FINAL REPORT

SAFER RESONANT ACOUSTIC MIXING METHODS FOR HIGH-VOLUME PRODUCTION OF PYROTECHNICS

SERDP Project WP- 2631

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14. ABSTRACT

The objective of this work was to develop and mature a resonant acoustic mixing (RAM) process to reduce the environmental, safety, and occupational health impacts currently observed in the mix-muller manufacturing process of Magnesium/Sodium Nitrate/Epoxy illumination compositions. All RAM compositions were observed to be more homogenous with similar/slightly lower sensitivity than the mix-muller produced materials. Performance testing showed that resonant acoustic mixed material produced similar burn times and similar/increased luminous efficiency to a mix-muller produced composition. In collaboration with Crane Army Ammunition Activity, three M485A2 illumination candles with RAM illumination composition were subjected to standard testing procedures and performed similarly to their mix-muller counterparts. Furthermore, projected benefits of a production-scale RAM process may result in significant increases to overall throughput, labor cost reduction of 61-96%, and a reduction in acetone used for cleanup operations by over 99%.

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Resonant acoustic mixing, RAM, pyrotechnic, environmental, safety, M485A2

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LIST OF ACRONYMS AND SYMBOLS

$	United States Dollar
Ø	Diameter
°C	Degrees Celsius
°F	Degrees Fahrenheit
ARDEC	U.S. Army's Armament Research, Development, and Engineering Center
CAAA	Crane Army Ammunition Activity
CCDC	U.S. Army's Combat Capabilities Development Command
cm	Centimeter
cP	Centipoise
cp	Candlepower
DSC/TGA	Differential scanning calorimetry and thermo-gravimetric analysis
ESD	Electrostatic discharge
g	Grams
g's	Acceleration relative to earth gravity
Gr	Granulation
H/D	Height to diameter ratio
IPA	Isopropyl alcohol
J	Joules
kg	Kilograms
L	Liter
lbs.	Pounds
Mg	Magnesium
min.	Minute
mj	Milljoules
ml	Milliliter
N	Newtons
$NaNO_3$	Sodium Nitrate
NSWC Crane	Naval Surface Warfare Center, Crane Division
oz.	Ounce
RAM	Resonant acoustic mixing
RDECOM	U.S. Army's Research, Development, and Engineering Command
s	seconds
SERDP	Strategic Environmental Research and Development Program
SON	Statement of need
PEG	Polyethylene Glycol
UHP	Ultra-high purity
W	Watts
wt. %	Weight percent

Acknowledgements

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Portions of the research described in this report took place at the Armament Research, Development, and Engineering Center (ARDEC). This center previously resided within the U.S. Army's Research, Development, and Engineering Command (RDECOM). After much of the work was completed, ARDEC was realigned into the Combat Capabilities Development Command (CCDC) and is now called Armaments Center.

ABSRACT

Objective

The objective of this work was to develop and mature a resonant acoustic mixing (RAM) process to reduce the environmental, safety, and occupational health impacts currently observed in the manufacture of the high volume pyrotechnic: Magnesium/Sodium Nitrate/Epoxy. These formulations are found in a variety of munitions including gun- and mortar-fired illumination projectiles. Common production methods for these materials can require personnel to manually scrape impellers during the mixing process while exposing them to over a hundred pounds of known sensitive pyrotechnic materials. In addition to safety concerns, large quantities of toxic solvents (e.g., acetone) are used to clean the many parts of these 1950's-era mixers (e.g., impeller or mix-muller mixers). Acetone poses environmental, occupational health, and safety risks, which make these processes unsustainable. The proposed RAM method could significantly reduce personnel hazards and solvent waste streams.

Technical Approach and Results

Three RAM processes were developed to reduce the environmental, safety, and occupational health risks currently observed in the mix-muller manufacturing process of Magnesium/Sodium Nitrate/Epoxy illumination compositions. In these processes, it was shown that the key mixing step is the incorporation of the high-viscosity cross-linking agent Versamid 140. All RAM mixed materials were observed to be more homogenous with similar/slightly lower sensitivity than the mix-muller produced materials. Performance testing showed that resonant acoustic mixed material produced similar burn times and similar/increased luminous efficiency to a mix-muller produced composition. As many of the Resodyn methodologies developed utilize solvent to lower the viscosity of the epoxy precursors, a number of lower-viscosity, commercially-available epoxy alternatives were also subjected to mechanical testing, performance testing, and inert RAM processing evaluation. In short, a number of low-viscosity curing agent alternatives appear to have promising RAM processing characteristics and minimal effect of combustion performance while being able to offer a range of mechanical properties to meet various application requirements.

For a pilot scale demonstration, the two-step RAM mix process was scaled from laboratory to concept scale (2 lb. batch size) with no change in ignition sensitivity. In collaboration with Crane Army Ammunition Activity, three M485A2 illumination candles with RAM illumination composition were subjected to standard testing procedures along side candles that were produced with the standard mix-muller process. All three RAM candles performed similarly to their mix-muller counterparts and demonstrated that RAM is a viable alternative to mix-muller mixers.

Benefits

A central benefit of RAM mixing is decreased operator exposure to production-scale quantities of sensitive explosives. Additional projected benefits of a production-scale RAM process may result in significant increases to overall throughput, labor cost reduction of 61-96%, and a reduction in acetone used for cleanup operations by over 99%.

1.0 EXECUTIVE SUMMARY

1.1 INTRODUCTION

Magnesium (Mg)/Sodium Nitrate ($NaNO_3$)/Epoxy formulations and their derivatives are a high volume pyrotechnic that is utilized in illumination and colored flare applications for the Army, Navy and Air Force (Figure 1) [1]. Such illuminant compositions are typically manufactured using impeller or mix-muller (Figure 2) based mixing methods which are hazardous because large volumes of relatively dry material are mechanically scraped by blades and/or wheels. Furthermore, these methods require personnel to be exposed to large quantities of sensitive pyrotechnic compositions during the mixing and cleaning process. In some mixing operations, personnel are required to repeatedly scrape impellers during the manufacturing-scale mixing of known sensitive material. In 2002 at the Crane Army Ammunition Activity (CAAA), an accident occurred in the similar mix-muller-based mixing process of "first-fire" ignition composition. This incident is thought to have been caused by the pinching of material in between some the many moving parts associated with the mix-muller process, resulting in extensive damage to various equipment and the mixing room. Furthermore, even though Mg/$NaNO_3$/Epoxy formulations do not require solvent during the mixing process, it is extensively used during cleaning of the equipment. It was estimated by CAAA personnel, that up to 80% of acetone used at the illumination production facility is used on cleaning mixing hardware. Therefore, the current mix-muller-based manufacturing of Mg/$NaNO_3$/Epoxy is an environmentally hazardous manufacturing process with substantial safety, occupational health risks as well as significant toxic solvent waste streams.

Figure 1. Illumination candles enhance the warfighter's capability to operate at night [2].

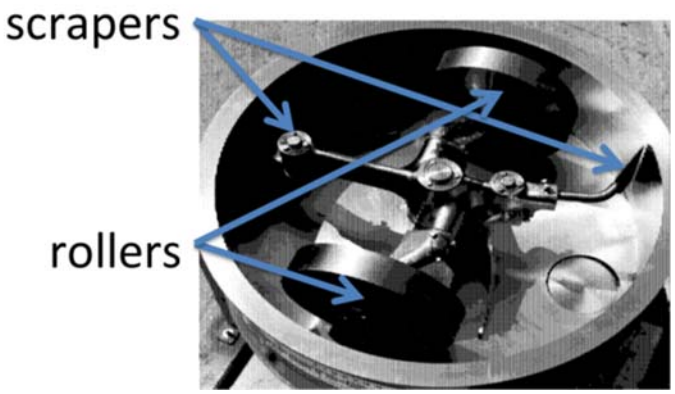

Figure 2. Example of a mix-muller mixer.

Resonant acoustic mixers (RAM) offered by Resodyn Corporation are fundamentally different than the traditional impeller and mix-muller-based mixing techniques while simultaneously offering several significant safety advantages. By sealing all of the constituents in a single static-dissipative container and shaking at low frequencies, the resonant acoustic mixer induces the powder to flow inside of the container without any moving parts touching the potentially sensitive composition. Having a manufacturing process that is entirely sealed in a static dissipative or conductive container greatly reduces the risk of accidental ignition by electro-static discharge (ESD), impact, friction, or pinching material between moving parts. Additionally, the sealed container does not require any technician interface with the potentially sensitive composition during the mixing process, as there are no impeller blades or mix-muller wheels in need of in-process scrape down. Production-scale RAM5 (Figure 3) and RAM55 acoustic mixers are commercially available and can to mix up to 80 and 920 lbs. in a single batch, respectively [3]. These commercially available acoustic mixers allow this technology to be considered for full-scale pyrotechnics manufacturing. In summary, RAM is a promising, scalable manufacturing process that could be used for environmentally benign mixing while also increasing personnel safety by reducing exposure with minimal solvent-based cleaning requirements.

Figure 3. Laboratory-scale LabRAM with 1 lb. maximum batch size (left); pilot-scale LabRAM IIH with 2.2 lb maximum batch size (center); production scale RAM5 with 80 lb. maximum batch size (right) [3].

1.2 OBJECTIVES

The objective of this project was to develop lower environmental impact resonant acoustic manufacturing processes for pyrotechnic compositions that are also scalable and safer than existing methods. Specifically, the manufacturing of Mg/$NaNO_3$/Epoxy illumination compositions were targeted. This project minimized the environmentally toxic solvents used in the cleanup process while also implementing the resonant acoustic mixing technique to increase personnel safety by minimizing overall technician exposure during the mixing process. The RAM method, being a highly effective mixing method, also produces compositions that are better mixed in less time than conventional impeller or mix-muller-based mixing methods. It is estimated that up to 80% of acetone solvent from the CAAA illumination manufacturing facility is used on cleaning mixing hardware. Therefore, this environmentally sustainable manufacturing method could significantly reduce personnel hazards and solvent waste streams from cleaning large mixing hardware.

1.3 TECHNICAL APPROACH

During the first phase of this program, research focused on developing laboratory-scale RAM methods for small-scale production of Mg/$NaNO_3$/Epoxy based compositions. Specifically, the RAM process of Mg/$NaNO_3$/Epoxy will be refined while verifying that important safety (e.g., electrostatic, impact and friction sensitivity) and performance metrics are met. During the second phase, the RAM methods will be matured using promising Mg/$NaNO_3$/Epoxy formulations. These compositions will be tested side-by-side with conventionally mixed Mg/$NaNO_3$/Epoxy compositions using a comprehensive set of performance, sensitivity, and mechanical strength tests. Lastly, the viability of this manufacturing method will be tested with pilot-scale manufacturing of selected compositions in 2 lb. batches. These acoustically mixed compositions will be pressed into candles using a full-scale flare configuration and tested side-by-side with conventionally produced flares using existing facilities, equipment, and processes for testing at NSWC Crane. This pilot-scale manufacturing demonstration will be examined with the advisement of CAAA which is the sole US supplier of mortar and illumination candles for the Army and Marine Corps. Ultimately, the matured mixing techniques developed during this project could be applied to a wide variety of similar illuminants and epoxy-based pyrotechnic manufacturing processes.

1.4 RESULTS AND DISCUSSION

1.4.1 LABORATORY-INVESTIGATION

Early mixing experiments attempting to achieve a homogenous mixture of the baseline illumination composition often yielded large, binder-rich areas. Early tests varied the order of addition of ingredients, mixing intensity, mix time, container size/aspect ratio, and fill fraction with little success. Early mixes often produced dense, binder-rich balls comprised mostly of the more viscous Versamid 140 curing agent (8,000-12,000 cP) as opposed to the less viscous epoxide-resin Araldite 507 (500-650 cP) [4, 5].

After understanding the inert mixing process and its potential safety concerns, live Mg/$NaNO_3$/Epoxy compositions were produced using the refined resonant mixing process. To evaluate the effects of the RAM technique on key pyrotechnic performance metrics, these compositions were subsequently pressed into 15 gram pellets and then subjected to performance, ignition sensitivity, thermal analysis and mechanical strength tests (see full report for details). At the end of the laboratory-scale performance study, several RAM processes were identified for

producing illumination compositions while verifying that important mechanical, safety, and performance parameters are equivalent or superior to traditionally mixed compositions.

Three RAM methodologies, shown in Figure 4, were developed after extensive inert mixing, live mixing, and sub-scale candle performance testing. These methodologies include a 1-step, 2-step, and 3-step process, each with their own mix routine, order of addition, and pros/cons from a technical perspective. The development of these processes also utilize vacuum processing which can significantly alter the flow inside of the container as well as pull off and recover any acetone solvent which may be utilized as a processing aide (1-3 rel. wt. %). An aging study showed that the 3-step RAM process (patent submitted, Appendix B: 2) could allow for a significant increase in manufacturing flexibility since the two precursor mixes could be mixed in bulk in advance and stored for the third mix to be performed only as needed. For full details, please see the full report.

