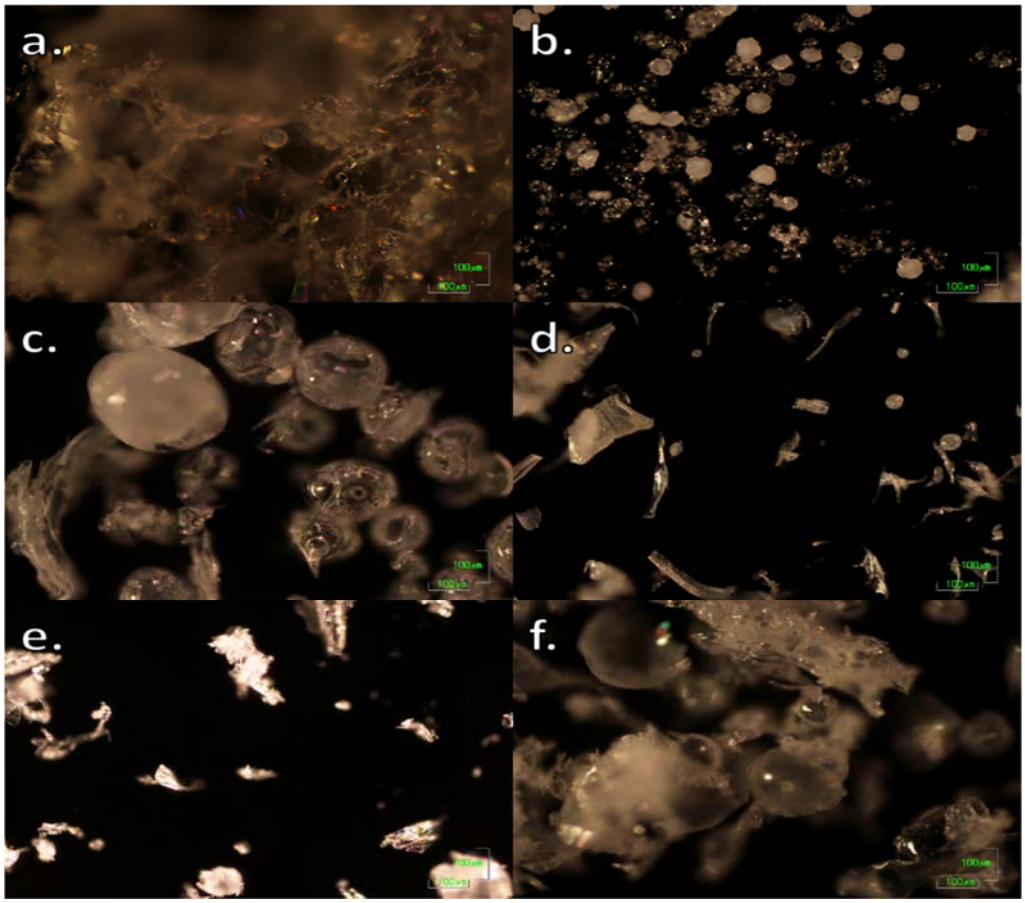


Figure 9: PETN encapsulated in PMMA by: a. acetone, 1hr; b. acetone, 2hr; c. toluene; d. toluene, hot; e. acetonitrile, 1hr; f. acetonitrile, 2hr

ETN is more readily soluble in water-immiscible organic solvents than PETN (Table 3). Dichloromethane (DCM) is often used for this method since it is very volatile and immiscible with water. It proved useful in encapsulating NaOH solutions in PMMA. ETN readily dissolves in DCM. Three methods using DCM were attempted; each created microspheres; however, the spheres were transparent, suggesting no ETN was inside (Figure 10 a-c). Acetone was also used as a solvent; but even with addition of NaCl, no capsules formed (Figure 10 d); instead, the solid recovered was a thin agglomeration of fibrous white solids. EtOAc proved to be the best solvent for ETN, yielding mostly clear microspheres (Figure 10 e). However, previous studies in our laboratory had shown that ETN recrystallized rather slowly;[1] therefore, in this case, the appearance of clear microspheres did not necessarily indicate empty microspheres.

Table 3: ETN/PMMA microspheres

Solvent	Temperature (°C)	Mix time (hrs)	Surfactant	Results
DCM	25	2	PVA	Figure 10 a
DCM	44	2	PVA	Figure 10 b
DCM	25	2	Triton	Figure 10 c
Acetone	25	2	PVA+NaCl	Figure 10 d
EtOAc	25	2	PVA	Figure 10 e

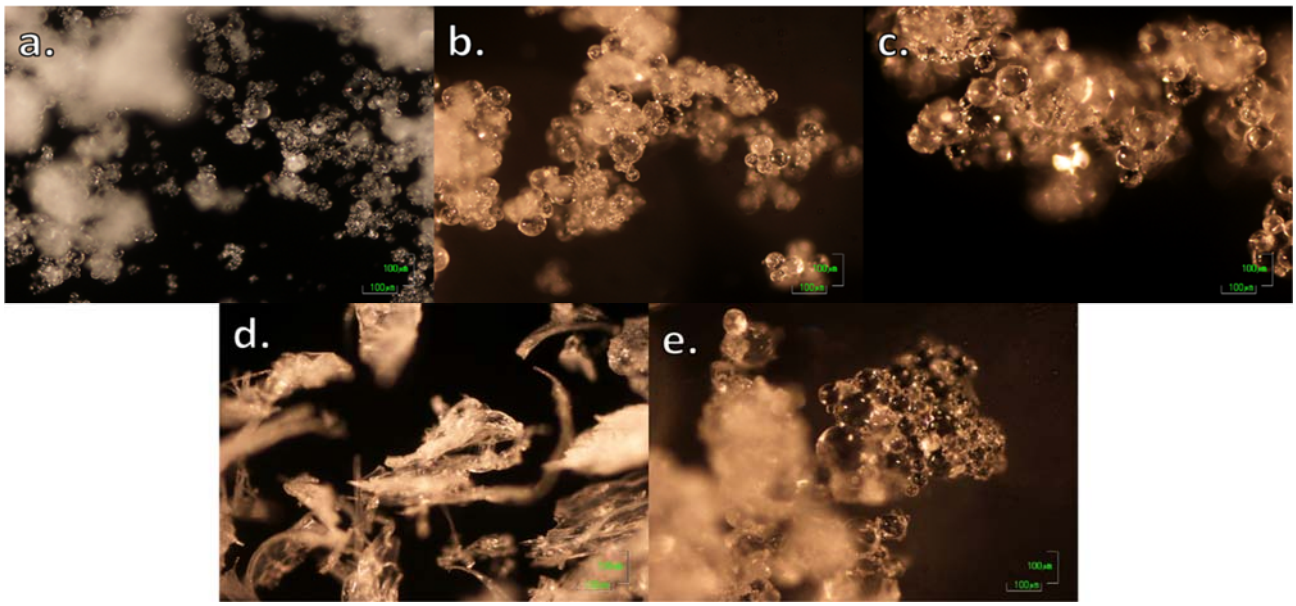


Figure 10: ETN in PMMA: a. DCM; b. DCM hot; c. DCM w/Trition; d. Acetone; e. EtOAc

