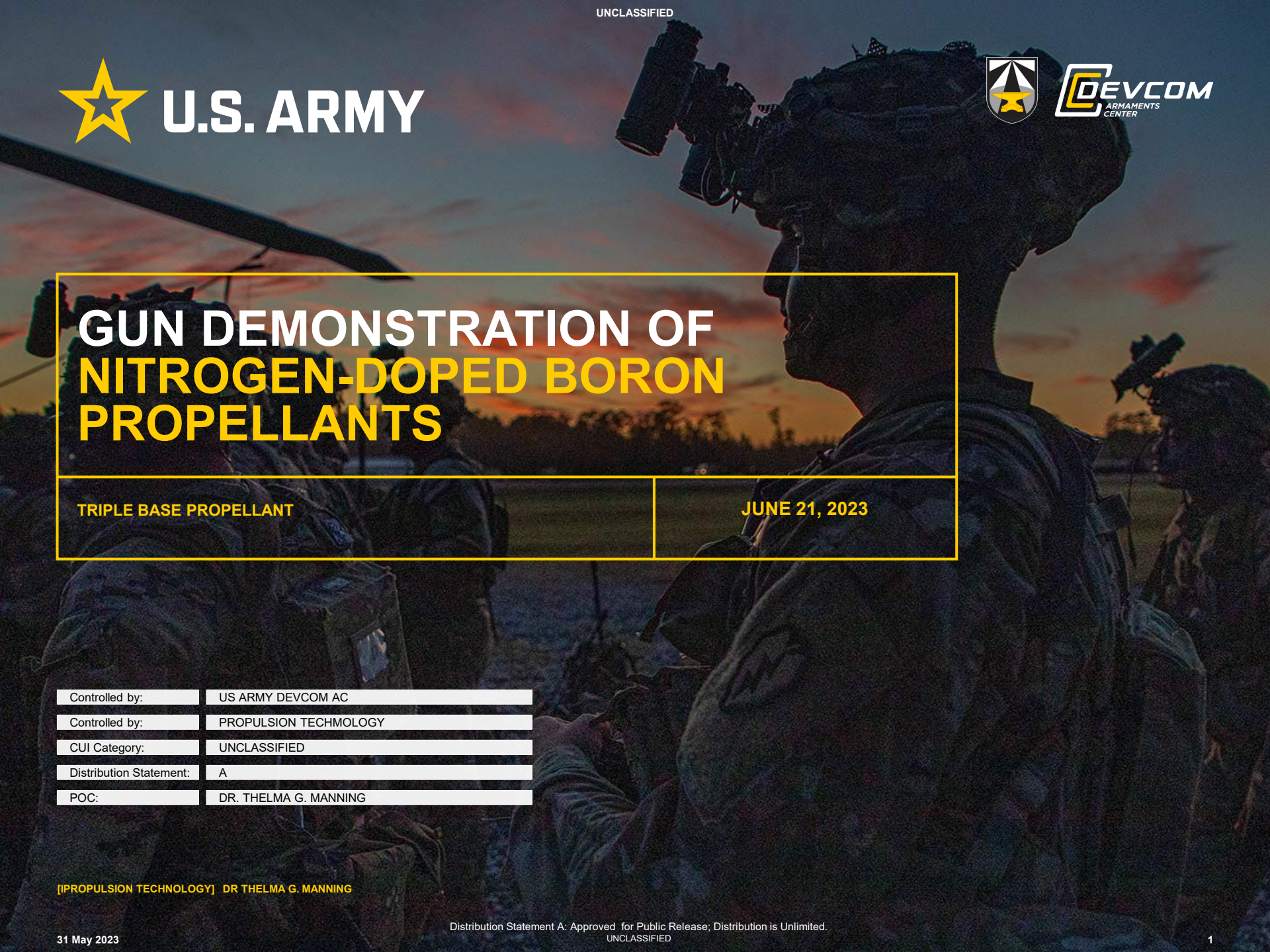

U.S. ARMY

DEVCOM ARMAMENTS CENTER

GUN DEMONSTRATION OF NITROGEN-DOPED BORON PROPELLANTS

TRIPLE BASE PROPELLANT

JUNE 21, 2023

Controlled by:	US ARMY DEVCOM AC
Controlled by:	PROPULSION TECHMOLOGY
CUI Category:	UNCLASSIFIED
Distribution Statement:	A
POC:	DR. THELMA G. MANNING

[IPROPULSION TECHNOLOGY] DR THELMA G. MANNING

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OUTLINE

- Introduction and Background
- Results and Discussion
  - Previous work
  - Preparation of BN
  - Compatibility Testing of Propellant Constituents
  - Manufacture of propellant
  - Firing Test Preparation Using 25mm Gun Test Fixture
  - Characterization and Testing
- Summary and Conclusion
- Future Plans
- Acknowledgement

INTRODUCTION
155MM ARTILLERY

- The currently fielded 155mm artillery propelling charge, M232/M232A1, has exhibited spiral wear and erosion problems.
  - This phenomenon has been attributed to a number of factors such as the wear reducing liner that contains Titanium Dioxide, Talc and wax, and the interaction of the propellant combustion. products on the projectile rotating band within the gun tube wall.
  - Modeling & Simulation studies performed from Benet Labs has determined that the reaction of Titanium Dioxide with the Talc and wax produced a residue that was hard to remove.
  - This product was an abrasive residue (number 80 ceramic grit) that built up in the gun barrel causing a spiral rifling imbalance and accelerated gun barrel erosion which markedly shortened gun barrel life.

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INTRODUCTION
155MM ARTILLERY

- Boron nitride is an interesting potential additive to propellants that could reduce gun wear effects in advanced propellants.
  - It has the properties of providing metal coating/lubricating steel hardening properties and nitrogen cooling.
  - During propellant 25mm gun firing, the additive will either form hexagonal boron nitride, which can provide a protective coating and lubricating barrier on the inside of the barrel walls, or oxidize to form boron oxide.
  - Boron oxide could also coat the barrel, or dope the steel with boron.
  - Additionally, because of its low molecular weight, boron nitride oxidation could help lower the propellant flame temperature.

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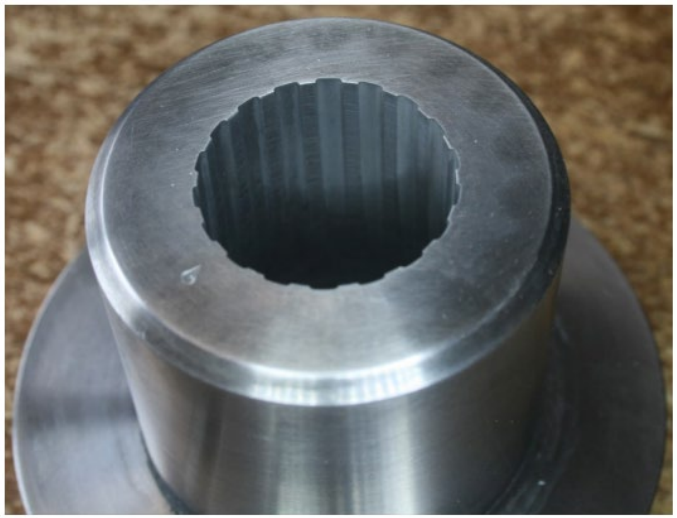
INTRODUCTION
155MM ARTILLERY

- For this testing, erosion test steel sleeves were used to enhance testing of the propellant samples (baseline and three additive levels for each propellant)
  - two different types of erosion sleeves were fabricated.