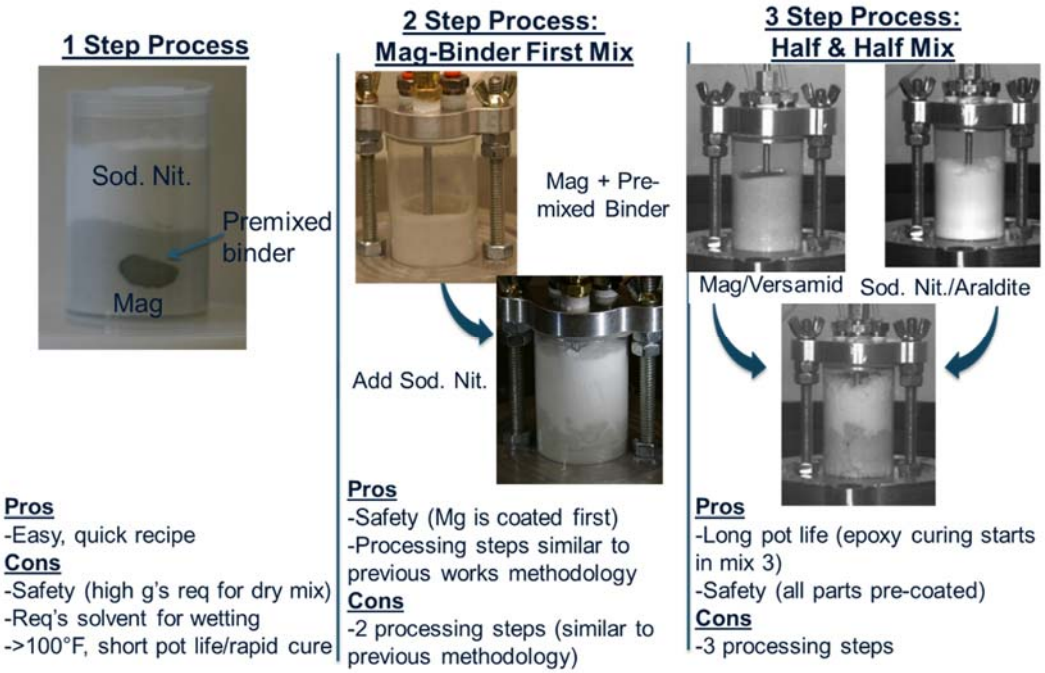

Figure 4. Overview of successful resonant mixing methodologies for epoxy-based pyrotechnics.

Table 1 shows the impact sensitivity of illumination composition prepared on a Resodyn via the previously described 1-step, 2-step, and 3-step processes as well as a mix-muller for comparison purposes. Overall, the Resodyn mixed compositions are similar or slightly less sensitive than the mix-muller produced materials. The Resodyn mixed compositions have low impact sensitivity, improved friction sensitivity over the mix-muller material, and similar ESD to the mix-muller material. This similar/slightly lower sensitivity is likely achieved because Resodyn produces more homogeneous mixtures as shown in Figure 5. Qualitatively, the mix-muller process typically produces "large hard chunks" of binder rich materials, while the refined Resodyn processes produce material the consistency of "wet sand". Overall, the sensitivity and thermal analysis (available in full report) show that materials produced by the Resodyn methods pose no additional safety risk over the mix-muller produced composition.

Table 1. Sensitivity data for illumination compositions produced by various methods.

Sample Info	Impact	BAM Friction	Rotary Friction				ESD
			Fire Energy (ft-lb)				
Description	50% Fire Energy (J)	Threshold energy (N)	Average	Lowest	Average time to react (s)	Response (# fired)	Maximum no-fire energy (mJ)
Mix-muller	34.2	54.0	122.9	45.3	4.4	8/10	125.0
1-Part Resodyn	>35.0	160.0	340.3	75.9	12.5	9/10	125.0
2-Part Resodyn	>35.0	80.0	283.0	55.9	10.6	10/10	180.0
3- Part Resodyn	33.8	120.0	262.4	133.2	9.8	8/10	125.0
RDX Standard	7.9	120.0	n/a	n/a	n/a	0/10	80.0
PETN Standard	--	48.0	--	--	--	--	--

*Blue indicates a very low hazard, green indicates a low hazard, yellow indicates a medium hazard, orange indicates a high hazard, and red indicates a dangerous hazard.

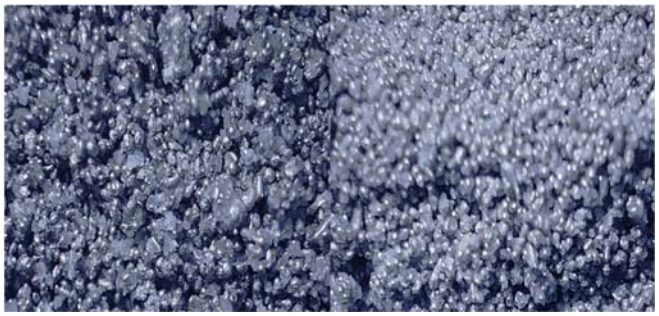

Figure 5. Microscopic images of the baseline illumination composition prepared with mix-muller (left) and Resodyn(right).

Generally, resonant acoustic mixed material can produce homogeneous compositions with similar burn times and similar/increased luminous efficiency to a mix-muller produced composition. Figure 6 shows images of ~15-gram combustion performance tests showing that candles produces qualitatively similar plumes. Figure 7 shows that the relative luminous efficiency is similar or slightly higher than the mix-muller composition. This performance is due, in part, to the increased homogeneity of the Resodyn process over the mix-muller.

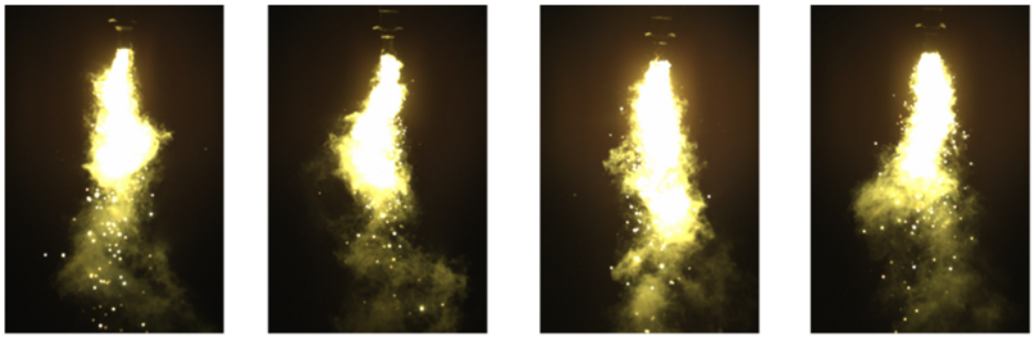

Figure 6. Images of performance testing of the baseline illumination compositions produced by various mixing methods.

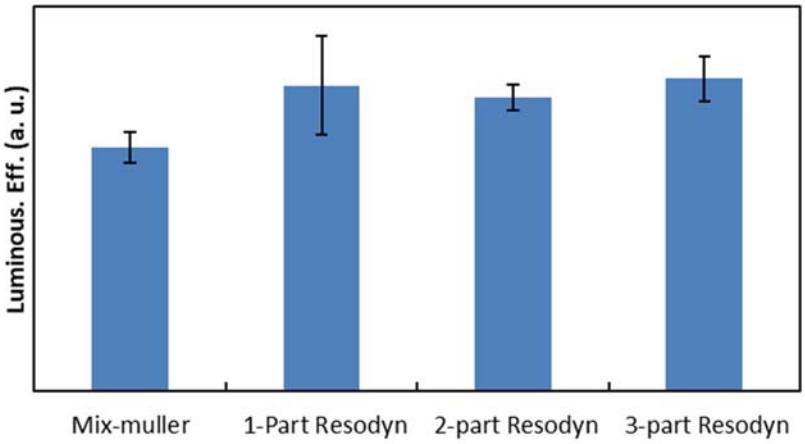

Figure 7. Relative luminous efficiency of the baseline illumination compositions produced by various mixing methods.

1.4.2 PILOT SCALE DEMONSTRATION

The final portion of this project partnered with CAAA to demonstrate and compare RAM-mixed illumination composition to the conventional mix-muller material in a full-scale flare configuration. CAAA annually produces thousands of Illuminating and Infrared Mortar Candles for 60mm, 81mm, & 120mm mortars as well as 105mm and 155mm artillery projectiles. Illuminating and Infrared projectiles, Figure 1, enhance our warfighter's capability to operate at night and compliment the capabilities of night vision equipment [6]. For this demonstration, M485A2 155-mm visible-light illuminating projectiles were used to compare the differences in performance between RAM-mixed and mix-muller mixed material. The exact formulation and manufacturing parameters for this demonstration are not listed as they are not approved for public release.

The M485A2 155-mm Illumination Round, Figure 8, is a relatively large pyrotechnic device that is used to light up the field during combat and training ranges. This item is fired from a howitzer with relatively high trajectories when the charge activates and a parachute opens, creating a bright light that lasts for several minutes as the parachute drifts to the ground [7].

Figure 8. M485A2 projectile (left) and illumination candle (right) [8].

In preparation for consolidation into the M485A2 155-mm Illumination Round hardware, nine 1-kilogram batches of illumination composition was prepared using the 2-step RAM process as previously described (see full report for additional details). Two CAAA engineers observed this mixing process reported that the RAM mixer has safety advantages and much faster mix times in

comparison to the conventional mixed-muller. After mixing, RAM composition were placed into drying pans while subsequent mixes were being performed. Prior to pressing into the final candle hardware, all mixes were allowed to partially-cure for at least 1.5 hours; 5 hours for the first mix. These pilot scale mixes were visibly observed to be very homogeneous with little to no noticeable clumps of material.

The 9 kilograms of RAM-mixed illumination composition was subsequently transferred to the CAAA production facility for pressing operations. Three M485A2 155-mm Illumination candles, Figure 9, were prepared using standard flare hardware and pressing procedures. In comparison to the mix-muller produced composition, CAAA technicians reported that the RAM material appeared homogeneous, with improved pot-life, and consolidated well using production tooling.

Figure 9. M485A2 candles made with RAM-produced illumination composition.

The three M485A2 illumination candles with RAM illumination composition were subjected to standard testing procedures along with standard mix-muller M485A2 illumination candles (Figure 10). All three RAM candles performed similarly to their mix-muller counterparts and passed all performance requirements (Figure 11). This demonstration shows that RAM is a viable alternative to mix-muller mixers and can be potentially used to produce candles with similar performance.

Figure 10. Testing of illumination candle at NSWC Crane photometric light testing tunnel.

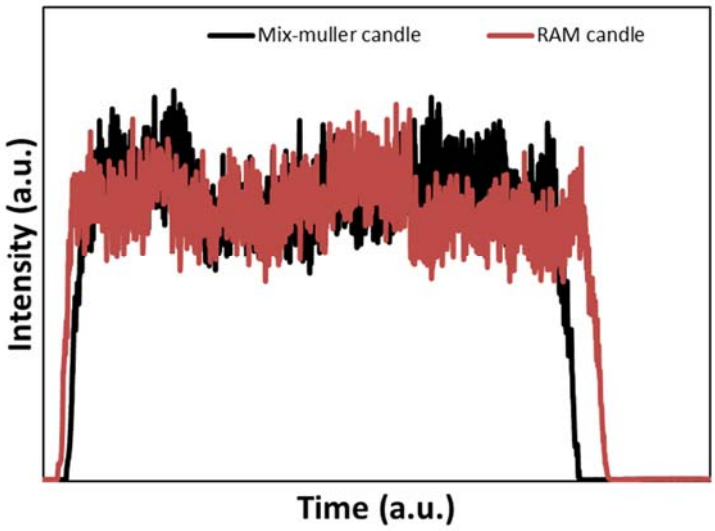

Figure 11. Comparison of arbitrary intensity plot for mix-muller and RAM candles.

1.4.3 ENVIRONMENTAL BENEFIT OF RAM PROCESS

According to CAAA personnel, up to 80% of acetone at their illumination manufacturing facility is used on cleaning the mix-muller hardware. For example, 1-2 gallons of acetone is typically spent cleaning the mix-muller after a pyrotechnic mix which can range in batch size from 27-57 kg (60-125 lbs.). This quantity of solvent is necessary to clean the mix-muller (regardless of the size of the mix) due to the excess surface area of the rollers and scrapers as well as many other hard-to-reach areas (Figure 2). It is significantly easier to clean RAM containers which are simple cylinders. In the pilot scale demonstration, a single rag wetted with acetone was sufficient to clean the container after each 1000-gram mix. A scaling analysis based off of the quantity of solvent used in the pilot scale demonstration (see full report) shows that using a RAM5 for a 57 kg (125 lb) mix instead of a mix-muller can result in a acetone reduction of 98.7%. It is noted that RAM solvent efficiency (e.g., the ratio of solvent needed for cleaning to the amount of material produced) increases significantly with batch size.

Table 2 shows an approximate cost analysis to highlight some of the potential cost savings of using a production scale RAM5 or RAM55 versus the common mix-muller. To produce approximately 1000 lbs. of composition, a mix muller would need approximately three technicians for 10 hours to produce 8- 125 lb. batches. A RAM 5/RAM55 could produce similar amounts of composition in 5 and 1.5 hours, respectively. These RAM5/RAM55 processes could result in labor saving of 61-96%. Similarly, acetone used for cleanup operations could be reduced by over 99% for either of the production scale RAM operations.