To determine if encapsulation of PETN and ETN was successful, differential scanning calorimetry (DSC) (using a TA Q100 and a scan rate of 20 degree/minute) was performed on samples of the neat and of the encapsulated explosives. Hermetically sealed aluminum pans held the samples—about 0.2 mg of the neat explosive or 1 to 2 mg of the microspheres. The PMMA encapsulated explosives examined (Figures 11 and 12) were created using EtOAc and mixing for 2 hours at

room temperature. EtOAc provided the most consistent results across the methods used for PETN. Both Figures 11 and 12 show an exotherm in the scan of the PMMA microspheres which corresponds to that of the un-encapsulated explosive, indicating the presence of the explosive in the microsphere. In the case of ETN/PMMA microspheres, it shows that, although visually the capsules appeared empty (clear and colorless), at least some ETN was present (Figure 12). Neither the PETN nor ETN microcapsules had an apparent endotherm near the melting temperature of the energetic. This may be due to 1) the energetic not solidifying after encapsulation, 2) remaining solvent in the PMMA microcapsule, or 3) simply the small amount of energetic present.

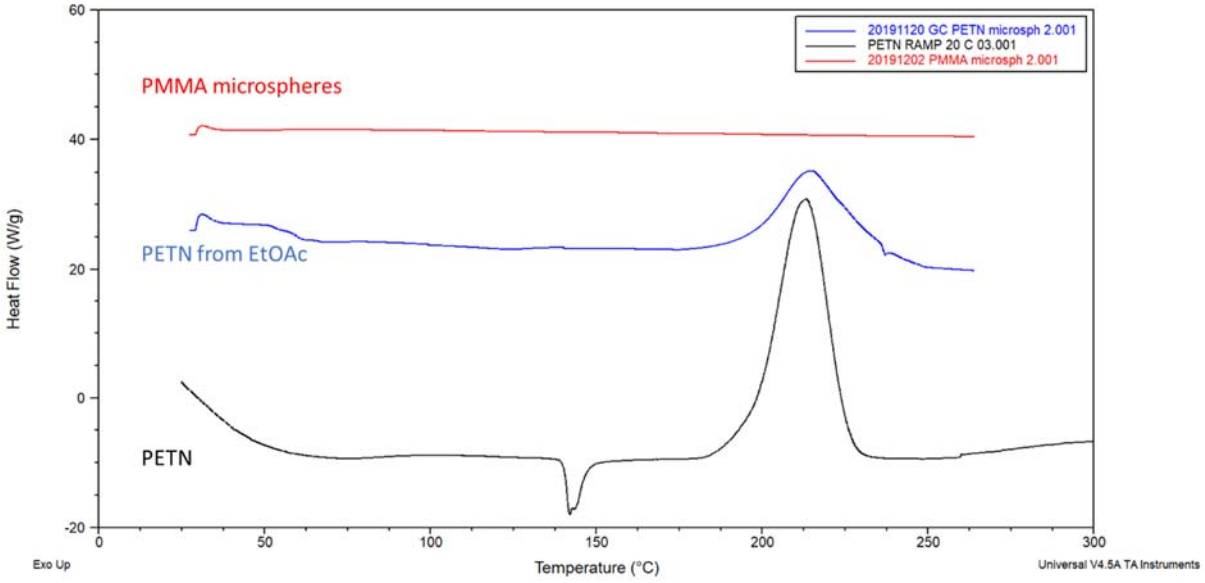


Figure 11: PETN DSC, 30-270°C at 20°C/min

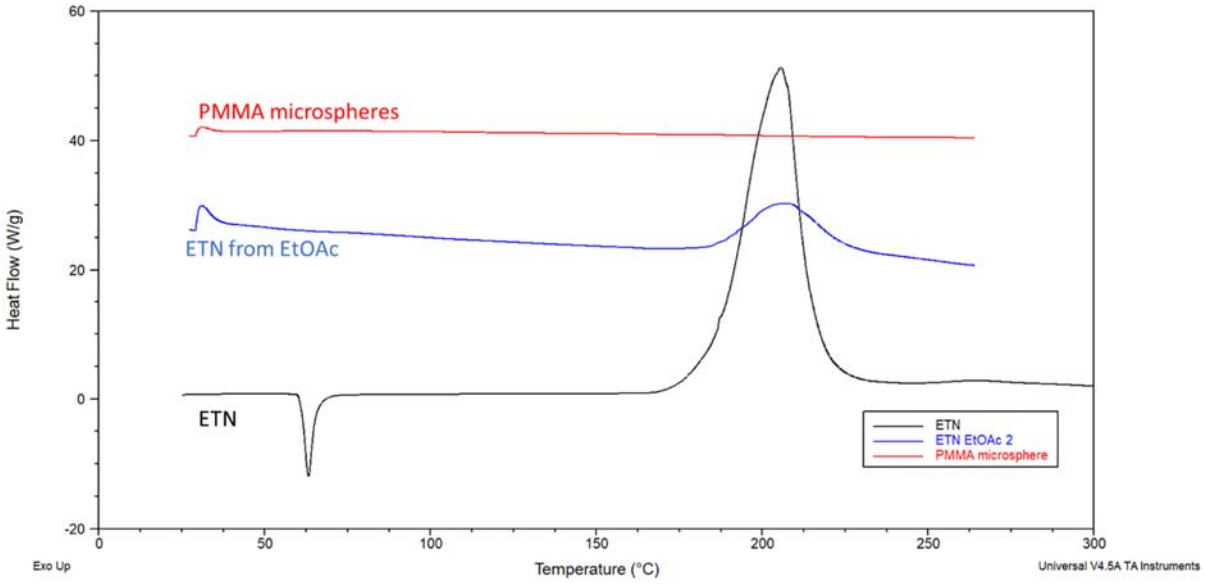


Figure 12: ETN DSC, 30-270°C at 20°C/min

Detonation Testing

To evaluate how added particles (encapsulated agents) affected the performance of an explosive inert glass microballoons (MB), glass microspheres (MS), or PMMA microspheres were added to an explosive. These tests were intended to provide guidance as to how many of the encapsulated microspheres could be added to an explosive formulation without negatively impacting its performance. It was expected that glass particles might have a different effect than the softer PMMA particles, but the commercial glass particles came in more reproducible sizes than our lab-made PMMA ones; thus, both were tested. It was necessary for our lab to prepare the adulterated explosive and to do so uniformly. The explosive, available and most appropriate for our formulation was RDX powder (wetted RDX Type II, Class 3). We formulated this initially with red gum (RG) and later with polyethylene wax (PE) (91% RDX: 9% PE). The low-density oxidized PE was Honeywell A-C 629; it allowed variable pellet density by pressing to different pressures (10 tons maximum pressure). This PRD/PE formulation[2] become the standard "booster" pellets for subsequent tests (Figure 13).

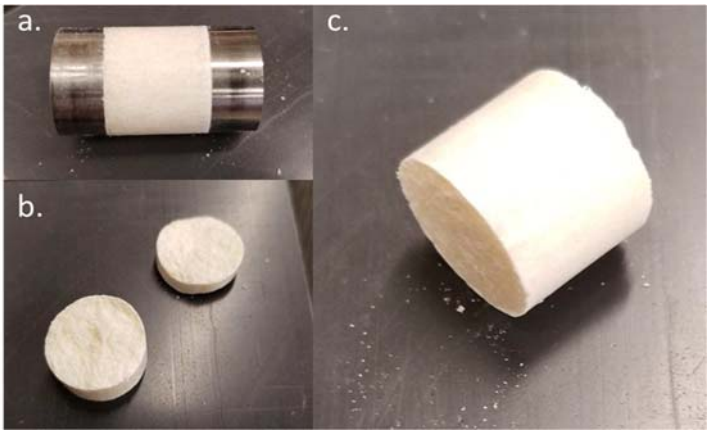


Figure 13. a) anvils stuck to pellet of RDX; b) pellet pulled apart; c) whole pellet.