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PREVIOUS WORK

Concept diagram showing how the propellant additive will provide a regenerative BN coating and hardening of the steel, resulting in decreased wear and erosion.

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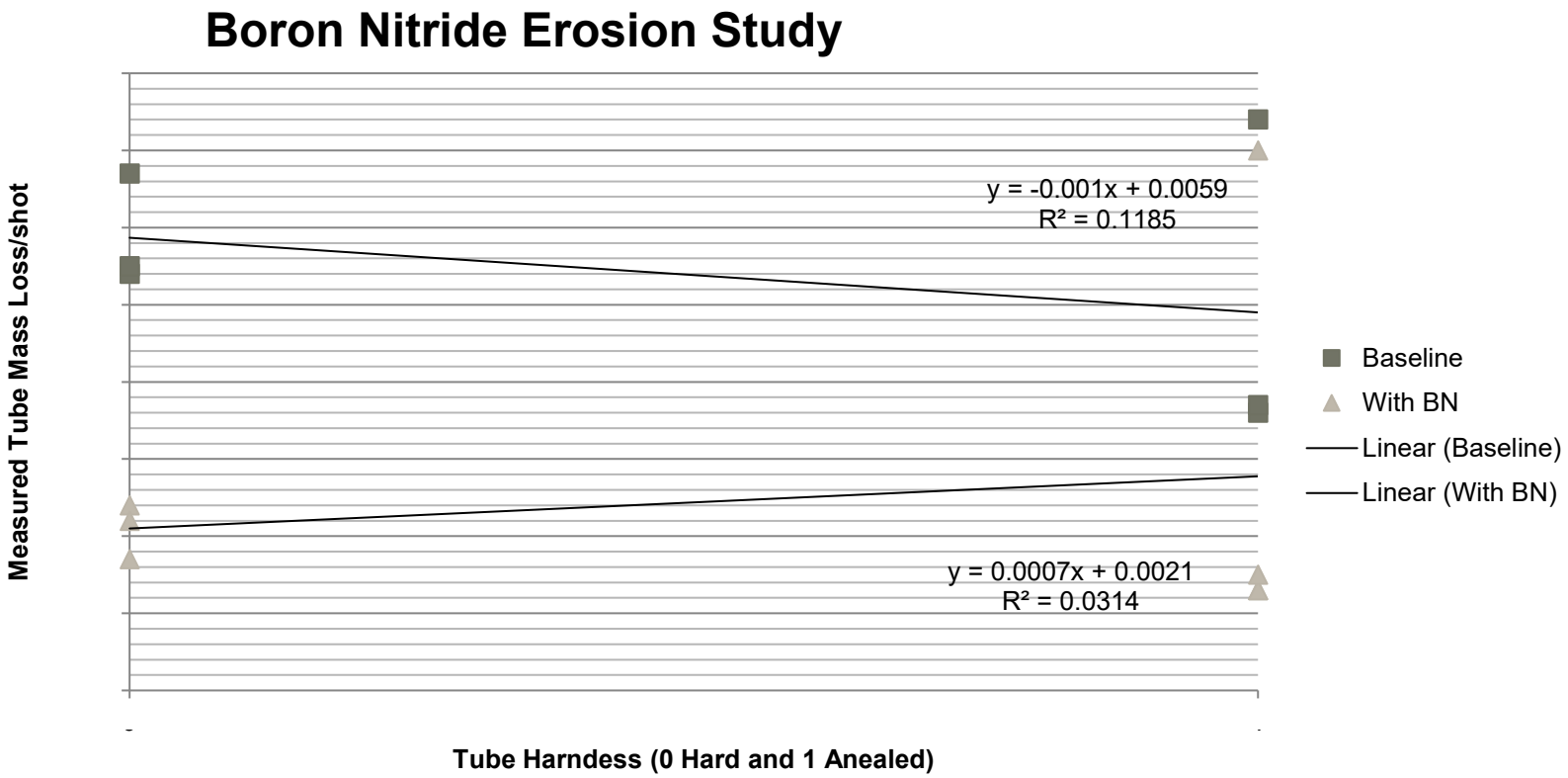
WEAR AND EROSION TESTING



Previous wear and erosion testing have demonstrated the technology provided a 2-3X reduction in wear and erosion, achieving TRL 5.

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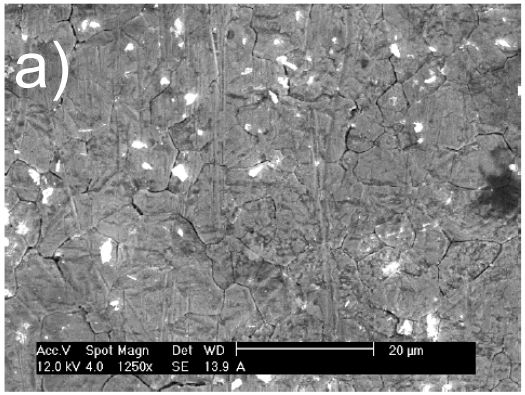
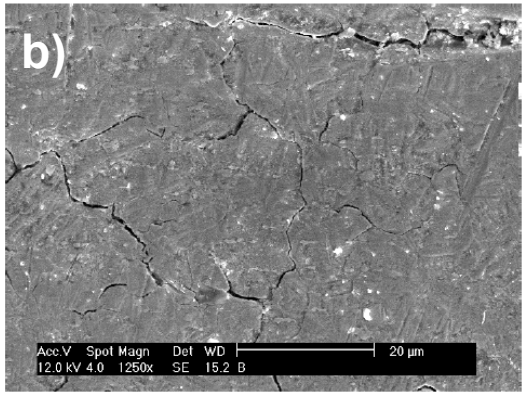
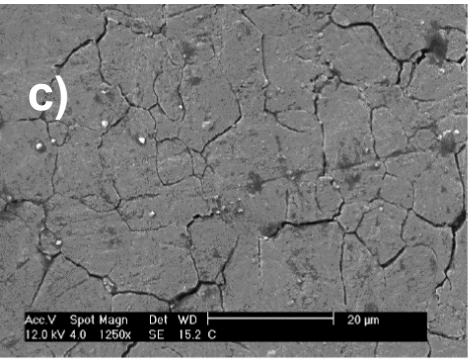
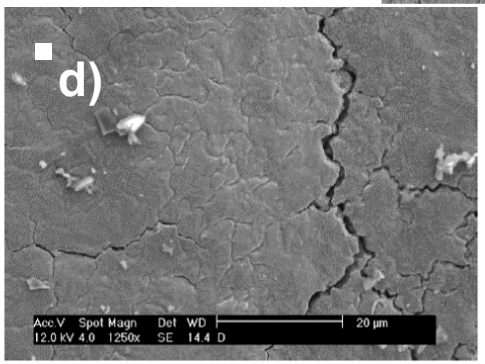
SCANNING ELECTRON MICROSCOPE