Table 2. Cost analysis of pilot scale RAM versus mix muller.

	Mix Muller	RAM5	RAM55
Total Quantity Produced (lbs.)	1000	960	924
Number of Mixes (#)	8	12	1
Batch size (lbs.)	125	80	924
	Materials		
Pyrotechnic Ingredients ($)	--	--	--
Cleanup acetone (gallons)	12	0.11	0.05
Cleanup acetone* ($)	$340.72	$3.17	$1.35
Acetone Reduction (%)	--	99.07%	99.60%
	Labor		
Labor (# personnel)	3	3	3
Labor (hours)	10	5	1.5
Total Labor** ($)	$3,000.00	$1,500.00	$450.00
Total Labor Savings (%)	--	61.25%	96.31%
Total cost savings ($)	--	$1,837.55	$2,889.37

*assumes $150/20L acetone

**assumes labor rate of $100/hr.

1.4.4 CONCLUSIONS

In this work, three resonant acoustic mixing (RAM) processes were developed to reduce the environmental, safety, and occupational health impacts currently observed in the mix-muller manufacturing process of Mg/$NaNO_3$/Epoxy illumination compositions. These methodologies include a 1-step, 2-step, and 3-step process, each with their own mix routine, order of addition, and pros/cons from a technical perspective. In these processes, it was shown that the key mixing step is the incorporation of the high-viscosity cross-linking agent Versamid 140. In sensitivity testing, all Resodyn mixed materials were observed to be more homogenous with similar/slightly lower sensitivity than the mix-muller produced materials. Performance testing resulted in resonant acoustic mixed material producing similar burn times and similar/increased luminous efficiency to a mix-muller produced composition. An aging study showed that the 3-step Resodyn mixing process (patent submitted) could allow for a significant increase in manufacturing flexibility since the two precursor mixes could be mixed in bulk in advance and stored for the third mix to be performed only as needed. As many of the Resodyn methodologies developed utilize solvent to lower the viscosity of the epoxy precursors, a number of lower-viscosity, commercially-available epoxy alternatives were also subjected to mechanical testing, performance testing, and inert RAM processing evaluation (see full report for details). Overall, a number of low-viscosity curing agent alternatives appear to have promising RAM processing characteristics and minimal effect of combustion performance while being able to offer a range of mechanical properties to meet various

application requirements. For a pilot scale demonstration, the two-step RAM mix process was scaled from laboratory to concept scale (2-lb batch size) with no change in ignition sensitivity. In collaboration with CAAA, three M485A2 illumination candles with RAM illumination composition were subjected to standard testing procedures along with standard mix-muller candles. All three RAM candles performed similarly to their mix-muller counterparts and demonstrated that RAM is a viable alternative to mix-muller mixers. Furthermore, projected benefits of a production-scale RAM process may result in significant increases to overall throughput, labor cost reduction of 61-96%, and a reduction in acetone used for cleanup operations by over 99%.

1.5 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

Future process development needs to address the effect of solvent as a process aide on the resulting mechanical properties of the flare. This is important as the artillery and mortar-fired illumination rounds experience some of the highest accelerations and spin rates of all fielded pyrotechnic flares. Alternative to using solvent as a process-aide, a number of promising lower-viscosity binder systems have been identified. Also, a solvent-less mix process that uses a cooled mixing vessel to keep the process temperature below 100 °F should be evaluated.

Per the full report, CAAA is interested in this mixing technology, but due to current high inventory levels of the various Mortar and Artillery-Fired Illumination Projectiles, the future production schedule, and interest in alternative mixing processes, is uncertain.

2.0 OBJECTIVE

2.1 SERDP RELEVANCE

As stated in the statement of need (SON) WPSON-16-03, the objective of this work was to develop and mature the resonant acoustic mixing technology to reduce the environmental, safety, and occupational health impacts currently observed in the manufacture of the high volume pyrotechnic Magnesium (Mg)/Sodium Nitrate ($NaNO_3$)/Epoxy. As requested in SON, this project started with laboratory evaluation of the manufacturing process while verifying that important safety (e.g., electrostatic, impact and friction sensitivity) and performance metrics were met. Important parameters such as material compatibility, processing time were documented for this new technique while observing process temperature. The viability of this manufacturing method was tested with pilot-scale manufacturing of selected compositions in 2 lb. batches. These acoustically mixed compositions were pressed into full-scale candles and tested side-by-side with conventionally mixed flares using existing facilities, equipment, and processes for lot acceptance testing at Naval Surface Warfare Center, Crane Division (NSWC Crane). As requested in the SON, this pilot-scale manufacturing demonstration was performed with the advisement of Crane Army Ammunition Activity (CAAA) which is the sole US supplier of mortar and illumination candles for the Army and Marine Corps. Ultimately, the matured mixing techniques developed during this project could be applied to a wide variety of similar illuminants and pyrotechnic manufacturing processes.

2.2 TECHNICAL OBJECTIVE

The objective of this project was to develop a lower environmental impact resonant acoustic manufacturing process for pyrotechnic compositions that are also scalable and safer than existing methods. Specifically, the manufacturing of Mg/$NaNO_3$/Epoxy illumination compositions were targeted. This project minimized the environmentally toxic solvents used in the cleanup process while also implementing the resonant acoustic mixing (RAM) technique to increase personnel safety by minimizing overall technician exposure during the mixing process. The RAM method, being a highly effective mixing method, also produces compositions that are better mixed in less time than conventional impeller or mix-muller-based mixing methods. It is estimated that up to 80% of acetone solvent from the CAAA illumination manufacturing facility is used on cleaning mixing hardware. Therefore, this environmentally sustainable manufacturing method could significantly reduce personnel hazards and solvent waste streams.

At first, research focused on developing laboratory-scale RAM methods for small-scale production of Mg/$NaNO_3$/Epoxy based compositions. Specifically, the RAM process was refined while verifying that important safety (e.g., electrostatic, impact and friction sensitivity) and performance metrics were met. Next, the RAM compositions were to be tested side-by-side with conventionally mixed Mg/$NaNO_3$/Epoxy compositions using a comprehensive set of performance, sensitivity, and mechanical strength tests. Lastly, the viability of this manufacturing method will be tested with pilot-scale manufacturing of selected compositions in 2 lb. batches. These RAM compositions will be pressed into full-scale flares and tested side-by-side with conventionally produced flares using existing facilities, equipment, and processes for testing at NSWC Crane. This pilot-scale manufacturing demonstration will be performed under the advisement of CAAA which is the sole US supplier of mortar and illumination candles for the Army and Marine Corps. Ultimately, the matured mixing techniques developed during this project could be applied to a wide variety of similar illuminants and epoxy-based pyrotechnic manufacturing processes.

3.0 BACKGROUND

$Mg/NaNO_3$/Epoxy formulations and their derivatives are a high volume pyrotechnic that are utilized in illumination and colored flare applications for the Army, Navy and Air Force (Figure 12) [1]. Some $Mg/NaNO_3$/Epoxy formulations from literature are shown in Table 3. Such illuminant compositions are typically made using impeller or mix-muller (Figure 13) based mixing methods which are hazardous because large volumes of relatively dry material are mechanically scraped by blades and wheels. Furthermore, these methods require personnel to be exposed to large quantities of sensitive pyrotechnic compositions during the mixing and cleaning process. In some mixing operations, personnel are required to repeatedly scrape impellers during the manufacturing-scale mixing of known sensitive material. In 2002 at CAAA, an accident occurred in the similar mix-muller-based mixing process of "first-fire" ignition composition. This incident is thought to have been caused by the pinching of material in between some the many moving parts associated with the mix-muller process, resulting in extensive damage to various equipment and the mixing room. Furthermore, even though $Mg/NaNO_3$/Epoxy formulations do not require solvent during the mixing process, it is extensively used during cleaning of the equipment. It was estimated by CAAA personnel, that up to 80% of acetone used at the illumination production facility is used on cleaning mixing hardware. Therefore, the current mix-muller-based manufacturing of $Mg/NaNO_3$/Epoxy is an environmentally hazardous manufacturing process with substantial safety concerns, occupational health risks, as well as significant toxic solvent waste streams.

Figure 12. Illumination candles enhance the warfighter's capability to operate at night [2].

Table 3. Examples of Mg/$NaNO_3$/Epoxy formulations in literature.

	Material	Weight (%)
Source: [1]	Magnesium	58
	Sodium Nitrate	37.5
	Binder	4.5
Source: [9]	Magnesium	52, 58
	Sodium Nitrate	35, 37
	Binder	13, 5
Source: [10]	Magnesium	50
	Sodium Nitrate	44
	Binder	6
Source: [11]	Magnesium	45.5-58
	Sodium Nitrate	37.5-45.5
	Binder	4.5-9

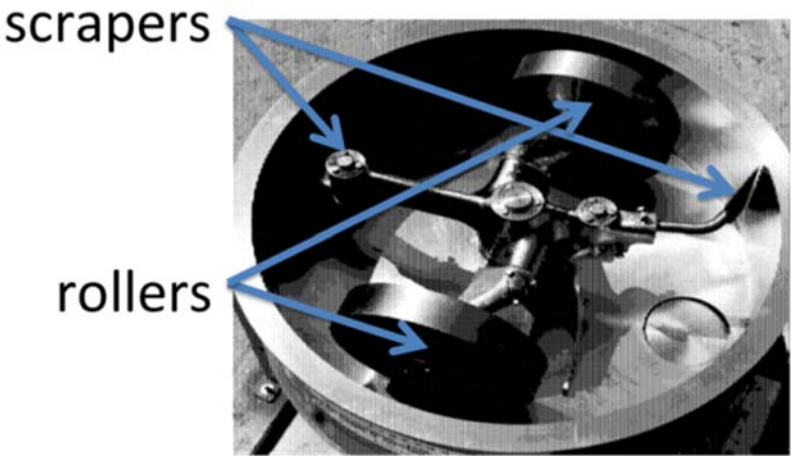

Figure 13. Example of a mix-muller mixer.

The resonant acoustic mixing (RAM) process was developed by Resodyn Corporation which was founded in 1994. Resonant acoustic mixers offered by Resodyn Corporation are fundamentally different than the traditional impeller and mix-muller-based mixing techniques while simultaneously offering several significant safety advantages. Conceptually similar to a paint shaker, the RAM process starts by sealing all of the constituents in a single static-dissipative container and shaking at low frequencies. Using an internal control mechanism, RAM generates a high level of energy by seeking and operating at the "resonant condition" which induces the powder to flow inside of the container without any moving parts touching the potentially sensitive composition. This mixer typically operates at 58-62 Hertz and is self-adjusting the displacement and acceleration (up to 100 g's) of the system to maintain the optimized resonant mixing condition [3]. Having a manufacturing process that is entirely sealed in a static-dissipative or conductive container greatly reduces the risk of accidental ignition by electro-static discharge (ESD), impact, friction, or pinching material between moving parts. Additionally, the sealed container does not require any technician interface with the potentially sensitive composition during the mixing process, as there are no impeller blades or mix-muller wheels in need of in-process scrape down.

The RAM method has been extensively used for laboratory-scale preparation (< 1 lb.) of energetic materials [12] including propellants [13, 3] and recently pyrotechnics [14, 15, 16] using

the LabRAM mixer shown in Figure 14. Rapid and thorough mixing is often obtained with excellent repeatability. Laboratory scale results indicate this mixing technique can be used for dry [14, 15, 16], semi-wet [13] and wet mixing [12] procedures. The RAM5 (Figure 14) and RAM55 acoustic mixers are commercially available and can to mix up to 80 and 920 lbs. in a single batch, respectively [3]. These commercially available acoustic mixers allow this technology to be considered for full-scale pyrotechnics manufacturing. In summary, RAM is a promising scalable manufacturing process that could be used for environmentally benign mixing while also increasing personnel safety by reducing exposure with minimal solvent-based cleaning requirements.

Figure 14. Laboratory-scale LabRAM with maximum 1 lb batch size (left); pilot-scale LabRAM with maximum 2.2 lb batch size (center); production scale RAM5 acoustic mixer with maximum 80 lb. batch size (right) [3].

4.0 MATERIALS AND METHODS

4.1 REACTIVE COMPOSITIONS

In this report, a baseline illumination formulation consisting of 55 wt. % Magnesium, 39 wt. % Sodium Nitrate, and 6 wt. % binder is assumed. This formulation is not representative of any in-service formulation and was chosen as an averaged formulation of those formulation available in open literature (Table 3). Table 4 summarizes the vendor information and nominal particle sizing for the commercially-available powders used within the experimental compositions. All live pyrotechnic compositions were initially mixed in 30-50 gram quantities for safety purposes. Unless otherwise noted, the binder used was a two-part thermoset-epoxy consisting of 70 wt. % Araldite 507 and 30 wt. % Versamid 140. Other epoxy binder systems that were explored in selected experiments are summarized in Table 5. For inert studies, glass media (60-120 mesh from McMaster-Carr) was used as a magnesium surrogate due to similar particle morphologies (Figure 15).

Table 4**.** Vendor information and composition of baseline illumination composition.