Once the baseline formulation was satisfactorily created, RDX was adulterated with inert glass microballoons (MB), glass microspheres (MS), or PMMA microspheres. K25 microballoons (25-90 μm, manufactured by 3M) are small, hollow, spherical particles; microspheres are similar but solid particles (44-90 μm); the PMMA microspheres are solid particles (60-80 μm). Each offers a different hotspot mechanism as well as a shock impedance match/mismatch due to their hollow or solid nature. They were mixed into the RDX at 5% and later 10% by volume. Volume ratios between RDX and the adulterant were chosen rather than percent mass because there is a difference in densities among glass microspheres (1.04 $g \cdot cm^{-3}$), glass microballoons (0.23 $g \cdot cm^{-3}$) and PMMA microspheres (0.47 $g \cdot cm^{-3}$). Using percent volume ensures that void volume in each of the mixtures is approximately the same.

Adulterated formulations were made in the same manner as the unadulterated RDX. A slurry of RDX and the adulterant was formed in water and heated to 80 °C; the emulsified PE wax was then mixed in. With vigorous mechanical stirring, the emulsion was broken upon addition diluted sulfuric acid, thus coating the solids in the slurry. The coated RDX/adulterant was filtered and dried. Visually, the adulterated formulations appeared identical to the unadulterated RDX/PE. The presence of microballoons or microspheres was confirmed by microscopy. After pressing, all formulations were imaged to assure the adulterant retained structural integrity.

The shot configuration used six to nine pellets stacked in a clear plastic tube (Figure 14). A small amount of petroleum jelly was placed between pellets to minimize air gaps. Unadulterated sample and adulterated samples were fired. The adulterated samples (6 pellets) were boosted using three RDX/PE unadulterated pellets. Shots were initiated horizontally, with RP-83 EBWs (Figure 15).

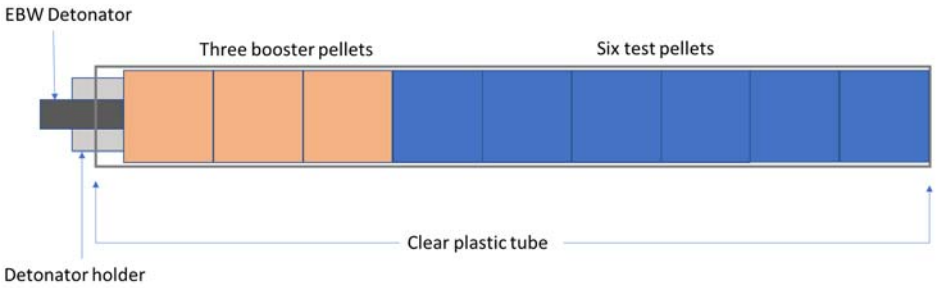


Figure 14: Shot configuration

Figure 15: Shot fixture with detonator

High-speed Camera Diagnostics

Data was collected using two high-speed cameras: an Optronis SC-10 streak camera and a SIMD 16 (Figure 16). The cameras were coupled using the SIMD beam-splitting port, which splits the light from the lens attached to the SIMD between both cameras. This allows both cameras to witness the shot from the same angle. The SIMD16 captures a total of sixteen frames, and for this shot series those were collected at a framing rate of 1.410 million frames per second. Detonation velocities were calculated by tracking the reaction front in each of these frames.