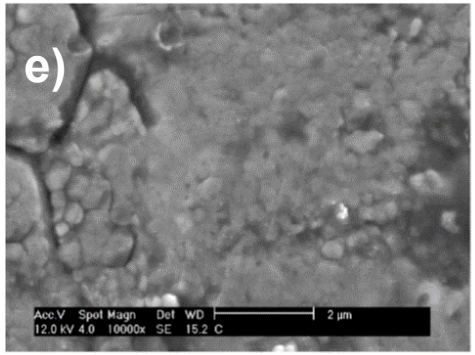
SEM surface images of: hardened steel inserts at 1,250 X magnification fired (a) in standard RPD-380, and (b) with BN / RPD-380 composite; unhardened steel insets at 1,250 X magnification fired (c) in standard RPD-380, and (d) with BN / RPD-380 composite; unhardened steel insets at 10,000 X magnification fired (e) in standard RPD-380, and (f) with BN / RPD-380 composite.

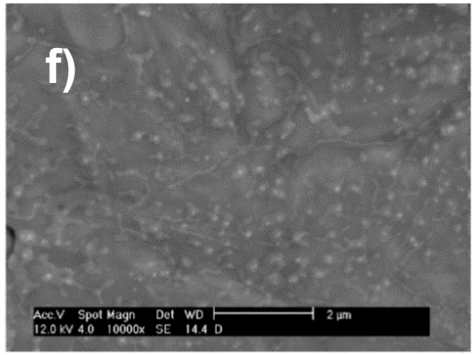












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OBJECTIVE OF THE PHASE II ENHANCEMENT PROJECT

The primary objective of the Phase II Enhancement project is to achieve TRL 6 for the BN additive technology through demonstration in sub-scale gun testing.

- Manufactured a second batch of BN to DEVCOM AC.
- Steel selection (4330V alloy) for Veritay's 25-mm apparatus was unanimously agreed upon.
- DEVCOM AC prepared propellant formulations and delivered them to Veritay for testing.

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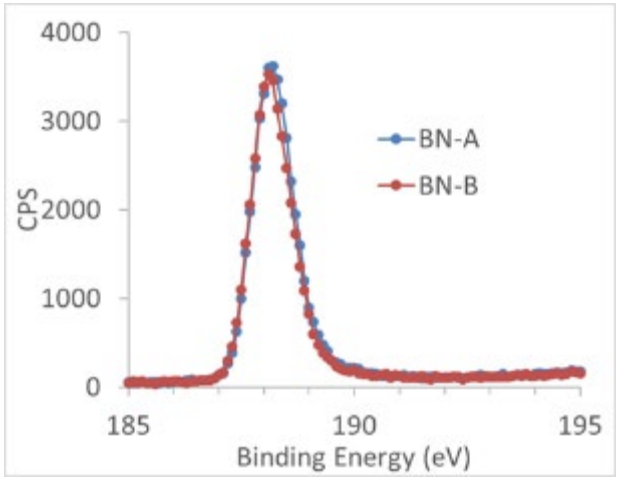
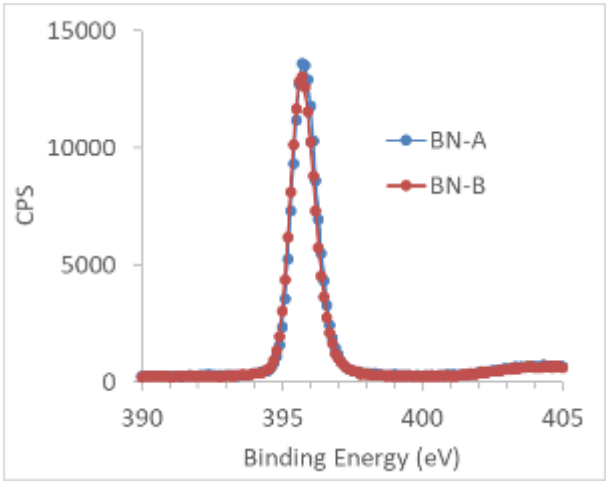
PREPARATION OF BN

Specification	Phase II BN	BN-A	BN-B
B:N Ratio	1:1 +/- 0.05	1:1 +/- 0.05	1:1 +/- 0.05
Oxygen Content	<10%	<10%	<10%
Surface Area	>20 m^2/g	>20 m^2/g	>20 m^2/g
Morphology	>50% spheres	5-25% spheres	25-50% spheres
Metal Composition	None (ICP or AAS)	None (ICP or AAS)	None (ICP or AAS)



(a) the B 1s spectra region for the BN samples delivered



(b) the N 1s spectra region for the BN samples delivered

- XPS analysis shows the materials are hexagonal boron nitride with the expected B:N ratios and less than 10% oxidation (no oxidation was detected).

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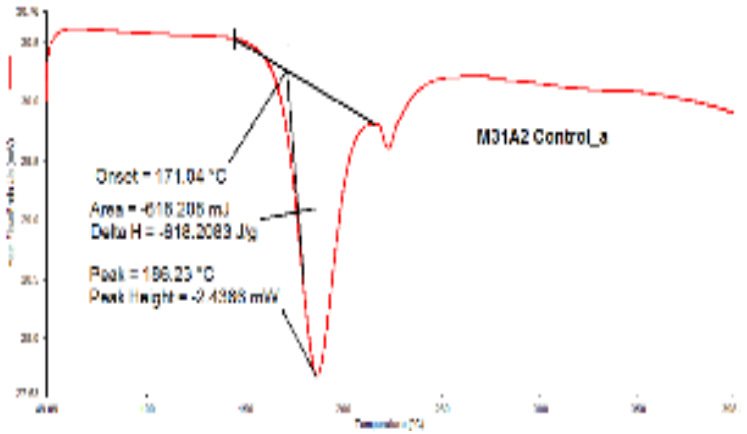
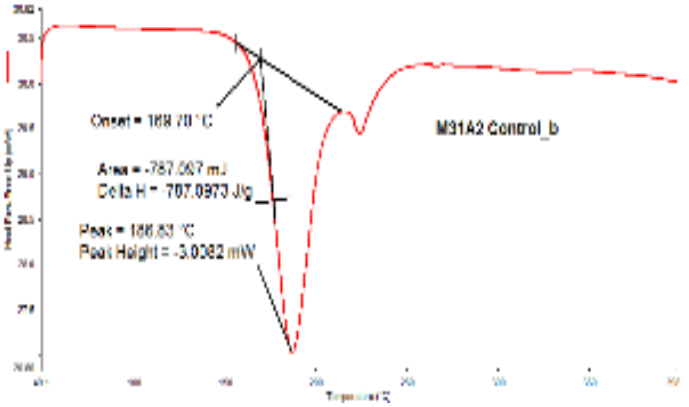
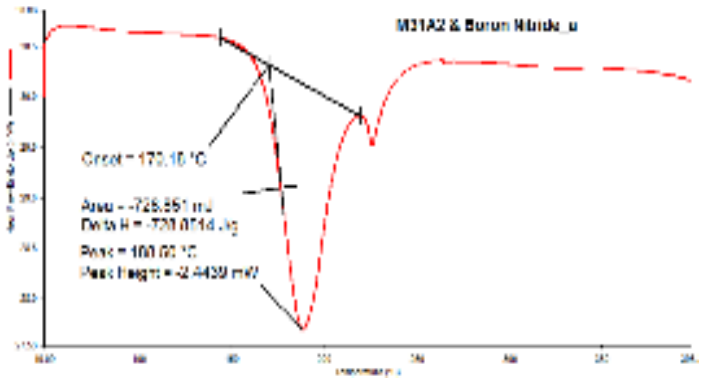
COMPATIBILITY TESTS IAW STANAG 4147