Reactant	Vendor	Nominal Particle Size	Nom. wt. %
Magnesium	Hart Metals, Inc.	MIL-DTL-382D, Gr. 17	55
Sodium Nitrate	Hummel Croton, Inc.	MIL-S-322C, Gr B	39
Araldite 507	Huntsman Advanced Materials Americas LLC	--	4.2
Versamid 140	Gabriel Phenoxies Inc.	--	1.8

Table 5. Modified epoxy-binder test matrix and their relative mixture ratios.

Name	Epoxy Resin (wt. %)	Curing agent (wt. %)	Polymeric Modifier (wt. %)
Historically-used epoxy systems (Baselines)			
V140B	Araldite 507(70)	Versamid 140 (30)	-
PS	Epon 813(33.3)	D.E.H. 24 Hardener (1.7)	Polysulfide LP-33 (65.0)
Commercially Available Epoxy Alternatives			
V150	Araldite 507(65)	Versamid 150 (35)	
V747	Araldite 507(67)	Versamid G-747 (33)	-
A506	Araldite 507(63.3)	Ancamide 506 (36.7)	-
J400	Araldite 507(64.5)	Jeffamine D400 (35.5)	-
JBlend	Araldite 507(57.1)	Jeffamine D400 (28.6)	Jeffamine D2000 (14.3)
V140S	Araldite 507(65.7)	Versamid 140 (34.3)	-
PEG10	Araldite 507(63)	Versamid 140 (27)	PEG 400 (10)
PEG15	Araldite 507(59.5)	Versamid 140 (25.5)	PEG 400 (15)
PEG20	Araldite 507(56)	Versamid 140 (24)	PEG 400 (20)

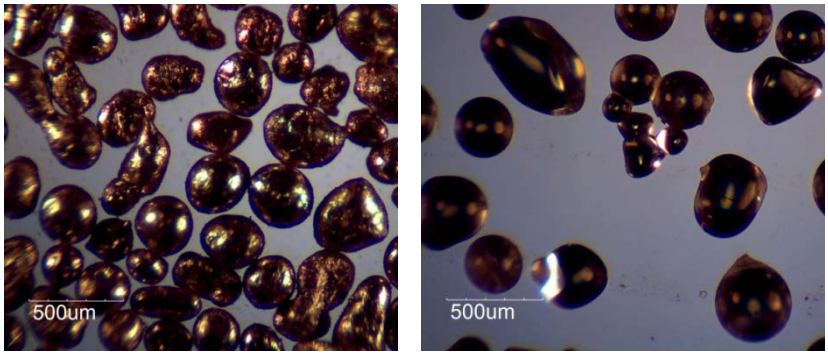

Figure 15. Magnesium (left) and glass media (right) particle morphology.

4.2 LABORATORY-SCALE MIXING OF PYROTECHNIC COMPOSITIONS

Laboratory-scale mixing of inert and live compositions was performed on laboratory scale LabRAM acoustic mixer with a custom-designed hold-down fixture [3]. Custom-instrumented mixing lids were designed to use with commercially available disposable containers while facilitating variable vacuum processing and mixture temperature recording. The container lid utilized a set of filters system to minimize energetic material in the vacuum lines. Inert mixes were performed in clear polypropylene Lacon® containers and live mixes were performed in electrostatic dissipative semi-transparent Statcon™ containers [17].

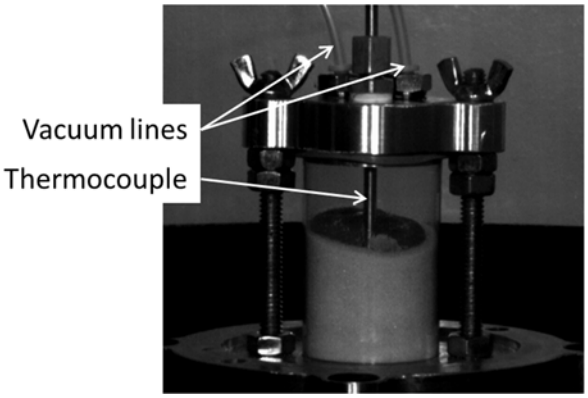

Figure 16. Custom mixing lid that allows thermocouple instrumentation and vacuum processing with commercially available containers.

In some cases, “hand-mixed” samples were prepared by mixing the ingredients with a metal spatula in a grounded metallic container until homogeneous.

For the 50-gram (g), sub-scale candles, the magnesium and sodium nitrate were dried in an oven for 18 h at 60 °C prior to blending. To prepare each composition, the binder components were added to a Hobart mixing bowl and vigorously mixed by hand with a wooden tongue depressor for 1 min. Magnesium was added and the mixture was blended mechanically with a B-blade for 10 min. The air-driven planetary mixer was turned off, sodium nitrate was added, and the mixture was blended for another 10 min. Then, the pyrotechnic mixture was transferred to a large ceramic bowl before being consolidated into pellets.

Pilot-scale mixing of inert and live compositions was performed on at LabRAM IIH with a custom-designed mix vessels and a custom designed hold-down fixture; images and descriptions of these fixtures will be presented in later sections [3].

4.3 COMBUSTION EXPERIMENTS

Live pyrotechnic compositions were pressed into experimental pellets or into fish-paper tubes of the same diameter. Figure 17 shows a typical experimental pellet and a schematic of how samples are mounted and inhibited with Miller-Stephenson's Epoxy 907 [18] to facilitate linear burning. Prior to pressing, mixtures were stored overnight at room temperature to achieve a partial-cure of the epoxy binder system. Experimental pellets of 0.75 inch diameter were pressed in two increments utilizing a 12 ton Carver press at a load of ~4500-5500 lbs. for ~10 seconds. Each pellet was comprised of a nominal mass of ~15 grams of composition with <5 grams of a thermite-based ignition slurry. After mounting, samples cured in an oven at 60 °C for 24 hours. Three to six pellets were prepared for each composition to provide statistical validity on the measurements. Pellets were ignited remotely by an electric match.

For the 50-gram, sub-scale candles, approximately 50 grams of energetic material was loaded into a kraft cardboard tube (8.00 cm length, 3.15 cm inner diameter) with the aid of a tooling die that held the tube (inner diameter of 3.37 cm). The powder was consolidated in one increment at a dead load of 4500 kg with a 10 second dwell time. The resulting pellets were coated with a thermate-based igniter composition (as an acetone slurry). Six candles were prepared and tested for each formulation. After coating, all candles were cured for 16 h in an oven at 60 °C.

Luminous intensity measurements were performed using SED 033 silicon detector photodiode fitted with a photopic response filter (Y-filter). The average luminous intensity is determined by averaging the steady-state intensity and therefore does not account for ignition and extinction transients. The luminous efficiency is calculated by integrating the temporal luminous intensity profile and dividing by the mass of the reacting pellet (~15 grams). The burn time was measured as the time difference at 5% of the maximum luminous intensity over the duration of the burn of the experimental pellet.

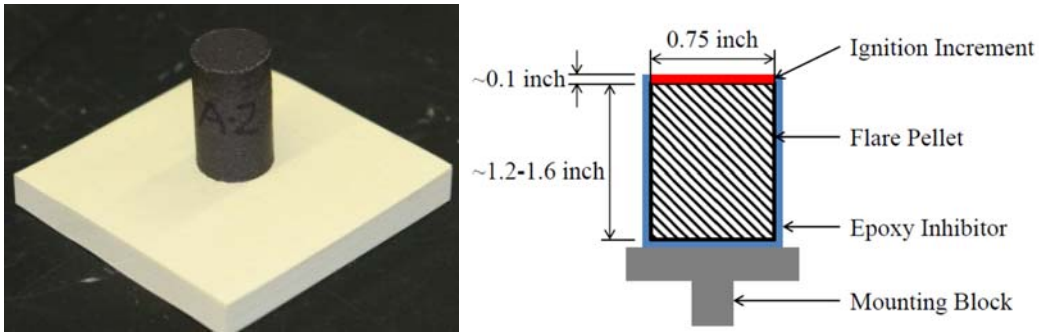

Figure 17. Image of 15 gram pyrotechnic pellet (left) and schematic of mounted and inhibited pellet (right).

4.4 SENSITIVITY AND THERMAL ANALYSIS

Sensitivity testing on selected formulations was performed according to NAVSEA Instruction 8020.5C and MIL-STD-1751A. [19, 20]. Electrostatic discharge, BAM friction, Rotary Friction, and impact sensitivities were determined in accordance with MIL-STD-1751A method 1031,

method 1023, and method 1013, respectively [20]. Differential scanning calorimetry and thermo-gravimetric analysis (DSC/TGA) scans were performed with a STA600 at 20 °C min^{-1} with UHP Nitrogen at 20 ml min^{-1}.

4.5 MECHANICAL PROPERTIES ANALYSIS

Mechanical properties were determined via an Instron 5969 Universal Test Machine, computer acquisition system, and Instron Bluehill 3 software. Nominal test conditions are shown in Table 6.

Table 6. Nominal Instron test parameters.

	Uniaxial Compression	**Splitting Tensile**
Pellet Dimensions (inches)	0.50 Ø x 0.75	0.50 Ø x 0.375
Pellet Mass (grams)	4	2
Strain Rate (inches/min.)	13	2.5
Values Obtained	Compressive strength Compressive strain Compressive Young's Modulus	Tensile strength estimate

5.0 RESULTS AND DISCUSSION

5.1 INERT MIXING STUDY

Early visualization of the flowing mixture through a transparent container permitted an in-depth understanding of how various parameters directly affected the internal mixing inside of a sealed jar. This process was first explored using an inert composition with similar particle size, density, and surface area to the Mg/$NaNO_3$/Epoxy compositions. A RAM container instrumented with a thermocouple was utilized to monitor heat generation during the mixing process because self-heating of a sensitive energetic composition is undesirable and was not understood in this type of mixing environment. Furthermore, heating of the epoxy binder could result in rapid curing which would be undesirable.

Early mixing experiments attempting to achieve a homogenous mixture of the baseline illumination composition often yielded large, binder-rich areas such as those shown in Figure 18. Early tests varied the order of addition of ingredients, mixing intensity, mix time, container size/aspect ratio, and fill fraction with little success. Early mixes often produced dense, binder-rich balls comprised mostly of the more viscous Versamid 140 curing agent (8,000-12,000 cP) as opposed to the less viscous epoxide-resin Araldite 507 (500-650 cP) [4, 5].

Figure 18. Images of early inert mixing attempts resulting in binder rich areas.

A subset of experiments (Figure 19, Table 7) investigated the effect of liquid viscosity on the ability to rapidly mix with the inert composition in a RAM environment. These experiments showed that only liquids with a viscosity <1800 cP readily incorporate into high >90% solids loaded powder mixtures. As the Versamid 140 is significantly higher than this limit, these and other, early experiments illustrated that a RAM method for epoxy-based pyrotechnics must be focused on integration of binder and wetting of all material while targeting “bulk-mixing regime”. The “bulk-mixing regime” is a flow pattern in which all of the material steadily flows within the container and is generally considered to result in optimum RAM mixing [21].

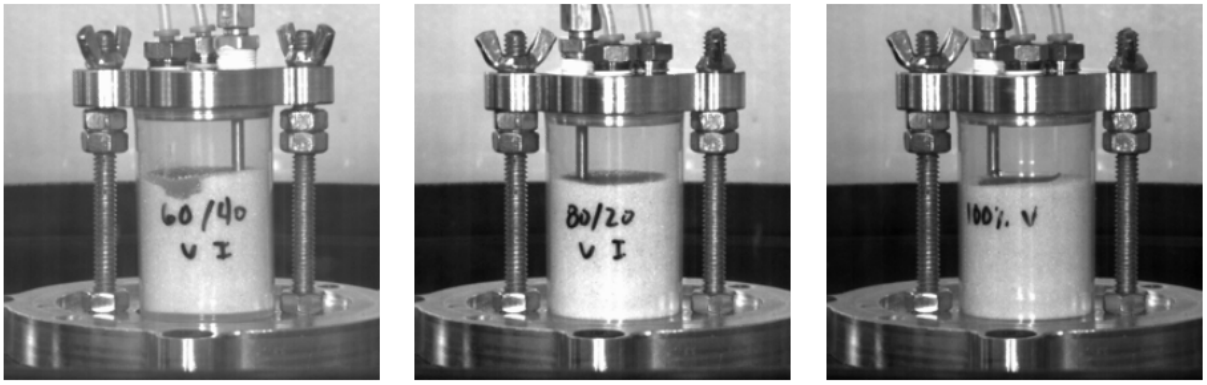

Figure 19. Images of mix experiments with varied epoxy viscosity via solvent dilution.

Table 7. Table of varied epoxy viscosities via solvent dilution.