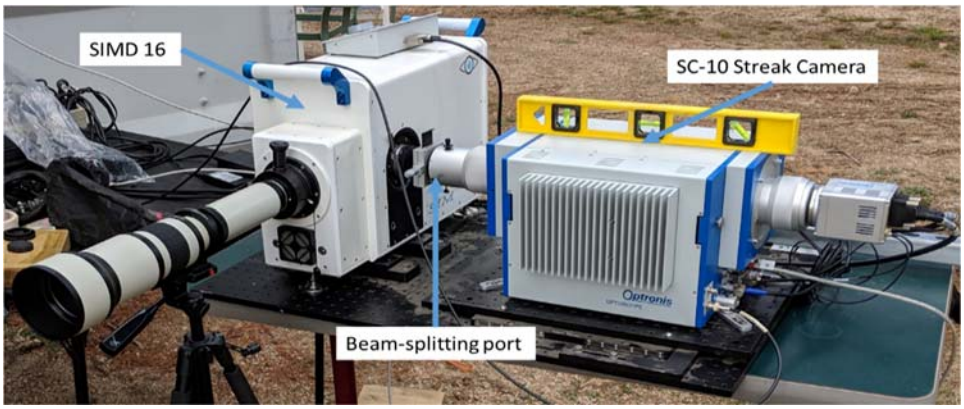


Figure 16: high-speed camera set-up

The baseline of RDX/PE was shot first; the data is found in Table 4, Plot 1, and Figure 17. Three pellets of the same unadulterated RDX/PE pellets preceded the adulterated pellets to ensure the detonation had time to stabilize after coupling to the booster pellets from the detonator. If there were a change in detonation velocity in the adulterated pellets, the streak record would exhibit a change in slope. The first frames of every shot show the front traveling through the booster pellets; these are marked in orange in the table and the plot. The frames from 13 to the end of the record were taken after the detonation front had left the pellets ("breakout"); these frames were not included in the calculation of the detonation velocity and are marked red. The three shots performed with the RDX/PE with 5% MS, MB, or PMMA formation are shown in Tables 5 to 7 and accompanying Plots 2-4 and Figures 18-20. The streak camera record is shown alongside the SIMD record. There is a small axis plotted in the streak record to indicate shot and streak direction. Table 7, Plot 5, and Figure 21 is data collected for a RDX/RG shot.

frame	time (μs)	position (mm)
1	7.8	0
2	8.509	3.29
3	9.218	10.75
4	9.927	17.84
5	10.636	23.91
6	11.345	29.09
7	12.054	33.90
8	12.763	39.97
9	13.472	46.17
10	14.181	52.24
11	14.89	57.43
12	15.599	63.12
13	16.308	72.23
14	17.017	79.82
15	17.726	83.74
16	18.435	88.67

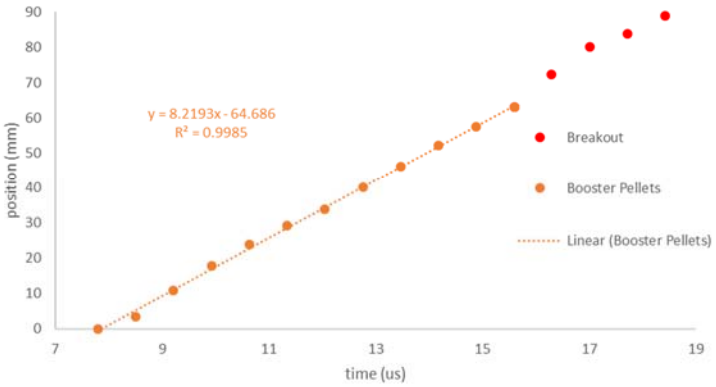


Table 4 and Plot 1: RDX/PE booster pellet calibration

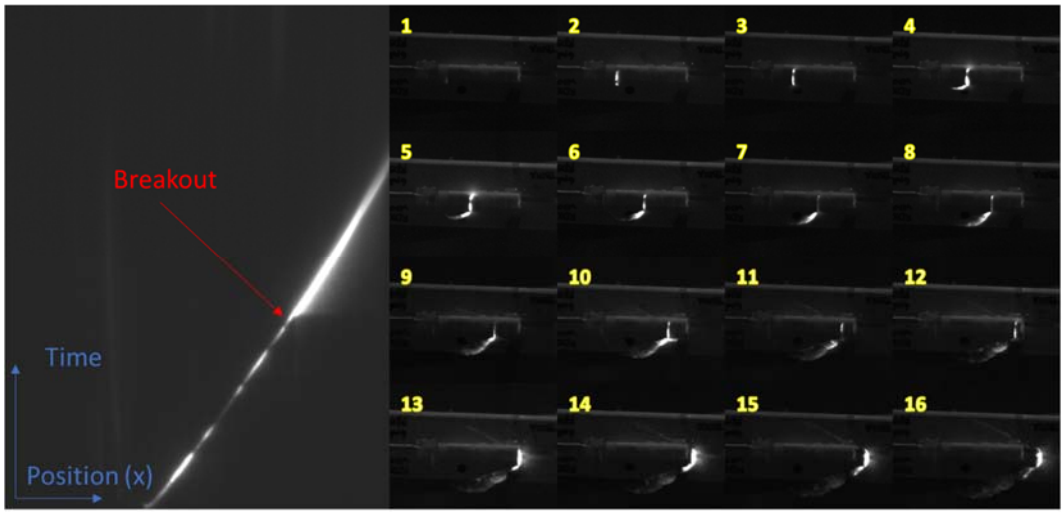


Figure 17: RDX/PE booster pellets, streak record (left), SIMD16 record (right)

frame	time (µs)	position (mm)
1	6.5	-
2	7.562	-
3	8.624	0
4	9.686	10.51
5	10.748	18.92
6	11.81	27.85
7	12.872	35.73
8	13.934	44.53
9	14.996	52.81
10	16.058	61.61
11	17.12	70.94
12	18.182	79.74
13	19.244	87.76
14	20.306	96.43
15	21.368	104.57
16	22.43	104.57