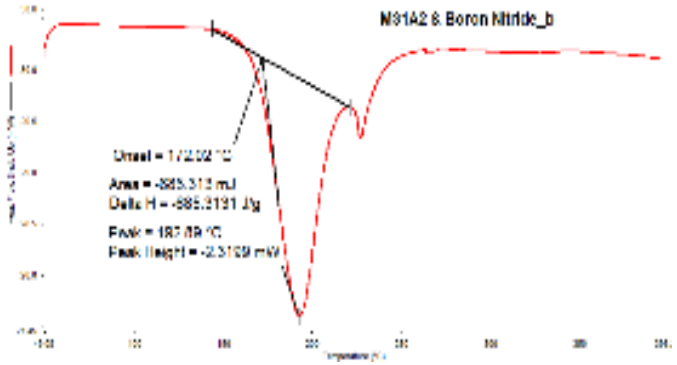
DSC scan for the M31A2 propellant as Control a.



DSC scan for the M31A2 propellant as Control b.



DSC scan for the M31A2 propellant with BN.



DSC scan for the M31A2 propellant with BN.

The M31A2 propellant control sample shown in Figures a -b, respectively, displayed an average peak temperature of 186.53 degrees Celsius.

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SUMMARY OF PEAK TEMPERATURES OF M31A2 PROPELLANT SAMPLES AND CONSTITUENTS FROM DSC TESTS

Samples	Peak Temp (°C)	Criteria	Result
M31A2 Control a	186.23		
M31A2 Control a	186.83		
M31A2/Boron Nitride_a	188.5	within or greater than 4 degrees shift to the right of M31A2 control	pass
M31A2/Boron Nitride_b	192.86	within or greater than 4 degrees shift to the right of M31A2 control	pass
M31A2/Titanium Dioxide_a	192.14	within or greater than 4 degrees shift to the right of M31A2 control	pass
M31A2/Titanium Dioxide_b	188.64	within or greater than 4 degrees shift to the right of M31A2 control	pass
M31A2/Talc_a	187.7	within or greater than 4 degrees shift to the right of M31A2 control	pass
M31A2/Talc_b	186.8	within or greater than 4 degrees shift to the right of M31A2 control	pass
M31A2/Talc/Titanium Dioxide_a	188.9	within or greater than 4 degrees shift to the right of M31A2 control	pass
M31A2/Talc/Titanium Dioxide_b	187.23	within or greater than 4 degrees shift to the right of M31A2 control	pass
M31A2/Talc/Titanium Dioxide/Boron Nitride_a	189.49	within or greater than 4 degrees shift to the right of M31A2 control	pass
M31A2/Talc/Titanium Dioxide/Boron Nitride_b	190.15	within or greater than 4 degrees shift to the right of M31A2 control	pass
M31A2/Talc/Boron Nitride_a	189.2	within or greater than 4 degrees shift to the right of M31A2 control	pass
M31A2/Talc/Boron Nitride_b	190.3	within or greater than 4 degrees shift to the right of M31A2 control	pass
M31A2/Titanium Dioxide/Boron Nitride_a	190.1	within or greater than 4 degrees shift to the right of M31A2 control	pass
M31A2/Titanium Dioxide/Boron Nitride_b	190.45	within or greater than 4 degrees shift to the right of M31A2 control	pass

Table 2: Summary of Compatibility Test Results

- A DSC decomposition peak temperature shift of 4 degrees Celsius or less is deemed compatible.
- Any shift towards a lower peak temperature of the explosive has some degree of incompatibility.
- The greater the shift towards lower temperatures; the greater the degree of incompatibility will be.
- A peak temperature shift of more than 20 degrees indicates incompatibility.
- A degree shift of more than 4 degrees Celsius to the right is also deemed compatible.

Based on test results shown in table, conducted IAW NATO/ U.S. military specifications STANAG 4147 (Chemical Compatibility of Ammunition Components with Explosives), M31A2 is deemed compatible when tested with all the constituent.

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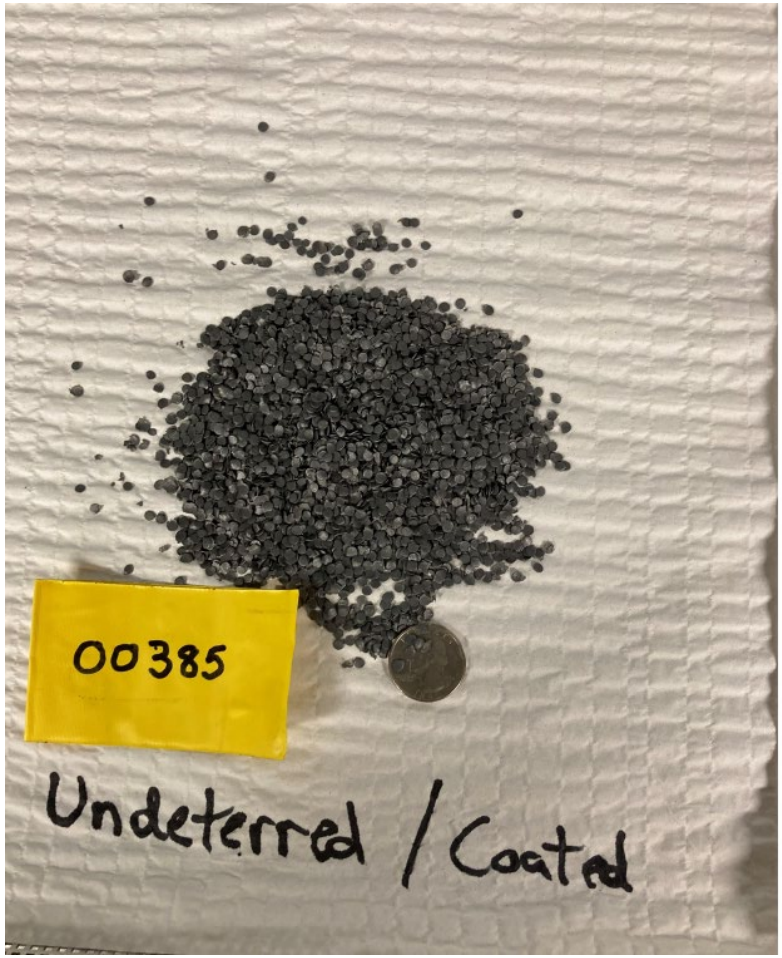
PROPELLANT GRAIN GEOMETRY

The grain dimensions were determined using Interior Ballistics High Velocity Gun (IBHVG2) code with a charge mass, a projectile mass and a target pressure.