Versamid 140/IPA	**20/80**	**40/60**	**60/40**	**80/20**	**100/0**
Viscosity (cP)	81	130	361	1822	8000-12000*

The most promising inert mixing occurred when the pre-mixed binder was loaded in the middle of the glass media with a slightly compacted sodium nitrate loaded on top (Figure 20). The binder would readily clump if in initial contact with the sodium nitrate or stick to the sides of the container. With this configuration, a test series was performed to explore the effect of fill fraction (50%, 75%, 95%), container size/aspect ratio (0.75 oz. -1.8 H/D, 1.5 oz. - 1.4 H/D) and mixer acceleration (40, 60, 80, 95 g's) on the RAM process. Figure 21 shows resulting RAM power density, final mixture temperature, and time to achieve homogeneity for all successful mixes in this inert mixing study; a successful mix is defined as a mix which achieved homogeneity. First, it was shown that no mixture achieved homogeneity at a 50% fill fraction at any mixer setting and mix times up to 15 minutes. It was also apparent that the high acceleration mixing conditions resulted in more efficient mixing (higher power density), faster mix times and lower final mixture temperatures. The 1.8 H/D container also had a wide variety of mixing conditions at the 75% fill fraction that achieved homogeneity while the 1.4 H/D container only achieved homogeneity at the 95% fill fraction and the 95 g's, 75% fill fraction condition. It was also observed that the conditions which produced higher final mixture temperatures resulted in a qualitatively stiffer final mixture. This was due to the epoxy binder system curing faster at higher temperatures; this binder combination has a known pot life of 4-6 hours. It was therefore determined that a final mixture temperature of <100 °F is desired to maintain the pot life of the mixture.

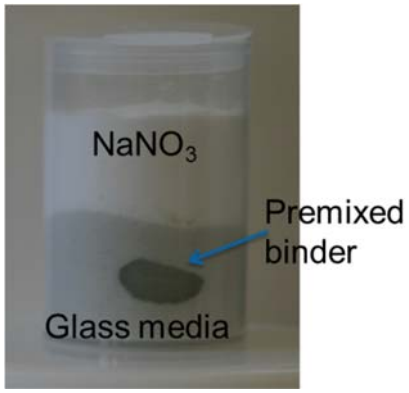

Figure 20. Optimized loading of ingredients for 1-step mixing process.

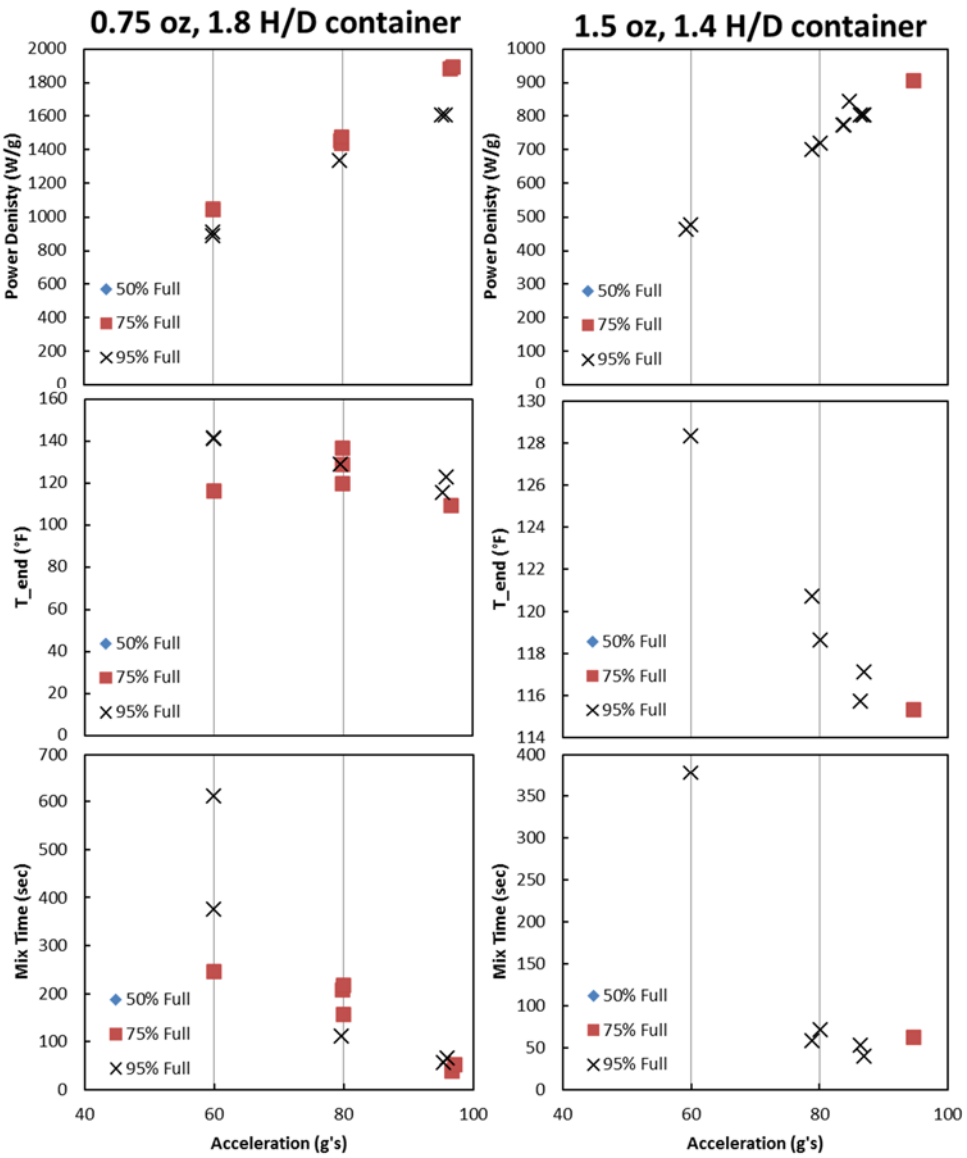

Figure 21. Resulting resonant mixing power density (top), final mixture temperature (middle) and time to achieve homogeneity (bottom) for mixes which achieved homogeneity in the inert mixing study.

5.2 LIVE LABORATORY-SCALE PERFORMANCE STUDY

After understanding the inert mixing process and its potential safety concerns, live Mg/$NaNO_3$/Epoxy compositions were produced using the refined RAM process. To evaluate the effects of the RAM technique on key pyrotechnic performance metrics, these compositions were subsequently pressed into 15 gram pellets and then subjected to performance, ignition sensitivity, thermal analysis and mechanical strength tests. In this report, luminous efficiency (cp-s/g) is reported a single indicator of performance. Ideally RAM mixed compositions were sought to be similar or superior to that of conventionally mixed compositions. At the end of the laboratory-scale performance study, several RAM processes were identified for producing illumination compositions while verifying that important mechanical, safety, and performance parameters are equivalent or superior to traditionally mixed compositions.

5.2.1 OVERVIEW OF SUCESSFUL MIXING METHODOLOGIES FOR EPOXY-BASED PYROTECHNICS

Three RAM methodologies, shown in Figure 22, were developed after extensive inert mixing, live mixing, and sub-scale candle performance testing. The development of these processes also utilize vacuum processing which can significantly alter the flow inside of the container as well as pull off and recover any acetone solvent which may be utilized as a processing aide (1-3 rel. wt. %). The following processes have been shown to consistently produce a homogenous mixture of the baseline illumination composition:

- 1 Step Mixing Process: Place Magnesium, premixed binder and acetone in one container as shown in Figure 20 and mix.
    - 30 seconds at 95 g's (no vacuum), 1.5 minutes at 65 g's (22" vacuum) or until homogeneous
    - Load container to ~90-95% fill fraction
    - The 1.5 wt. % acetone with the pre-mixed binder and vacuum processing helps to keep the mix temperature <100 °F
- 2 Step Mixing Process: First mix Magnesium, premixed binder and 1.5 wt. % acetone in a container. Then after achieving desired homogeneity, add sodium nitrate and acetone (optional) and continue mixing until completion.
    - Step 1 – Mag + Pre-mixed Binder
        - 30 seconds at 65 g's (no vacuum), 1.5 minutes at 65 g's (22" vacuum) or until homogeneous
        - This mix is made as "master batch" at 60% fill fraction
        - The 1.5 wt. % acetone with the pre-mixed binder and vacuum processing helps to keep the mix temperature <100 °F
    - Step 2 – Add Sodium Nitrate
        - 30 seconds at 65 g's (no vacuum), 1.5 minutes at 65 g's (22" vacuum) or until homogeneous
            - Target 100% fill fraction with light compression (resulting mixture fill fraction will decrease to ~90% once mixing begins)
        - The optional ~1.5 wt. % acetone with the pre-mixed binder and vacuum processing helps to keep the mix temperature <100 °F
- 3 Step Mixing Process: First, mix Magnesium and Versamid 140 and acetone until homogeneous. Next, in a separate container, mix sodium nitrate, araldite and acetone (optional) until homogeneous. Last, add portion of each precursor mix and acetone (optional) into a separate container so that the resulting ingredient ratios reflect that of Table 1, and mix until completion.
    - Step 1 – Magnesium + Versamid
        - 30 seconds at 65 g's (no vacuum), 1.5 minutes at 65 g's (22" vacuum) or until homogeneous
            - This mix is made as "master batch" at ~90% fill fraction
        - Mixture may go over 100 °F (no fuel/oxidizer or resin/curing agent)
        - Low acetone/versamid pre-mixture necessary (~2.5 wt. % acetone)
    - Step 2 – Sodium Nitrate + Araldite
        - 30 seconds at 95 g's (22" vacuum), 1.5 minutes at 65 g's (22" vacuum) or until homogeneous

- This mix is made as "master batch" at ~90% fill fraction
- Mixture may go over 100 °F (no fuel/oxidizer or resin/curing agent)
- Partial compaction of sodium nitrate when loading container is recommended
- Low acetone (~1.5 wt. %)

o Step 3 – First Half + Second Half

- 15 seconds at 95 g's (no vacuum), 1.5 minutes at 65 g's (ramp to 22" vacuum) or until homogeneous
  - Target 85-90% fill fraction
- Mag/Versamid on bottom, optional ~2 wt. % acetone, Sodium Nitrate/Araldite on top

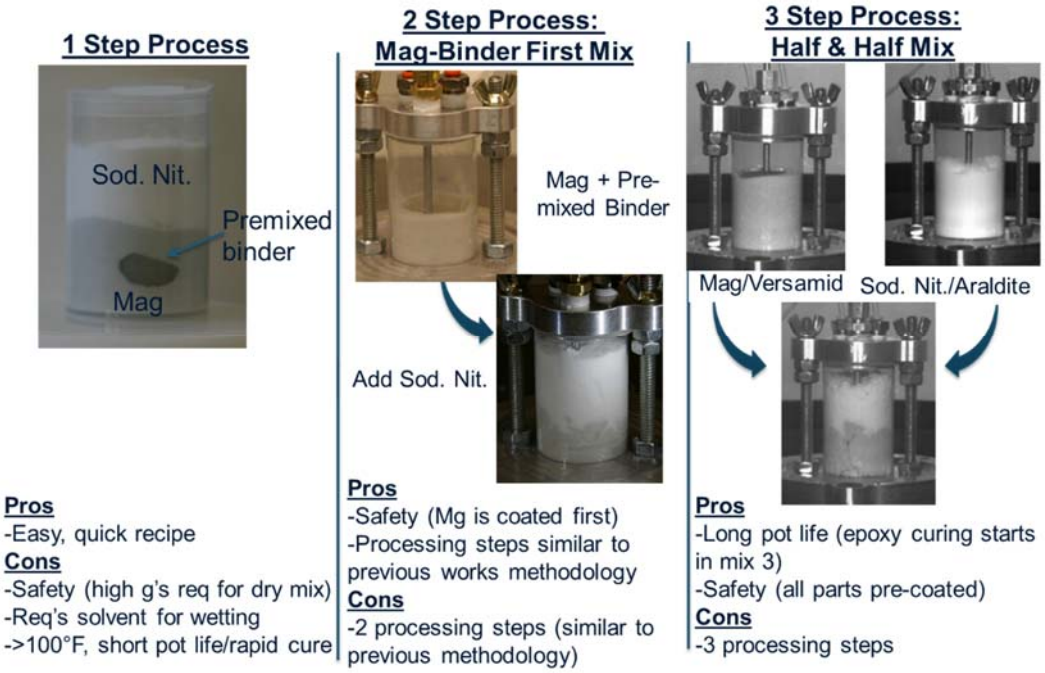

Figure 22. Overview of successful resonant mixing methodologies for epoxy-based pyrotechnics.

Other general lessons learned and best practices of RAM of epoxy-based pyrotechnics:

- General RAM of Epoxy-based Compositions
  - ~90% fill fraction, yields optimum mixing
  - Over filling a container can yield sporadic Resodyn response/errors
  - The loading of ingredients into the container is important
  - If not using solvent, try to minimize/eliminate epoxy on walls of container during loading
  - Using solvent in a mixing process incorporates any binder on the walls of the mixing container back into the mix
  - When vacuum processing, start low g's to start wetting material to minimize sucking powders into vacuum lines
  - Mixes can take several minutes to develop, must be patient
  - High vacuum greatly reduces temperature increase due to friction
  - Vacuum processing with solvent (e.g., acetone) causes a temperature drop due to endothermic evaporation and is an effective way of controlling process temperature

- Rounded container bottom helps reduces material sticking in corners
- An overnight room-temperature partial-cure is recommended prior to subsequent pressing to minimize binder migration in the final oven cure

- Thoughts on Solvent Use
  - Acetone was shown to more favorable than isopropyl alcohol due to its higher vapor pressure (aka – it was difficult to quickly evaporate the alcohol under vacuum)
  - A little bit of solvent (1.5-2.5 wt. %) greatly increases mixing efficiency with the correct container
  - Solvent addition minimizes epoxy residues on container walls
  - With moderate vacuum, 97% solvent extraction is possible within ~3 minutes
  - Solvent recovery and recycling is possible with a solvent trap or cold finger in the vacuum line

5.2.2 LABORATORY SCALE SENITIVITY AND THERMAL ANALYSIS

Table 8 shows the impact sensitivity of illumination composition prepared on a Resodyn via the previously described 1-step, 2-step, and 3-step processes as well as a mix-muller. Overall, the RAM compositions are similar or slightly less sensitive than the mix-muller produced materials. The RAM compositions have low impact sensitivity, improved friction sensitivity over the mix-muller material, and similar ESD to the mix-muller material. This similar/slightly lower sensitivity is likely achieved due to more homogeneous mixtures and better coated particles as shown in Figure 23. Qualitatively, the mix-muller process typically produces "large hard chunks" of binder rich materials, while the refined RAM processes produce material the consistency of "wet sand".