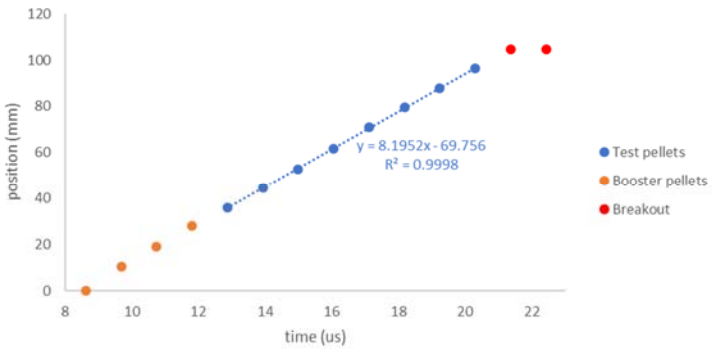


Table 5 and Plot 2: RDX/PE +5% MS

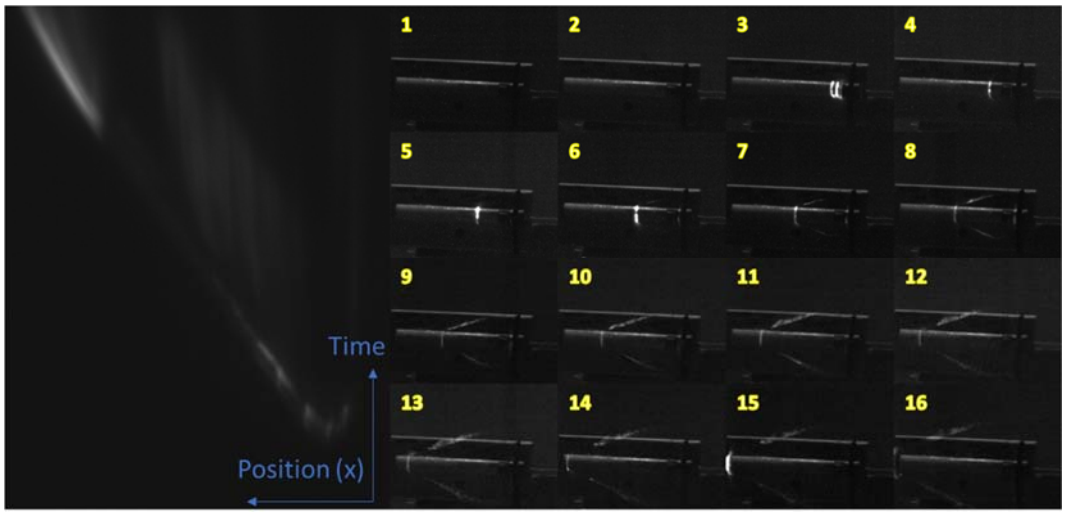


Figure 18: RDX/PE +5% MS, streak record (left), SIMD16 record (right)

frame	time (µs)	position (mm)
1	6.5	-
2	7.562	-
3	8.624	0.00
4	9.686	10.17
5	10.748	20.07
6	11.81	28.02
7	12.872	35.06
8	13.934	43.79
9	14.996	52.66
10	16.058	61.26
11	17.12	69.60
12	18.182	78.85
13	19.244	86.80
14	20.306	96.19
15	21.368	99.19
16	22.43	123.82

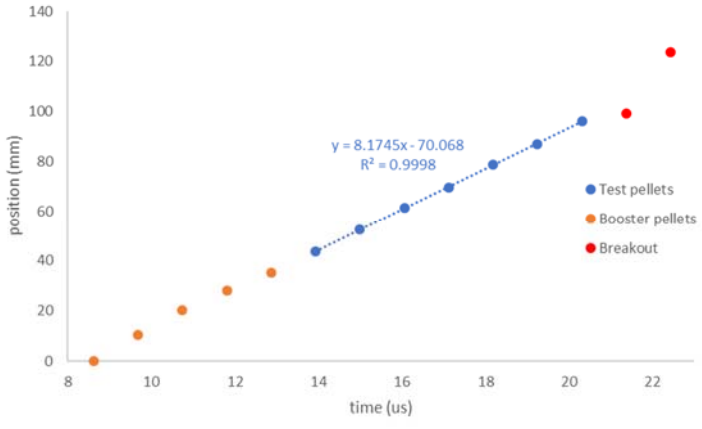


Table 6 and Plot 3: RDX/PE +5% MB

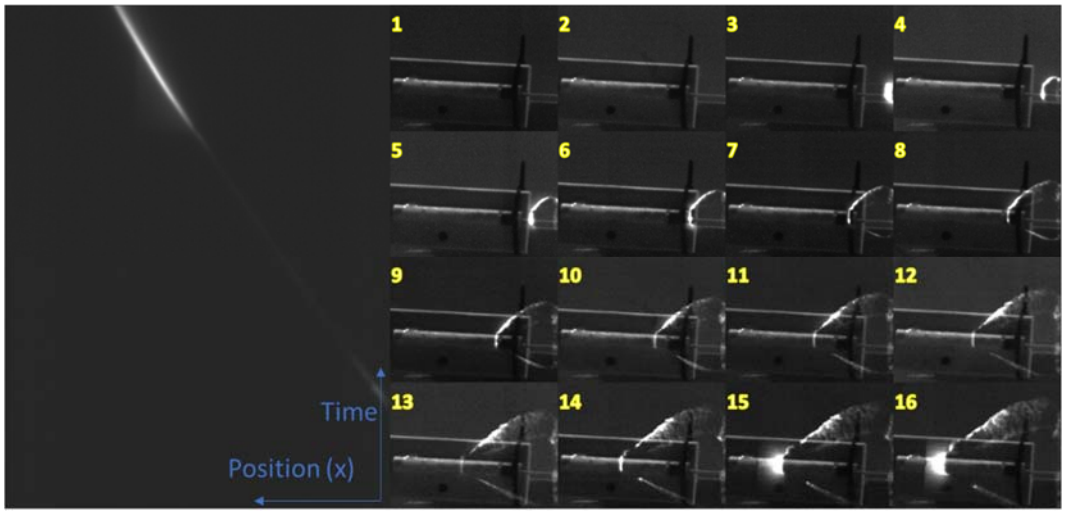


Figure 19: RDX/PE +5% MB, streak record (left), SIMD16 record (right)

frame	time (µs)	position (mm)
1	8	0.00
2	9.098	8.87
3	10.196	18.05
4	11.294	27.07
5	12.392	36.84
6	13.49	45.56
7	14.588	54.44
8	15.686	63.31
9	16.784	72.18
10	17.882	81.80
11	18.98	89.93
12	20.078	98.80
13	21.176	108.12
14	22.274	117.59
15	23.372	125.87
16	24.47	133.23