MANUFACTURED M31A2 MODIFIED PROPELLANTS



Lot # RDD21A-00385-A1
Graphite Coated and Undeterred

Lot # RDD21A-00385-A2
Graphite Coated and Deterred

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BALLISTICS TESTING IN 25MM MANN BARREL

- A ballistic workup was performed for each propellant in an instrumented 25mm Mann Barrel.
- The cartridges were drilled to measure chamber pressure and velocity was obtained through break strips.
- Charge mass was limited to 65 – 66 grams of propellant, owing to the lower bulk (settling) density of the flake propellant grain compared to that of a 7-perf cylindrical grain.
- This prevented our ability to load the cartridges to the loading density that was assumed for the IBHVG2 calculations, which resulted in a lower chamber pressure than predicted.

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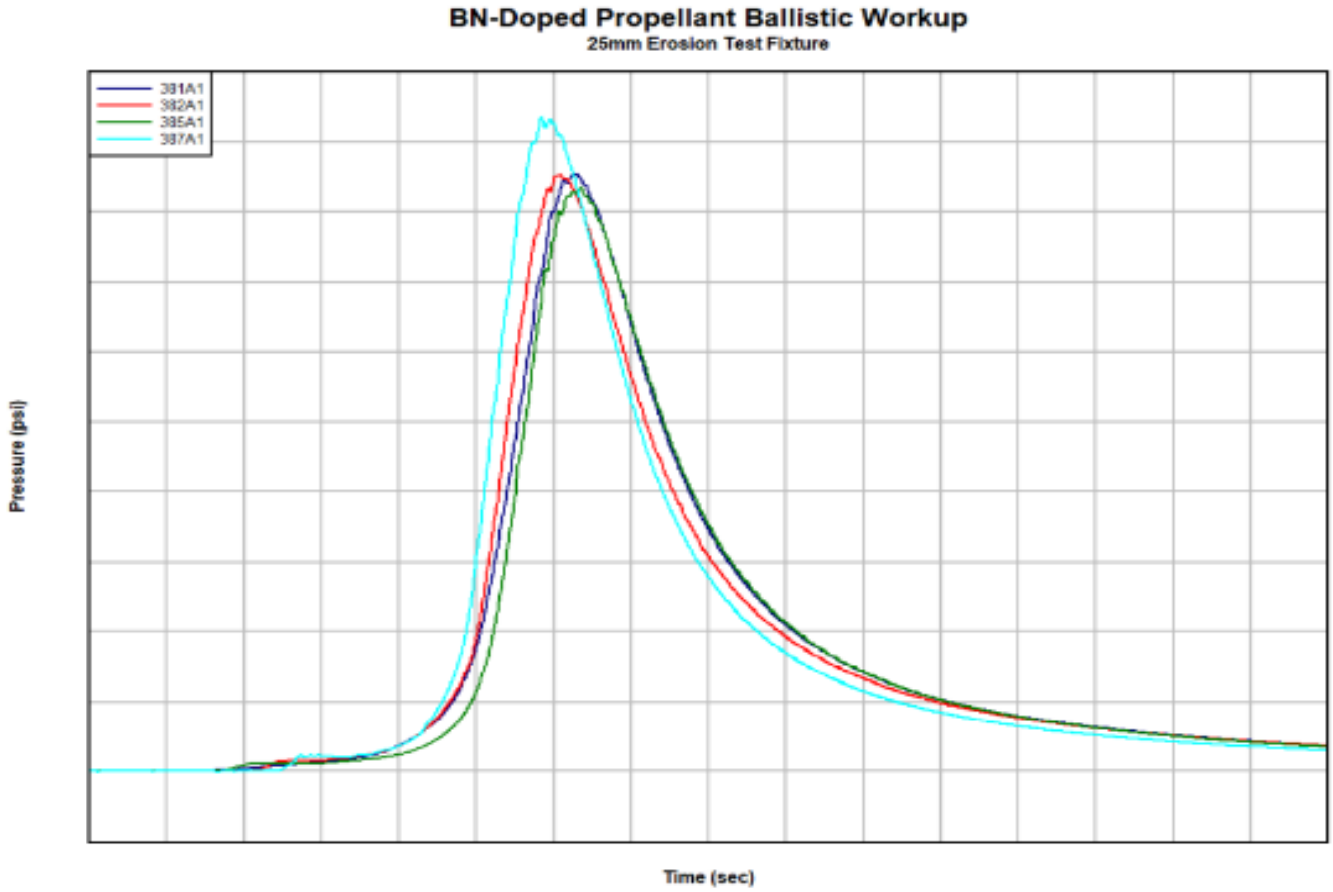
BALLISTICS TESTING IN 25MM MANN BARREL

- The muzzle velocity generated is a reasonable surrogate for a howitzer (around 3000fps). All shots used only the undeterred propellant variant. The resulting peak chamber pressure and velocity are shown in the following table .

Propellant	Charge Mass grams	Loading Density grams/cc		Chamber Pressure psi	Velocity ft/sec
381A1	65	0.686		42688	2943
383A1	65	0.686		42613	2953
385A1	66	0.696		41745	2927
387A1	65	0.686		46744	3001

BALLISTICS TESTING IN 25MM MANN BARREL



The resulting peak chamber pressure and velocity from IBHVG2 Modelling and Simulations Code. Pressure vs. time curves for all four propellants. All of the propellants were well behaved with no ignition issues or pressure anomalies.

BALLISTICS TESTING IN 25MM MANN BARREL

- Despite the chamber pressure and velocity being lower than predicted in the IBHVG2 models,
  - They are within the range of what would be experienced in a howitzer gun system.
  - Given the time constraints of this program, testing proceeded with the propellant loadings.
  - Consequently, 30 cartridges has been prepared of each propellant variant for test firing in the 25mm ETF.