Table 8. Sensitivity data for illumination compositions produced by various methods.

Sample Info	**Impact**	**BAM Friction**	**Rotary Friction**				**ESD**
			Fire Energy (ft-lb)				
Description	50% Fire Energy (J)	Threshold energy (N)	Average	Lowest	Average time to react (s)	Response (# fired)	Maximum no-fire energy (mJ)
Mix-muller	34.2	54.0	122.9	45.3	4.4	8/10	125.0
1-Part Resodyn	>35.0	160.0	340.3	75.9	12.5	9/10	125.0
2-Part Resodyn	>35.0	80.0	283.0	55.9	10.6	10/10	180.0
3- Part Resodyn	33.8	120.0	262.4	133.2	9.8	8/10	125.0
RDX Standard	7.9	120.0	n/a	n/a	n/a	0/10	80.0
PETN Standard	--	48.0	--	--	--	--	--

Blue indicates a very low hazard, green indicates a low hazard, yellow indicates a medium hazard, orange indicates a high hazard, and red indicates a dangerous hazard.

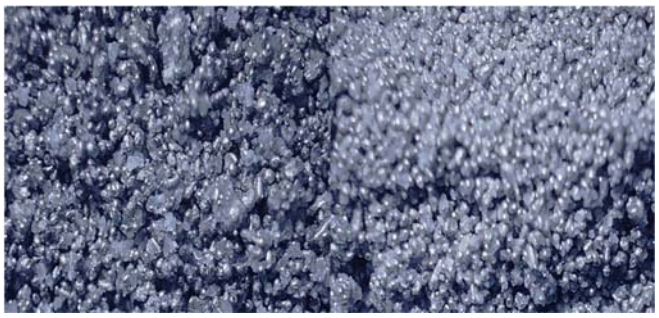

Figure 23. Microscopic images of the baseline illumination composition prepared with mix-muller (left) and Resodyn(right).

DSC/TGA scans of the ingredients of the baseline illumination composition are shown in Figure 24. The DSC/TGA scans of the illumination compositions (mixed by various methods) are shown in Figure 25. Derived ignition temperature and exothermicity data from these scans are summarized in Table 9. In comparison to the mix-muller material, the heatflow curves from the RAM compositions show no new features. Additionally, a "hand mixed" sample is also presented for reference. The ignition temperatures of the Resodyn compositions are also similar or higher than that of the mix-muller reference material; resulting in similar thermal ignition thresholds (within 35°C). Additionally, each of RAM compositions have similar exothermicity to the mix-muller reference material (within 10%). The three-part RAM material did exhibit a slightly higher ignition temperature (and a modified TGA curve) then the rest of the samples. This may be due to a less homogeneous mixture or a by-product of the acetone processing agent. Overall, the sensitivity and thermal analysis show that materials produced by the Resodyn methods pose no additional safety risk over the mix-muller produced composition.

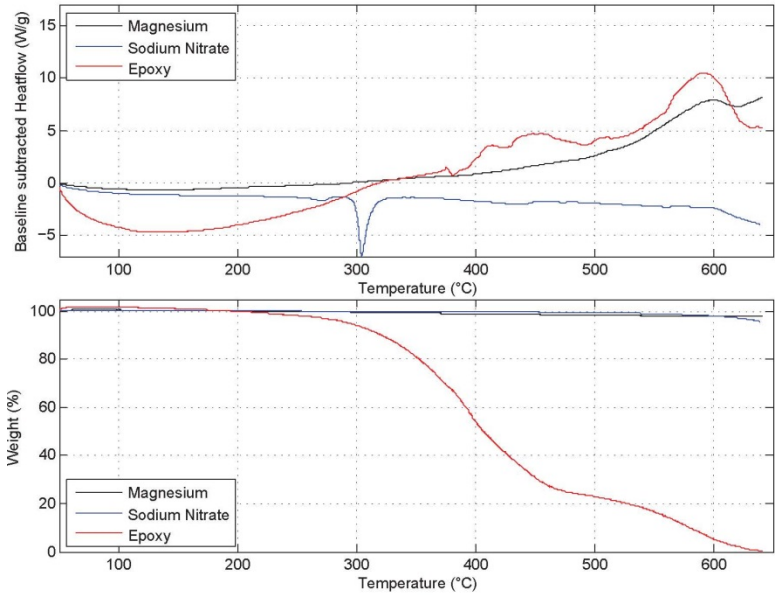

Figure 24. DSC/TGA scans of individual ingredients in Table 4 illumination composition.

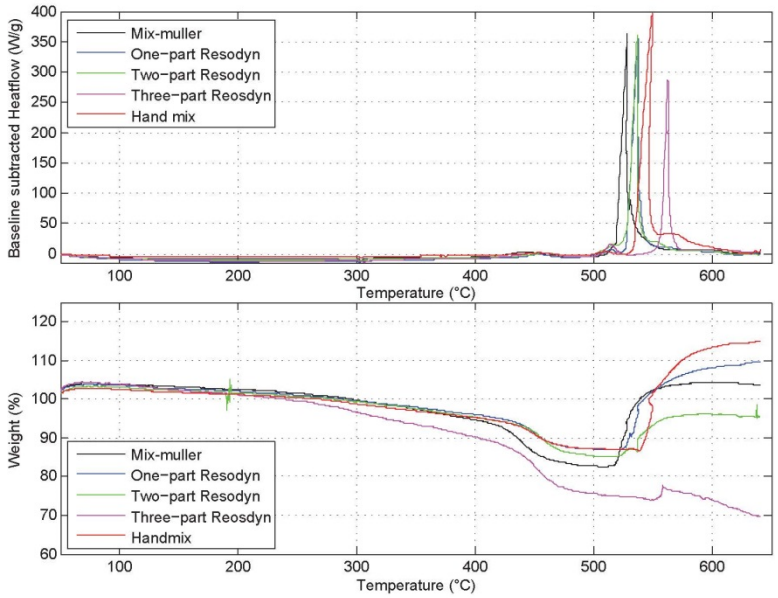

Figure 25. DSC/TGA scans of illumination composition mixed by various methods.

Table 9. Summary of DSC/TGA analysis of illumination compositions mixed by various methods.

Sample	Ignition Temperature (°C)	Peak Exotherm Temperature (°C)	Peak Exothermicity (W/g)
Mix-muller	518.8	528.4	363.0
One-part RAM	527.6	537.9	354.5
Two-part RAM	529.4	536.9	360.7
Three-part RAM	555.5	562.6	286.3
Hand Mixed	534.6	549.3	396.6

5.2.3 EFFECT OF MIXING METHODOLOGY ON COMBUSTION PERFORMANCE

Generally, resonant acoustic mixed material can produce homogeneous compositions with similar burn times and similar/increased luminous efficiency to a mix-muller produced composition. Figure 26 shows images of ~15-gram combustion performance tests showing that candles produces qualitatively similar plumes. Figure 27 shows that the relative luminous efficiency is similar or slightly higher than the mix-muller composition. It is due, in part, to the increased homogeneity of the RAM process over the mix-muller.

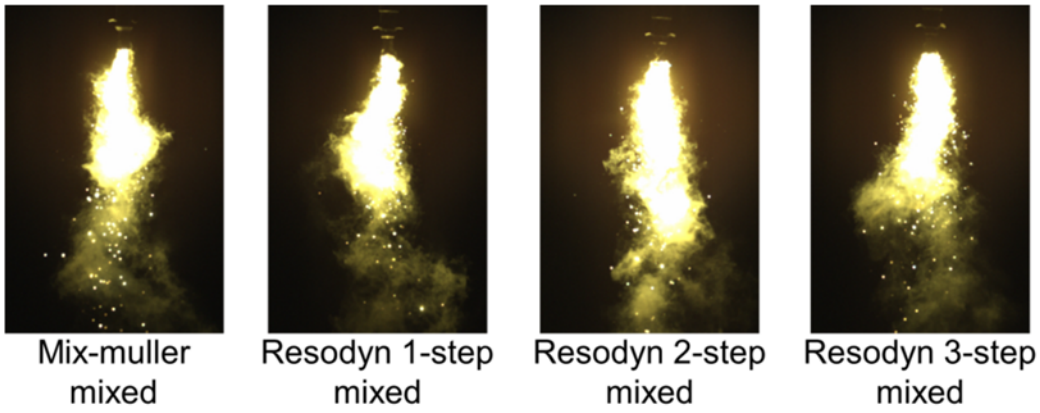

Figure 26. Images of performance testing of the baseline illumination compositions produced by various mixing methods.

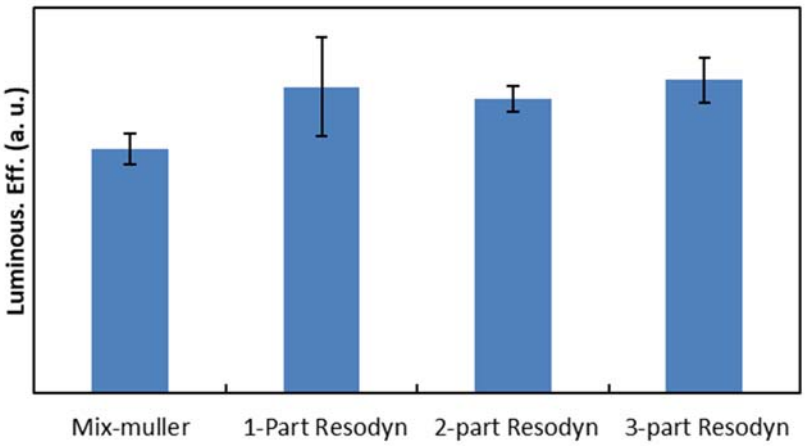

Figure 27. Relative luminous efficiency of the baseline illumination compositions produced by various mixing methods.

5.2.4 AGING OF PRE-CURSORS ON 3-STEP MIXING METHODOLOGY

One benefit of the 3-step RAM process (Figure 22) is that the first two mixing steps are non-energetic and do not affect the pot life of the final mix; fuel/oxidizer and epoxy resin/curing agent are both segregated until the final mixing step. This could allow for a significant increase in manufacturing flexibility as the two precursor mixes could be mixed in bulk (no energetic hazard) in advance, allowing for the third mix to be performed only as needed. It is noted that the third mixing step can also be accomplished in as little at 10-15 seconds due to both liquid ingredients already being thoroughly dispersed into their respective fuel/oxidizer powder. However, the storage compatibility of the precursor mixes of Magnesium/Versamid 140 and Sodium Nitrate/Araldite 507 was not known. Therefore, the ability to store the precursors 0-3 months prior to the final energetic mixing step was investigated. Figure 28 shows the effect of aging of pre-cursors on luminous efficiency 3-step RAM produced illumination composition. This study shows that the no significant change in luminous efficiency over the 3 months of storage. This indicates that the two precursor mixes could be performed in advance to be stored and used as needed. It should be noted that each of precursors need to be stored in air-tight containers as the epoxy components are known to degrade by absorption of water vapor and carbon dioxide over time.

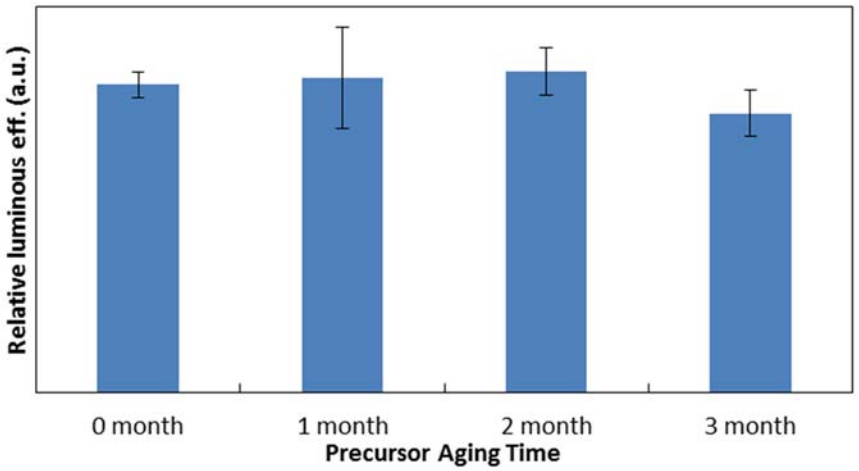

Figure 28. Effect of aging of pre-cursors on luminous efficiency 3-step mixing produced illumination composition.