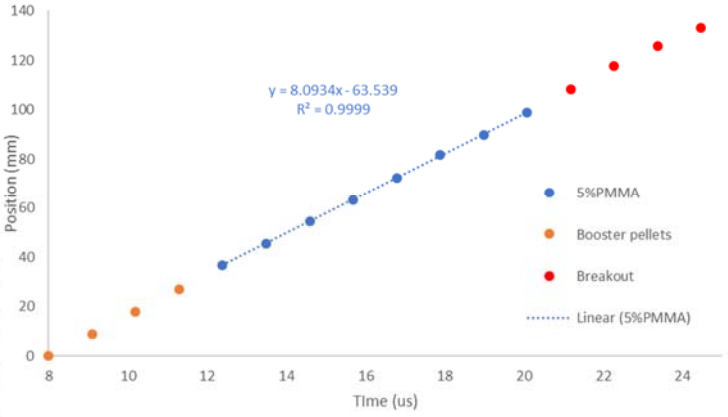


Table 7 and Plot 4: RDX/PE +5% PMMA

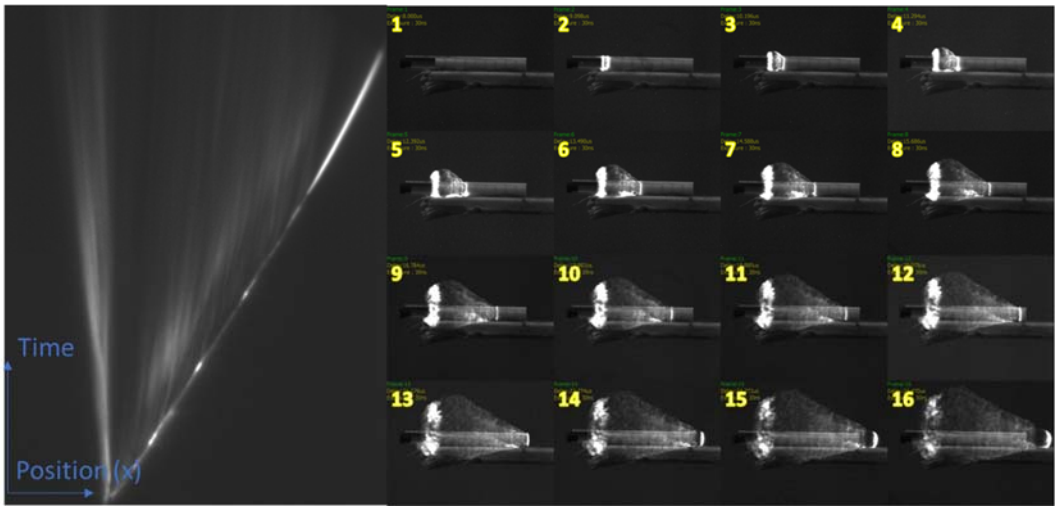


Figure 20: RDX/PE +5% PMMA, streak record (left), SIMD16 record (right)

frame	time (µs)	position (mm)
1	6.5	
2	7.296	
3	8.092	
4	8.888	0
5	9.684	8.9568696
6	10.48	14.656696
7	11.276	23.206435
8	12.072	27.277739
9	12.868	35.623913
10	13.664	40.305913
11	14.46	47.837826
12	15.256	52.926957
13	16.052	61.27313
14	16.848	69.82287
15	17.644	100.76478
16	18.44	103.6147

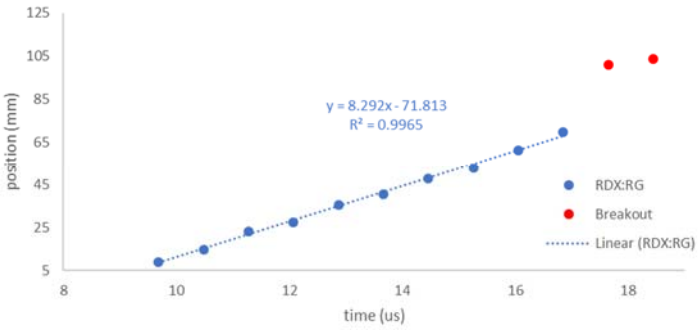


Table 8 and Plot 5: RDX/RG

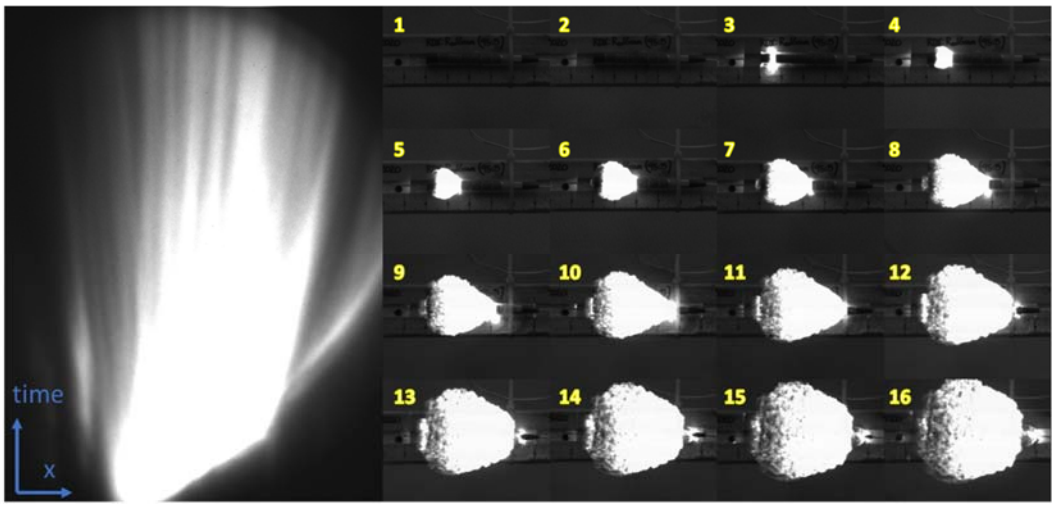


Figure 21: RDX/RG, streak record (left), SIMD16 record (right)

Table 9: Summarized high-speed camera results

Formulation	g/cm^3	km/s (SIMD16)	km/s (SC-10)
RDX/PE	1.72	8.219	8.03
RDX/PE	1.70	8.298	8.65
+ 5% MS	1.73	8.195	8.15
+ 5% MB	1.69	8.175	8.69
+ 5% PMMA	1.67	8.028	8.66
+ 5% PMMA	1.67	8.093	8.52
RDX/RG	1.72	8.292	-
RDX/RG	1.61	8.268	8.68

Conclusions

Detonation tests of the pellets indicate there was no substantial loss in performance of the RDX formulation when adulterated 5% by volume with either glass or PPMA microparticles. The performance of all adulterated formulations tested were within 3% the detonation velocity of the booster pellets and supported a steady detonation throughout the length of the test fixture. Thus, it is likely any of the microspheres could be used without significant reduction in the normal performance of the munition. RDX/PE pellets with 10% MS, MB, or PMMA adulterants have been prepared for testing to determine if this level of adulteration can also be tolerated. This will better inform how much additive can be added and still meet performance requirements. The more reactive agent that can be embedded in the explosive, the less effective (i.e. the less catalytic) that agent needs to be.