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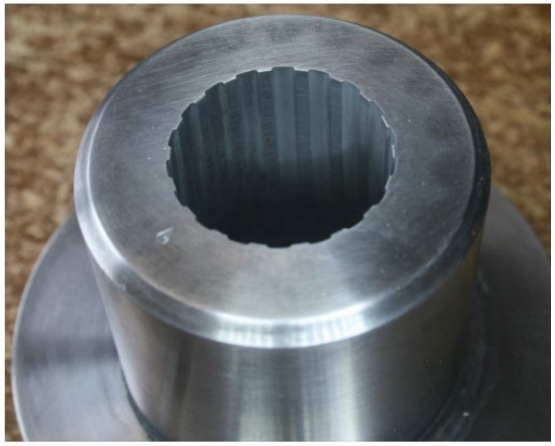
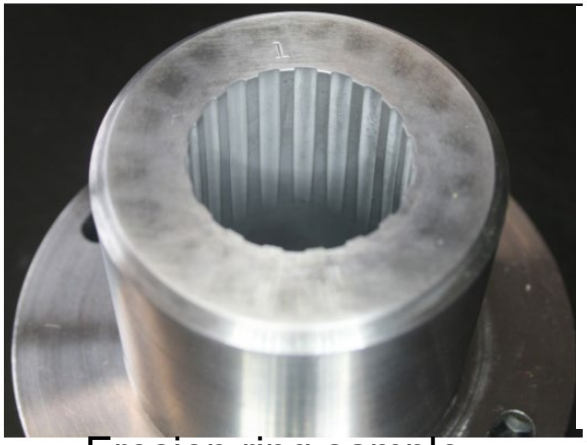
HELMEL COORDINATE MEASURING MACHINE (CMM) AT TEN LOCATIONS ON EACH RIFLING LAND AND GROOVE

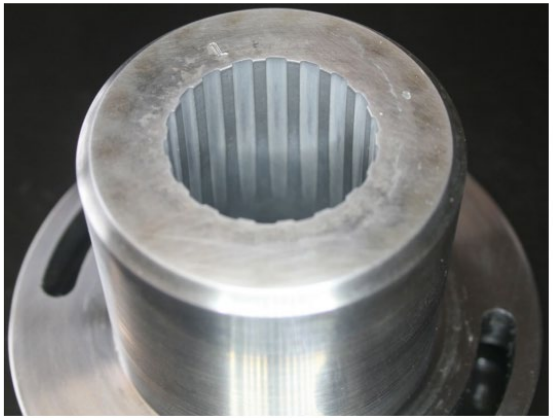
Photograph of an unfired insert showing grooves on the landings from machining.



Erosion ring sample number 2 after firing 50 shots with propellant 382A1.



Erosion ring sample number 3 after firing 50 shots with propellant 385A1.



Erosion ring number 4 after firing 50 shots with propellant 387A1.

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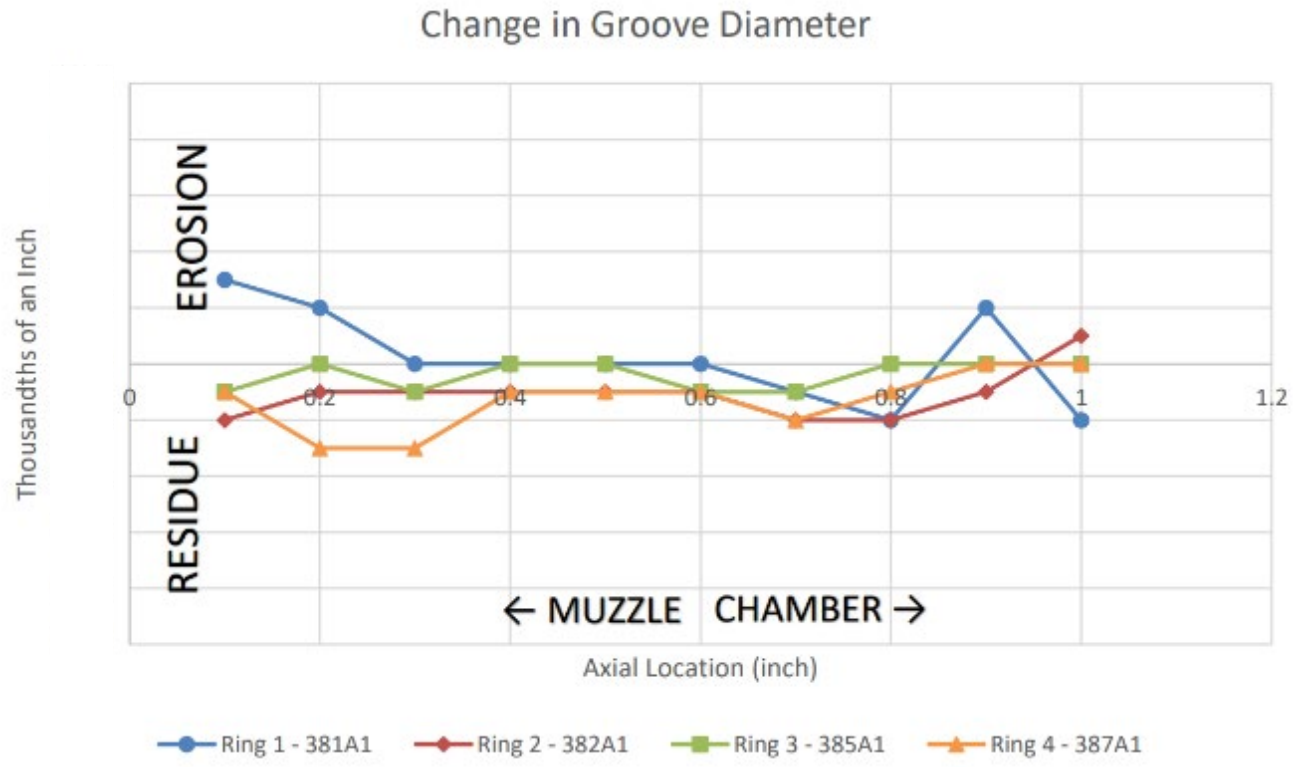
CHANGE IN GROOVE DIAMETER



Change in rifling groove diameter after 50 shots (2nd test series)