5.2.5 EFFECT OF EPOXY ON MECHANICAL PROPERTIES OF ILLUMINATION COMPOSITIONS

Artillery and mortar-fired illumination rounds experience some of the highest accelerations and spin rates of all fielded pyrotechnic flares. In these systems, the pyrotechnic binder plays a key role in determining the mechanical properties of the pyrotechnic candle. In this section, the effect of the epoxy binder on a pyrotechnics' resulting mechanical properties, combustion efficiency, and RAM processing is explored. Table 5 shows the epoxy-binder test matrix and their relative mixture ratios that were explored in this section. These binder systems were hand mixed, pressed into the sample configurations in Table 6 and subjected to uniaxial compression and splitting tensile testing as shown in Figure 29. Figure 30 shows the compressive young modulus and compressive strength of the pyrotechnic composite materials and of the virgin cured epoxy system. The two baseline composite materials (V140-B and PS-B) exhibited a wide range of elasticity and compressive strength. This shows that a wide range of mechanical properties can potentially achieve the strenuous application requirements of illumination rounds. Significant differences between the elasticity of the bulk polymer and composite material were noted though general trends were consistent. The elasticity of the V140-B can be readily altered by varying the curative ratio (V140S) or by the addition of PEG at ratios of 10-20% wt. The addition of PEG increases the elasticity of the material while significantly reducing the compressive strength of the composite. It is noted that the young modulus and compressive strength of epoxy from technical data sheet may be used to estimate of the approximate properties of a composite material. Overall, 9 commercially available low-viscosity epoxy systems were processed into live-pyrotechnic composite materials and subjected to mechanical properties testing. The results showed that a range of properties are achievable with similar mechanical properties in the range of historically-used epoxy systems.

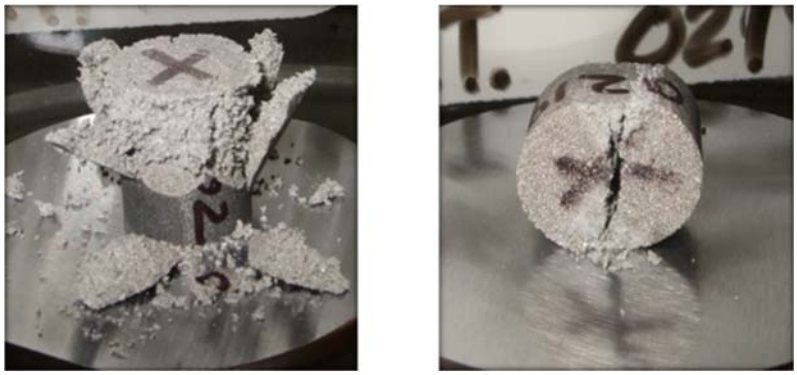

Figure 29. Images of uniaxial compression (left) and splitting tensile testing (right) of live pyrotechnic pellets.

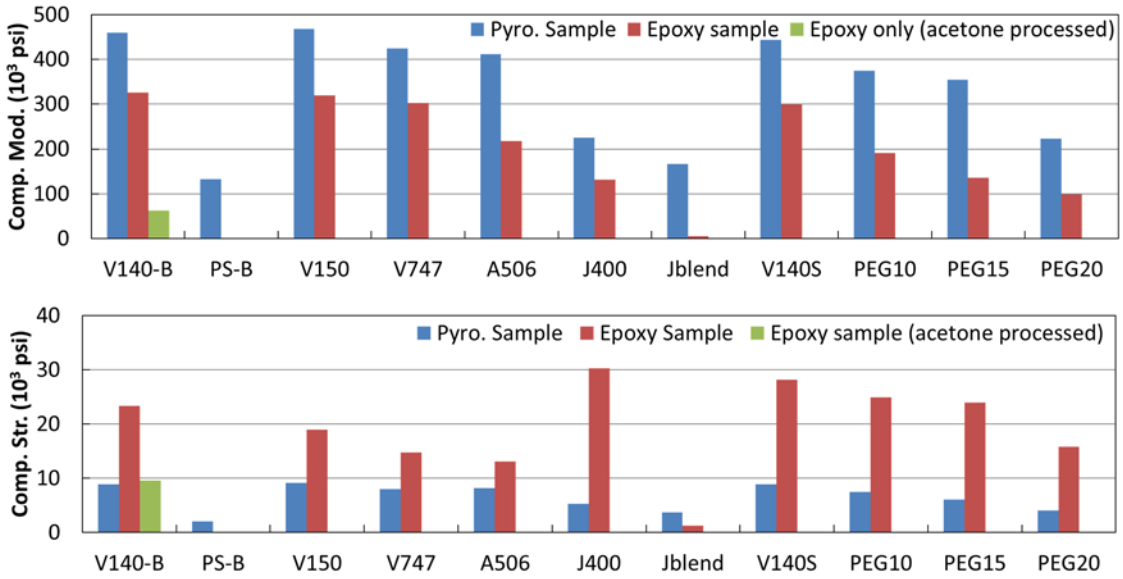

Figure 30. Effect of epoxy binder system on the compressive modulous (top) and compressive strength (bottom) of the baseline illumination composition. "Epoxy sample" refers to the material properties of the virgin cured epoxy system with no solids loading. "Epoxy only (acetone processed)" reflects the mechanical properties of the epoxy system that was processed with an acetone procesing aide similar to that used during RAM processing.

The use of acetone as a processing aide was also shown to increase the elasticity and decrease the strength of the epoxy system (Figure 30). While the mechanical strength is still within the two baseline composite materials (V140-B and PS-B), the elasticity of the acetone sample was outside the range of the historical epoxy systems. Additional work is needed to explore the effect of an acetone processing aide on the resulting mechanical integrity of the final illumination composition. This is particularly important due to the previously noted accelerations and spin rates of these items.

5.2.6 EFFECT OF EPOXY ON COMBUSTION PROPERTIES OF ILLUMINATION COMPOSITIONS

In addition to effects on mechanical properties, binder systems can potentially affect the combustion performance of a pyrotechnic candle**.** Therefore, the various epoxy systems were also tested as 50-gram, sub-scale candles at the Armament Research, Development, and Engineering

Center (ARDEC) photometric light testing facility (Figure 31). Figure 32 shows that 8 of 10 systems epoxy alternatives yield similar combustion performance within 10% of luminous efficiency of the V140-B baseline system. Additionally, the polysulfide based binder was more energetic than all of the binders tested. Addition of 20% PEG yields up to a 7% increase in combustion efficiency while significantly modifying the mechanical properties. Overall, a number of low-viscosity curing agent alternatives appear to have minimal effect of combustion performance while being able to offer a range of mechanical properties to meet various application requirements.

Figure 31. Photometric light testing of 50 gram pyrotechnic candles at ARDEC.

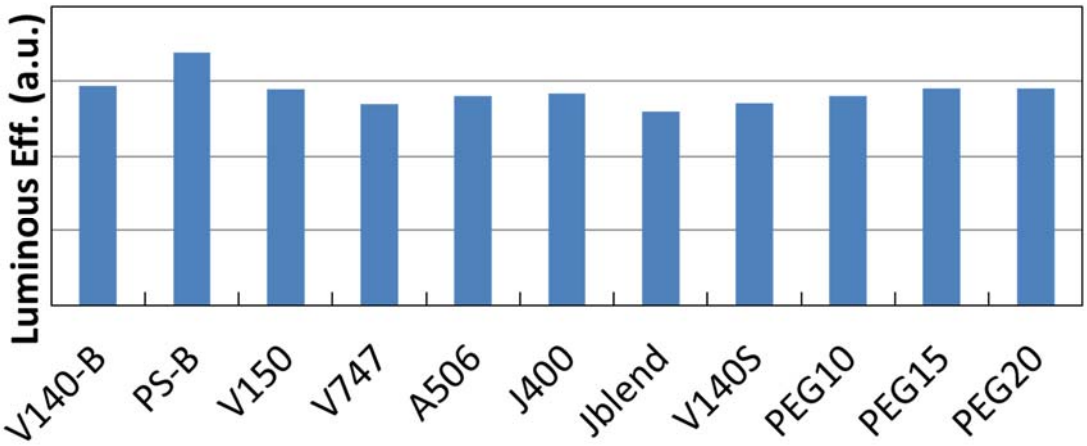

Figure 32. Effect of epoxy binder system on the combustion performance of the baseline illumination composition.

5.2.7 EFFECT OF EPOXY ON RAM PROCESSING OF ILLUMINATION COMPOSITIONS

The effects of curing agent viscosity on quality of mixing were observed and qualitatively assessed. Mixes consisting of inert fuel surrogate, sodium nitrate, and binder systems were prepared on the LabRAM operating at 65 g's of acceleration for two minutes. Wetting steps consisting of 85 g's loads for five seconds were also incorporated at the beginning and/or end of some mixes. Mixes were prepared in the 1-step loading configuration (Figure 20), with no pre-

mixing of binder or use of solvent-processing aides. Table 10 lists curative and modifier viscosities, as well as the qualitative assessment of mix homogeneity. Every system tested yielded a final mix containing binder-rich spheres. As viscosity decreased, these binder-rich areas decreased in both volume and number. Though no mixes were able to achieve complete homogeneity, all containing lower viscosity curing agents mixed better than the baseline Versamid 140. Mixes containing PEG modifiers yielded similar results to the baseline system. It is expected that, with optimization, some of these systems could achieve homogeneity without the use of pre-mix steps or processing aides.

Table 10. Curing agent and modifier viscosity at 25°C with qualitative assessment of mix homogeneity.

Nomenclature	Curing Agent Viscosity (cP)	Modifier Viscosity (cP)	Mix Homogeneity
V140B	8000 - 12000	N/A	Poor
V150	2000 - 4000	N/A	Fair - Poor
V747	200 - 500	N/A	Fair
A506	250	N/A	Fair
J400	21	N/A	Good
Jblend	21	247	Good
V140S	8000 - 12000	N/A	Poor
PEG10	8000 - 12000	> 7.3*	Poor
PEG15	8000 - 12000	> 7.3*	Poor
PEG20	8000 - 12000	> 7.3*	Poor

*Viscosity only given for 100°C

5.3 SCALE-UP RAM PROCESS TO CONCEPT SCALE

The primary goal during the scale-up study was to test the viability of the described 2-part RAM technique (Section 5.2.1) with pilot-scale mixing of Mg/$NaNO_3$/Epoxy based compositions. Using the favorable laboratory-scale sensitivity and thermal analysis (Section 5.2.2), NSWC Crane's local Material, Process, Equipment and Facility Review Committee approved larger-scale mixing up to 1 kg (2.2 lbs.). Custom mixing containers (Figure 33) were designed to evaluate the two-step mixing process at 32, 50, 100, 200 and 1000-gram batch sizes.

Figure 33. Custom mixing container for scaling analysis on LabRAM IIH.

5.3.1 POWER-DENSITY SCALING ANALYSIS

In previous work by Resodyn Corporation, similar mixing times were achieved by matching the calculated power-density between laboratory and production scales of thick pastes [22]. The power density (W/kg) is defined as the amount of power going into the mixture per unit mass of mixture. Figure 34 shows how the power density of the inert 2-part RAM process varies with batch sizes from 32 to 250 grams. Using the 2-part mix process on a LabRAM IIH, significantly less power per gram of material is needed to mix larger batch mixes. Practically, this means that this process should be able to be easily scaled to larger mixes beyond that demonstrated in this report. However, it was observed that when starting a larger mixture, the mixer power would often temporarily spike during the first few seconds of the mix. This can be avoided on larger mixes by slowly ramping up the acceleration during the first 10 seconds of the mix routine. A similar relationship was observed for live mixes between 32 to 1000 grams for live mixes and is shown in Figure 35.

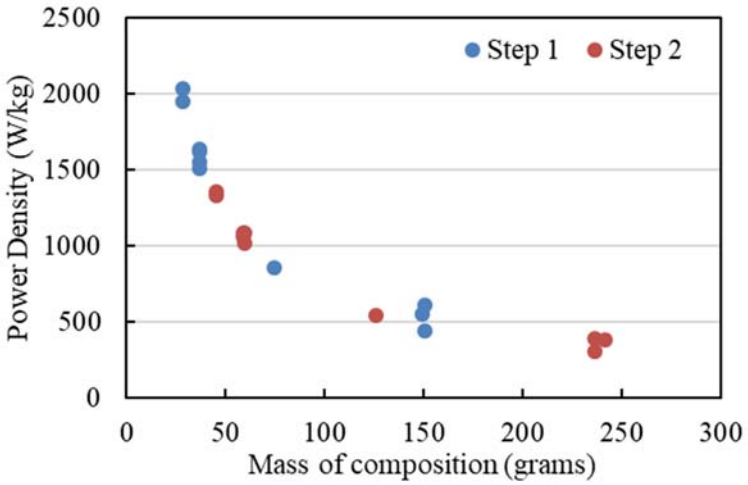

Figure 34. Inert composition scaling analysis for 2-part RAM process.