The degradation agents tested have had insufficient catalytic activity to digest the explosive without aid of a second agent to thoroughly distribute them throughout the explosive article. In the case of sodium hydroxide, rain would suffice; but in some regions accidental trigger is a distinct possibility, and in others it is almost completely unavailable. The possibility of encapsulated water microspheres was discarded when we learned during the ARO workshop on this topic, that no encapsulation can ensure water remains capsules long term. A second concerned brought out by that workshop is the environmental fate of the degradation product of the explosive. To date that issue has only been explored for nitrocellulose.[3-5]

Sensitizing insensitive explosives with more sensitive explosives awaits initiation testing to assess how well the concept works. Yet, passing that bar would only be the beginning for a battery of safety and performance testing. Triggering issues do not exist with this approach which is both a positive and a negative for this approach.

Future Directions

As stated above, the increase in voids in an explosive formulation provides more hotspots when the formulation is under shock loading, which aids in the propagation of the shock. We have suggested, but not yet tried, both shape-memory polymers and gas generators for this role.

A number of memory-shape polymers have been reported (Appendix B), but most are not readily available. A cheap and commercially available memory shape polymer are pre-stretched polystyrene (PS) sheets. Commercial PS products like Shrinky Dinks sell for about a dollar for an 8.5”x11” sheet. These shrink to 40% of their original area and become nine times thicker upon heating,[4] as the stress held in the plastic is converted to mechanical energy. When stretched PS sheets are exposed to their glass transition temperature (100 °C) or above, they rapidly contract to their pre-stretched dimensions. In theory, this is an accessible trigger for creating heterogeneities in an explosive formulation to transform, on-demand, an insensitive explosive into one easier to initiate.[5] (Figure 22) This level of heating is neither high enough to cause hazardous explosive decomposition nor low even to be activated accidentally.

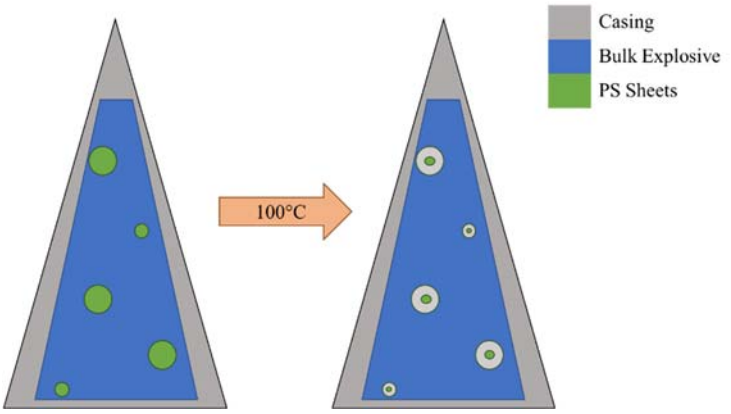


Figure 22: PS sheets creating voids in bulk by shrinking after heating

Another way of creating voids in an explosive formulation post-manufacturing is activating a species which generates gas. We have searched the literature for species which generate significant volumes of gas and do so with a reasonable triggering mechanism (Appendix C). In exploring gas generators, two features were noted--the ability to store a significant amount of gas per mass additive; and the mode of triggering gas release. Some complexes require a great deal of heat to desorb the stored gas. Although the goal was to make the explosive more easily initiate. High heat would not allow controlled, safe initiation. The most promising to date is $Mg(NH_3)_6Cl_2$ which has been studied for solid-state hydrogen storage.[6,7] The decomposition of $Mg(NH_3)_6Cl_2$ generates ammonia, which, when hydrogen is desired, is catalytically converted to N_2 and H_2. (Figures 23, 24) For the purposes of creating stress fractures, creating ammonia gas inside the explosive may be sufficient to sensitize the explosive formulation. This decomposition can be affected at reasonable temperatures starting at 80 ºC.

$$Mg(NH_3)_6Cl_2 \rightarrow MgCl_2 + 6NH_3$$

Figure 23: Thermal decomposition reaction of $Mg(NH_3)_6Cl_2$

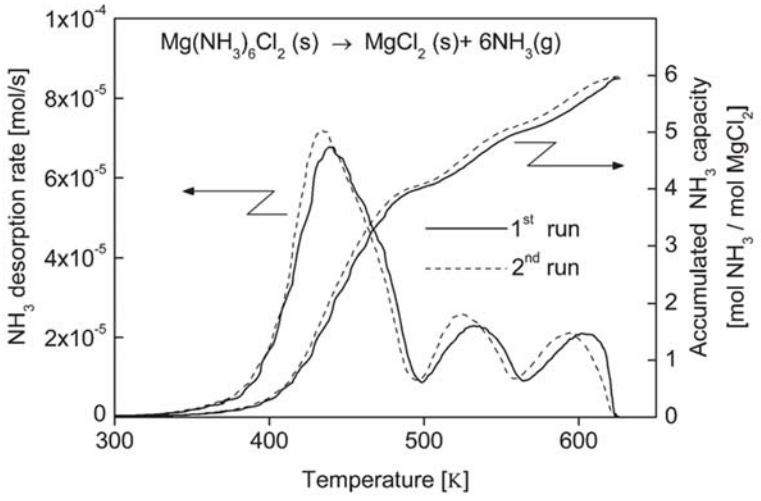


Figure 24: Ammonia gas generation by $Mg(NH_3)_6Cl_2$ vs temperature[6]

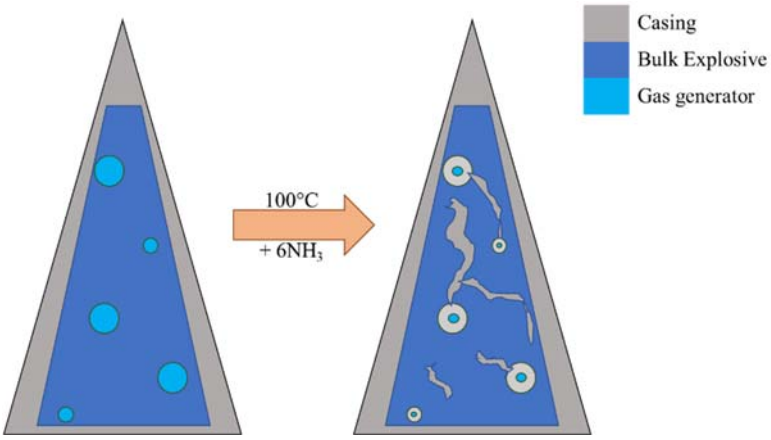


Figure 25: Gas generators fracturing the bulk charge after activation

Solid-state gas generators imbedded in an explosive formulation could increase the void space by releasing gas which could form microchannels effectively reducing the density of the bulk (Figure 25). These small cracks and voids would act as hotspots in the bulk explosive and would increase the shock sensitivity and ease initiation of the bulk.