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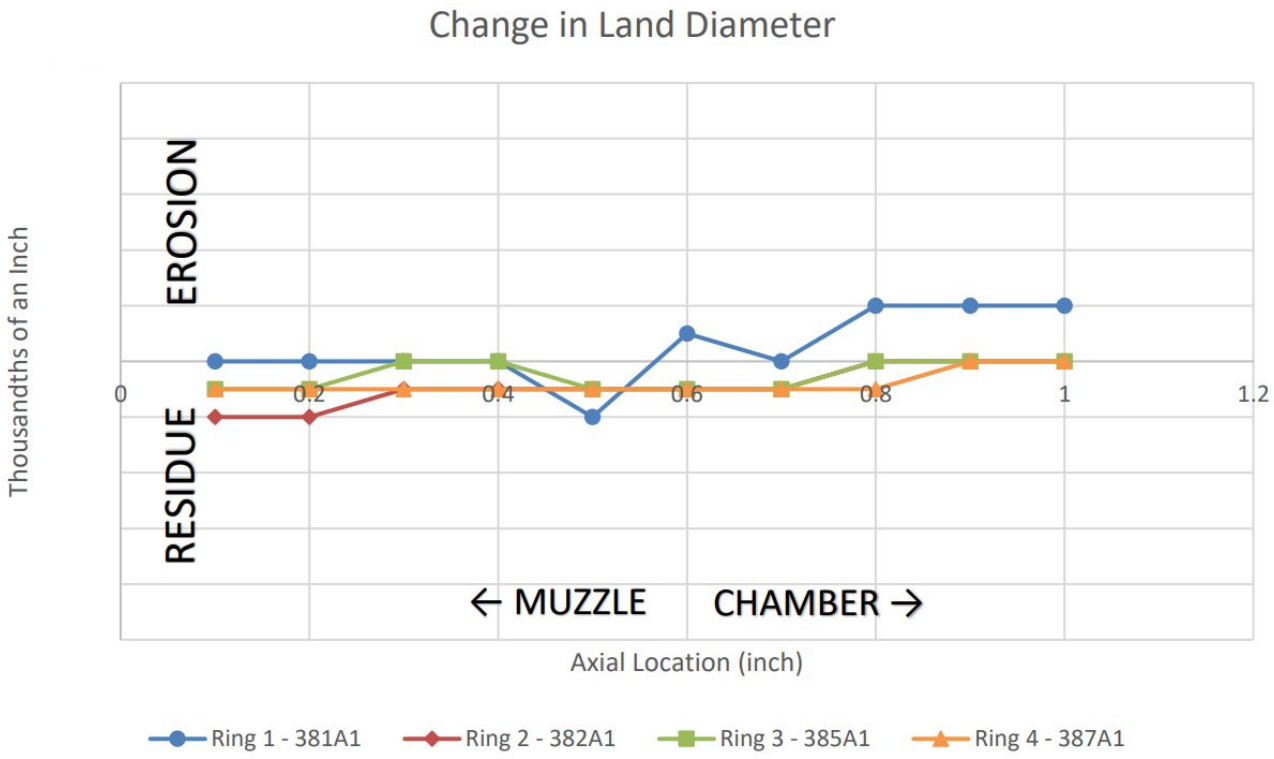
CHANGE IN LAND DIAMETER



Change in land diameter after 50 shots (2nd test series).

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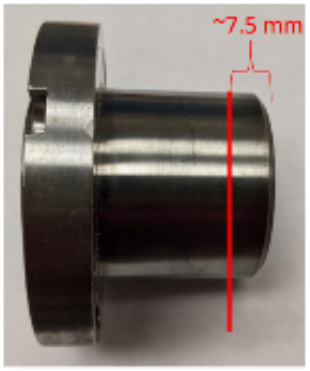
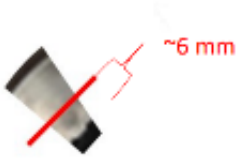
INSERT SAMPLES POSTMORTEM ANALYSIS

Step 1.) Cut ~7.5 mm off the end



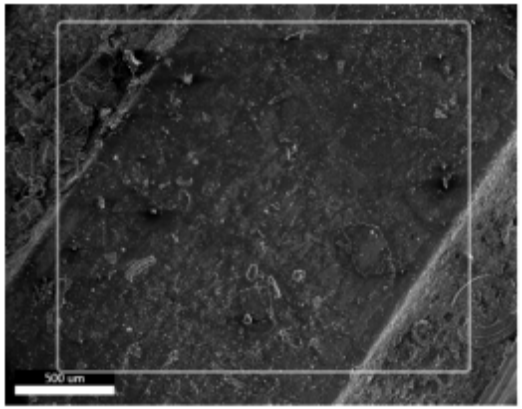
Step 2.) Cut out 5 slices with ridges

Step 3.) Cut ~6 mm sample from the ridge for each slice

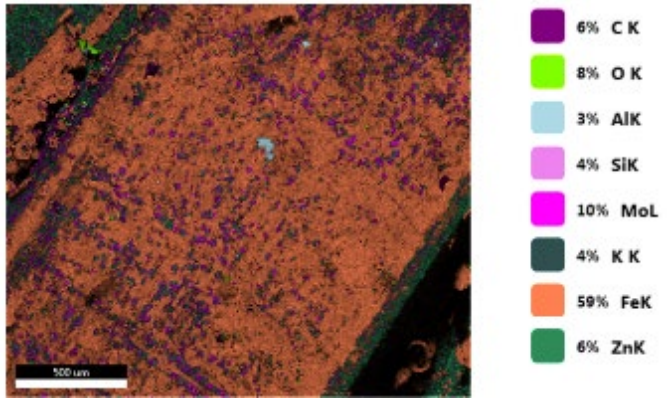


- Analysis techniques include Scanning Electron Microscopy (SEM), X-ray Photo-electron Spectroscopy (XPS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis, and Moh's hardness testing.
- Samples for the analyses were taken from the same location of each insert.
  - The muzzle end of each insert was cut off approximately 7.5 mm from the end.
  - Next, slices with an individual ridge (or "lands") were cut from the sample ring. Each land was reduced to a 6 mm depth without disturbing the surface of the ridge / lands.
  - Moh's hardness testing, SEM imaging, and XPS analysis was performed on the lands near the center (3-4 mm from the muzzle tip). ICP analysis was performed on the entire 6 mm x 6 mm x 7.5 mm lands sample.

SCANNING ELECTRON MICROSCOPE ANALYSIS

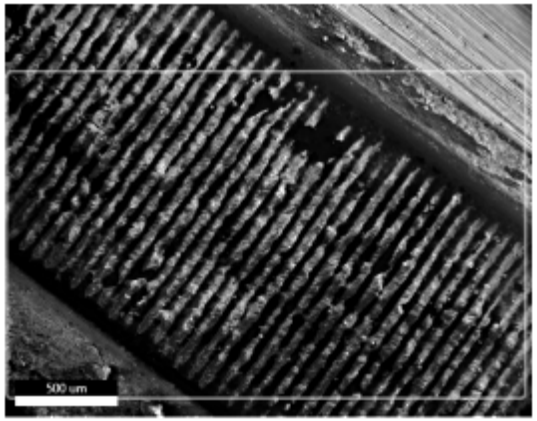


SEM analysis of sample #1

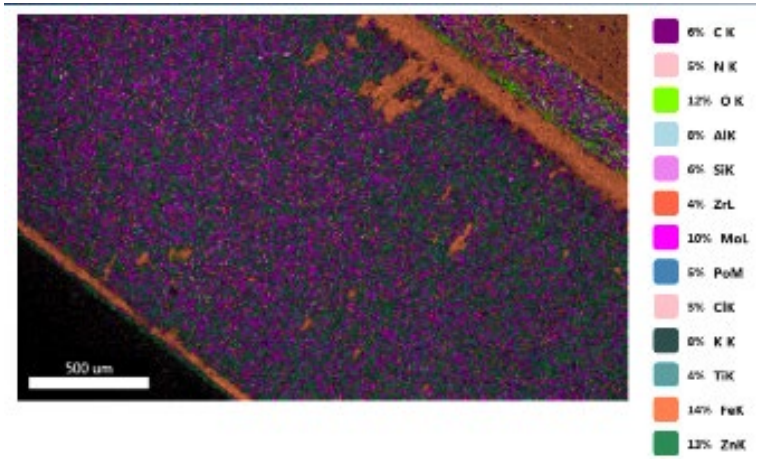


EDAX analysis of sample #1

(left is visual image, right is the elemental analysis by mass).