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Appendix A

Table A: List of Considered Digestion Agents

Degradant	Form	Conditions	Solvent	Target	Reference
Ag/TiO_2	Mesoporous NP	25 °C	$EtOH/NaBH_4$	4-nitotoluene	[1]
Cu	NP	110 °C, irradiated w/microwave and ultrasound	Ethylene glycol and water	Nitrobenzene	[2]
Pt	On nanocarbon, hydrogenation	80 °C	None	Nitrobenzene	[3]
Ru	Hydrogeneration	60 °C	None	Nitrobenzene	[4,5]
Cu/Ag/Au	Micelles of alloy	25 °C	Surfactants	4-nitrophenol	[6]
Ni-B	Nano-amorphous material	50 °C	Hydrazine/water		[7]
Fe	NP	25 °C	Water	Nitroarenes	[8]
Pd	NP	90 °C	Water	Nitroarenes	[8]
Co	NP	25 °C	Water $NaBH_4$	4-nitrophenol	[9]
Mg/Pd	Alloy	25 °C	Water/MeOH	TATP	[10]
Mg/Pd/Ni	Nano-micron particles	25 °C	Water/hydrophobic solvent	TATP	[11]
Fe/Pd/Ni	Nano-micron particles	25 °C	Water/hydrophobic solvent	TATP	[11]
$FeBr_2$/thiols	solution	65 °C	CD_3CN	TATP	[12]
Fe/Pd	Micro particles on carbon	25 °C	Toluene	TNT/RDX	[13]
Ni/Pd	Micro particles on carbon	25 °C	Toluene	TNT/RDX	[13]
NaOH	solution	100 °C	Water	TNT/RDX	[14]

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Appendix B

Shape-Shifting Material Review

It would be beneficial to store mechanical energy in small additives which would be co-formulated with the explosive and triggered intentionally by an external stimulus. Doing so would allow for the density of the bulk formulation to be changed on demand. Explosive performance, sensitivity, and initiability are all dictated by the density of the explosive.

Table B: List of some Shape-memory polymers (SMPs)

Compound	Stimulus	Activation condition	Elongation at break (%)	Commercially available	Source
F5-C6	Heat	65 °C	514	No	[1]
F10-C3	Heat	65 °C	575	No	[1]
F10-C6	Heat	65 °C	503	No	[1]
SMP A-1	Heat	71 °C	1175	No	[2]
SMP A-2	Heat	74 °C	818	No	[2]
SMP A-3	Heat	74 °C	674	No	[2]
SMP A-4	Heat	71 °C	623	No	[2]
SMP A-5	Heat	67 °C	606	No	[2]
Fe_3O_4-SMP	Radio wave	296 kHz	N/A	No	[3]
SMP-H1	UV light	365 nm	N/A	No	[4]
Azo LC	UV light	365 nm	N/A	No	[5]
Nafion	Heat	80 °C	25	Yes	[6]
Polystyrene	Heat	100 °C	40	Yes	[7]

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Appendix C

Gas Generator Review

Complexes, which have been patented for gas generation, e.g. $Cu(NH_3)_4(NO_3)_2$, $Co(NH_3)_3(NO_2)_3$, or $Co(NH_3)_6(ClO_4)_3$, show a large loss in mass when they degrade but require flame for initiation.[1] In addition, these complexes are capable of detonating when confined.[2] Adding metal complexes that require flame to initiate or could detonate given confinement would make the ordnance more hazardous to the end user. Other gas generators do not require flame but do need extreme heat to decompose fully. Metal hydrides (M^+H^-) have been investigated as a source of hydrogen gas.[3–6] These complexes have a range of gas desorption temperatures ranging from 125-500 °C.[7] By mass these complexes do not deliver much gas making them less than ideal when the additive can be only a small percent of the munitions' mass.

Metal organic frameworks (MOFs), which are porous solids with high surface area, can store a great deal of gas; however, the absorption of gas is done at very low temperatures (-196 °C) or very high pressures (>5 atm).[8–10] Some MOFs, like BPDC-$(NO_2)_4$, can lose up to 68% of their original mass when heated;[11] but due to the low energy density of the MOF, it is a poor choice to add to a formation. MOFs require impracticable conditions to store appreciable volumes of gas.

Azides (MN_3) are energetic complexes that release N_2 gas when they decompose.[12] Some are extremely sensitive to the point they are considered primary explosives.[13] Although this rules them out for the proposed application, it is intriguing that a few in this class, on AgN_3 and PbN_6, can undergo decomposition using magnetic fields (5 kV/m).[14] Thermal decomposition is also possible, but even the commonly used azide, NaN_3, does not release gas until about 275 °C.[15] This temperature is too high for most organic military explosives.

Soft X-rays (energies less than 5 keV and wavelengths greater than 0.2 nm) are able to degrade some polymers.[16,17] Added plastics would not be expected to increase the sensitivity of an explosive. However, they would not provide the same level of gas generation as some of the inorganic complexes. Only poly(ethylene succinate) loses an appreciable fraction of initial mass after irradiation.[17] To degrade plastics using soft x-rays, an appropriately powerful x-ray generator would be needed to penetrate the metal casing of the munition as well as the bulk of the explosive formulation.

Solid-state hydrogen generators can store hydrogen in forms other than hydrides. Ammonium (NH_3) can be used; and as a ligand to a metal, it can be released with heating.[18] Complexes like $Mg_2(NH_3)_6Cl_2$ store 9% by mass of hydrogen.[18] When heated passed 80 °C $Mg_2(NH_3)_6Cl_2$ releases ammonia gas (NH_3) which can then be directed over a catalyst to break it into N_2 and H_2 gas.[18] For the purposes of using a gas generating complex to form voids in an explosive formulation, the generation of ammonia gas would without further refinement would be sufficient. With this complex releasing gaseous ammonia at relatively low temperatures it could be added to explosive formulations with energetics that have phase transitions above 100 °C. Gentle heating of ordinance could be performed remotely, and temperatures could be kept low enough to not cause thermal initiation of the bulk explosive.

Appendix C References

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