SEM analysis of sample #3



EDAX analysis of sample #3

(left is visual image, right is the elemental analysis by mass, sample #3, which had the highest BN loading in the propellant, showed the most-defined ridges.).

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BORON CONTENT

Table 7. Results of ICP-MS analysis of the insert boron content after firing.

	Sample #1 (381A1)	Sample #2 (382A1)	Sample #3 (385A1)	Sample #4 (387A1)
B Content Measured	<10 ppm	<10 ppm	30 ppm	<10 ppm

	B	C	N	O	Na	Al	Si	S	Cl	K	Ca	Ti	Fe	Zn	Ba	Pb	Bi
Sample #1	2.6	71.5	3.3	12.8	0.4	0.4	3.1	1.6	1.5	0.6	0.2	<0.1	0.4	1.0	0.1	0.1	0.2
Sample #2	5.0	70.4	4.7	11.7	0.2	0.6	1.6	1.7	1.6	0.3	0.2	<0.1	0.3	1.4	<0.1	<0.1	<0.1
Sample #3	22.1	37.7	18.4	14.0	-	1.1	2.0	1.2	1.1	0.2	0.3	-	0.2	1.6	<0.1	0.1	<0.1
Sample #4	5.4	75.0	4.0	8.7	0.2	0.1	2.1	1.5	1.5	0.6	0.1	0.4	0.1	0.2	-	<0.1	<0.1

[a] Normalized to 100% of the elements detected. XPS does not detect H or He.
[b] A dash line "-" indicates the element is not detected.
[c] A less than symbol "<" indicates accurate quantification cannot be done due to weak signal intensity.
[d] A question mark "?" indicates species may be present at or near the detection limit of the measurement.

Table 8. Atomic Concentrations (in mole %) [a, b, c, d]

Table 10: Nitrogen Chemical States (in % of Total N[a])

	BN	Organic N	B:N (as BN)	B:N (total N)
Sample #1	77	23	1.00	0.77
Sample #2	84	16	1.26	1.07
Sample #3	97	3	1.24	1.20
Sample #4	90	10	1.49	1.34

[a] Values in this table are percentages of the total atomic concentration of the corresponding element shown in Table 8.

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MOH'S HARDNESS TESTING

	Sample #1 (381A1)	Sample #2 (382A1)	Sample #3 (385A1)	Sample #4 (387A1)
Surface Hardness Measured	4.5	4.5	5.5	5.5

Results from Moh's Hardness Testing.

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SUMMARY AND CONCLUSIONS

- Successful processing of the undeterred and deterred propellants, compatibility testing, vacuum thermal stability, and the upcoming 25mm wear and erosion gun testing.
- Based on test results shown in table 2, which were conducted in accordance with the defining criteria of IAW NATO/ U.S. military specifications.STANAG 4147 (Chemical Compatibility of Ammunition Components with Explosives), M31A2 is deemed compatible when tested with Boron Nitride, Titanium Dioxide, and Talc combinations utilizing DSC thermal procedures.
- Pressure vs. time curves for all four propellants are complete. All of the propellants were well behaved with no ignition issues or pressure anomalies.
- Despite the chamber pressure and velocity being lower than predicted in the IBHVG2 models, they are within the range of what would be experienced in a howitzer gun system. Given the time constraints of this program, testing proceeded with the propellant loadings. Consequently, 30 cartridges has been prepared of each propellant variant for test firing in the 25mm ETF.

SUMMARY AND CONCLUSIONS

- A scalable and economical process for production of BN nano-particles has been developed. These particles were confirmed to be spherical, with an average size less than 200 nm, and can be dispersed in propellants using the conventional solvent approaches. The particles were confirmed to not destabilize nitro-cellulose based propellants, such as the RPD-380, Accurate No. 2, and IMR 4198.

- To simulate the interaction of BN nano-particles with gun barrels under combustion environments, steel inserts were fired in a closed bomb test chamber in the presence of IMR-4198 propellant compositions with and without the BN additive.

- Samples fired with BN additive in the propellant showed signs of less oxidation in this testing. XPS showed that boron oxide coated the surface of samples fired with BN additive, and less iron was present on the surface in samples that were less oxidized.

SUMMARY AND CONCLUSIONS

- SEM and EDAX analysis showed stark differences in surface morphology and composition for samples fired with or without BN additive. Samples fired with BN had a boron oxide surface coating of flat platelets, and seemed to lack significant iron oxide (less than 10%). Samples fired without BN were covered with pits, bumps, and octahedral crystals indicative of Fe_3O_4. Hardness testing of the insert surfaces was performed to quantify any differences between samples, but the results for these samples were inconclusive.

- Further wear and erosion testing was conducted at DEVCOM Labs using RPD-380 propellant with and without BN. In these tests, the BN additive was demonstrated to reduce wear and erosion by a factor of 2-3 in the limited testing (up to 4 rounds). Post-test characterization at pH Matter found only a small amount of boron remained on the surface after firing and cleaning. However, ppm levels of boron doping can harden steel, and an increased hardness was observed in unhardened steel fired with boron nitride additive. SEM imaging showed less surface crack density in the samples fired with boron nitride. Important considerations for any further tests are an alternate grain form to allow larger bomb loading density, and the corresponding larger amount of propellant necessary for that condition, as well as to support a sufficient number of firings to generate supportable statistical conclusions.

- In light of the promising results, further wear and erosion testing of the BN propellant additive was conducted in a sub-scale 25-mm gun test to simulate the conditions of 155 mm artillery during a Phase II Enhancement project. The BN additive appeared to have a positive effect on reducing wear and erosion in the gun tests. All compositions showed reduced erosion versus the baseline material, but samples with high BN or BN with other additives showed the most promising results based on SEM imaging and Moh's hardness testing. Further, the analysis techniques all agreed that the sample fired with more BN had significantly more BN coating and the most well-defined machine grooves after firing. These results appear to agree with previous small-scale tests that demonstrated a 2-3X reduction in wear and erosion for propellants containing BN.

FUTURE WORK

The results on the Enhancement work bring the technology to a TRL 6. Recommended future work includes further testing of the additive with more-corrosive propellants and full-scale gun tests.

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