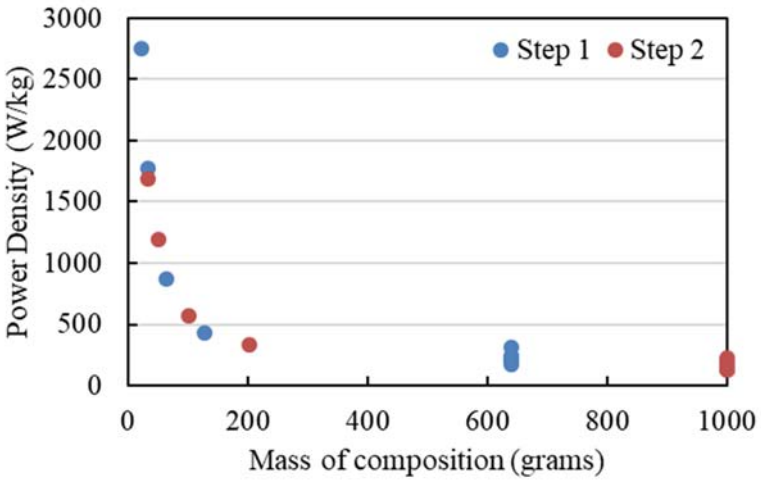

Figure 35. Live composition scaling analysis for 2-part RAM process.

5.3.2 SENSITIVITY ANALYSIS OF SCALED MIXES

Table 11 shows the sensitivity analysis of the two-part mix process in batch sizes ranging from 32 to 200 grams. The sensitivity of the pyrotechnic material made using the2-part process was similar regardless of batch size. Some variance in the rotary friction data is common for these types of pyrotechnics and does not indicate any change in material sensitivity. Overall, the sensitivity analysis is similar to that presented in Section 5.2.2 and no additional hazards are expected in larger batch size mixes.

Table 11. Sensitivity data for 2-part RAM illumination compositions produced in various batch sizes.

Sample Info	Impact	BAM Friction	Rotary Friction				ESD
			Fire Energy (ft-lb)				
Description	50% Fire Energy (J)	Threshold energy (N)	Average	Lowest	Average time to react (s)	Response (# fired)	Maximum no-fire energy (mJ)
32-gram mix	>35.0	216.0	95.8	31.9	3.8	10/10	125.0
50-gram mix	>35.0	324.0	203.7	16.0	8.0	9/10	80.0
100-gram mix	>35.0	360.0	146.4	51.5	5.4	9/10	125.0
200-gram mix	34.6	252.0	96.7	44.4	3.6	7/10	80.0
RDX Standard	7.8	128.0	1624.36	1624.36	59	1/10	20.0
PETN Standard	--	72.0	--	--	--	--	--

Blue indicates a very low hazard, green indicates a low hazard, yellow indicates a medium hazard, orange indicates a high hazard, and red indicates a dangerous hazard.

5.4 PILOT SCALE DEMONSTRATION

The final portion of this project partnered with CAAA to demonstrate and compare RAM-mixed illumination composition to the conventional mix-muller material in a full-scale flare configuration. CAAA annually produces thousands of Illuminating and Infrared Mortar Candles for 60mm, 81mm, & 120mm mortars as well as 105mm and 155mm artillery projectiles. Illuminating and Infrared projectiles, Figure 12, enhance our warfighter's capability to operate at night and compliment the capabilities of night vision equipment [6]. For this demonstration, M485A2 155-mm visible-light illuminating projectiles were used to compare the differences in

performance between RAM-mixed and mix-muller mixed material. The exact formulation and manufacturing parameters used in this demonstration are not approved for public release.

5.4.1 ITEM DESCRIPTION

The M485A2 155-mm Illumination Round, Figure 36, is a relatively large pyrotechnic device that is used to light up the field during combat and training ranges. This item is fired from a howitzer with relatively high trajectories when the charge activates and a parachute opens, creating a bright light that lasts for several minutes as the parachute drifts to the ground [7].

Figure 36. M485A2 projectile (left) and illumination candle (right) [8].

5.4.2 DEMONSTRATION OF PILOT-SCALE RAM MIXING

Prior to consolidation into the M485A2 155-mm Illumination Round hardware at CAAA, nine 1-kg batches of illumination composition was prepared using the 2-step RAM process as described Section 5.2.1. 3- 1-kg mix containers, Figure 37, were designed and manufactured for this pilot-scale demonstration. These mixes were prepared using a LabRAM IIH at the NSWC Crane Navy flare prototyping facility over the course of 3 hours. Two CAAA pyrotechnic engineers observed this mixing process and reported that the RAM process has several safety advantages and much faster mix times than the currently used mix-muller. After mixing, RAM composition were placed into drying pans, Figure 38, while subsequent mixes were being performed. Prior to pressing into the final candle hardware, all mixes were allowed to partially-cure for at least 1.5 hours; 5 hours for the first mix. These pilot scale mixes were visibly observed to be homogeneous with little to no noticeable clumps of unmixed material. As shown in Figure 37, >99.5% of the RAM processed material easily poured out of the container with <0.5% material needing to be scraped out of the container with a non-conductive wooden tongue-depressor.

Figure 37. Image of pyrotecnic residue in pilot-scale RAM mix container(left) and on lid(right).

Figure 38. 1 kg of RAM mixed illumination composition during final pilot-scale demonstration.

The 9 kg of RAM-mixed illumination composition was subsequently transferred to the CAAA production facility for pressing operations. Three M485A2 155-mm Illumination candles, Figure 39, were prepared using standard flare hardware and pressing procedures. In comparison to the mix-muller produced composition, CAAA technicians reported that the RAM material appeared homogeneous, with improved pot-life, and pressed well using production tooling. After 5 hours, from the start of mixing, The RAM mix material was still loose and able to be pressed after 5 hours from the start of mixing. According to the CAAA operators, the maximum pot life for mix-muller composition is 4-5 hours after which it would have to be thrown out because of how hard and unworkable it becomes.

Figure 39. M485A2 illumination candle produced with RAM-produced illumination composition.

5.4.3 PERFORMANCE COMPARISON OF RAM AND MIX-MULLER PRODUCED ILLUMINATION CANDLES

The three M485A2 illumination candles with RAM illumination composition were subjected to standard testing procedures along with standard mix-muller M485A2 illumination candles (Figure 40). Figure 41 shows an illumination candle before and after testing at the NSWC Crane photometric light testing tunnel. All three RAM candles performed similarly to their mix-muller counterparts and passed all light intensity requirements (Figure 42). This demonstration shows that RAM is a viable alternative to mix-muller mixers and can be potentially used to produce candles with similar performance.

Figure 40. Testing of illumination candle at NSWC Crane photometric light testing tunnel.

Figure 41. Image of M485A2 candles with RAM illumination composition before (left) and after radiometric testing (right) at the radiometric light testing tunnel.

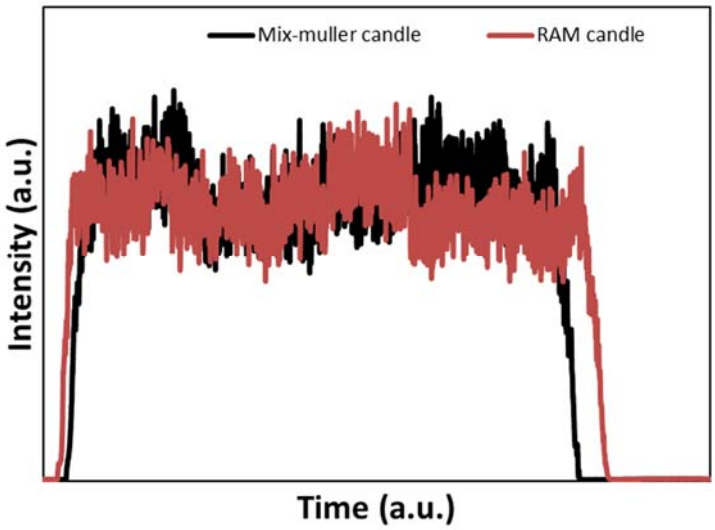

Figure 42. Comparison of arbitrary intensity plot for mix-muller and RAM candles.

5.5 ENVIRONMENTAL BENEFIT OF PILOT SCALE RAM MIXING

According to CAAA personnel, up to 80% of acetone at their illumination manufacturing facility is used on cleaning the mix-muller hardware. For example, 1-2 gallons of acetone is typically spent cleaning the mix-muller after a pyrotechnic mix which can range in batch size from 27-57 kgs (60-125 lbs). This quantity of solvent is necessary to clean the mix-muller (regardless of the size of the mix) due to the excess surface area of the rollers and scrapers as well as many other hard-to-reach areas (Figure 13). It is significantly easier to clean RAM containers which are simple cylinders. In the pilot scale demonstration, a single rag wetted with acetone was sufficient to clean the container after each 1-kg mix and a couple q-tips to clean the lid's vacuum ports. A scaling analysis based off of the quantity of solvent used in the pilot scale demonstration (Table 12) shows that using a RAM5 for a 57 kg (125 lb) mix instead of a mix-muller can result in a acetone reduction of 98.7%. It is noted that RAM solvent efficiency (e.g., the ratio of solvent needed for cleaning to the amount of material produced) increases significantly with batch size.

Table 12. Scaling analysis for cleaning mixing equipment; RAM versus mix-muller.

Mixer	Batch size (kgs)	Acetone (g)	Solvent Efficiency (grams acetone / kg comp)
LabRAM	0.1	0.9	8.7
LabRAM IIH	0.2	1.4	6.9
	1	4.1	4.1
RAM5	27.0	36.7	1.4
	36.0	44.5	1.2
RAM55	57.0	59.9	1.1
	250.0	161.1	0.6
	419.0	227.4	0.5
Mix-muller	27.2	4491.4	165.0
	36.3	4491.4	123.8
	56.7	4491.4	79.2

5.6 COST ANALYSIS OF PILOT SCALE RAM MIXING

Table 13 shows an estimated cost analysis to highlight some of the potential cost savings of using a production scale RAM5 or RAM55 versus the common mix-muller. To produce approximately 1000 lbs of composition, a mix muller process would need approximately 3 technicians for 10 hours to produce 8- 125 lb batches. Using the processes developed in this work, RAM 5/RAM55 may be to be able to produce similar amounts of composition in 5 and 1.5 hours, respectively. These RAM5/RAM55 processes could result in labor saving of 61-96%. Similarly, acetone used for cleanup operations could be reduced by over 99% for either production scale RAM operations.

Table 13. Cost analysis of pilot scale RAM versus mix muller.

	Mix Muller	RAM5	RAM55
Total Quantity Produced (lbs.)	1000	960	924
Number of Mixes (#)	8	12	1
Batch size (lbs.)	125	80	924
	Materials		
Pyrotechnic Ingredients ($)	--	--	--
Cleanup acetone (gallons)	12	0.11	0.05
Cleanup acetone* ($)	$340.72	$3.17	$1.35
Acetone Reduction (%)	--	99.07%	99.60%
	Labor		
Labor (# personnel)	3	3	3
Labor (hours)	10	5	1.5
Total Labor** ($)	$3,000.00	$1,500.00	$450.00
Total Labor Savings (%)	--	61.25%	96.31%
Total cost savings ($)	--	$1,837.55	$2,889.37

*assumes $150/20L acetone

**assumes labor rate of $100/hour

6.0 CONCLUSIONS AND IMPLICATIONS FOR FUTURE RESEARCH/IMPLEMENTATION

6.1 CONCLUSIONS

In this work, three RAM processes were developed to reduce the environmental, safety, and occupational health impacts currently observed in the mix-muller manufacturing process of Magnesium/Sodium Nitrate/Epoxy illumination compositions. These methodologies include a 1-step, 2-step, and 3-step process, each with their own mix routine, order of addition, and pros/cons from a technical perspective. In these processes, it was shown that the key mixing step is the incorporation of the high viscosity cross-linking agent Versamid 140. In laboratory-scale sensitivity testing, RAM materials were observed to be more homogenous with similar/slightly lower sensitivity than the mix-muller produced materials. Performance testing resulted in resonant acoustic mixed material producing similar burn times and similar/increased luminous efficiency to a mix-muller produced composition. An aging study showed that the 3-step RAM process (patent submitted) could allow for a significant increase in manufacturing flexibility since the two precursor mixes could be mixed in bulk in advance and stored for the third mix to be performed only as needed.

As an alternative to using acetone as a processing aide, a number of lower-viscosity, commercially-available epoxy alternatives were also subjected to mechanical testing, performance testing, and inert RAM processing evaluation. In general, mechanical data trended in an expected manner relative to the type of curing agent used. Amidoamine-cured resins showed the highest mechanical properties and largely agreed with expected values. PEG-modified resins showed reduction of mechanical properties in relation to an increase in weight percent of PEG used. Most of the epoxy alternatives, with one exception, maintained luminous efficiency within 10% of the baseline Versamid 140 system. It is expected that with further development some of epoxy alternatives could achieve homogeneity without the use of pre-mix steps or processing aides. Overall, a number of low-viscosity curing agent alternatives appear to have promising RAM processing characteristics and minimal effect of combustion performance while being able to offer a range of mechanical properties to meet various application requirements.

For a pilot scale demonstration, the two-step RAM mix process was scaled from laboratory to concept scale (2-lb batch size). In collaboration with CAAA, three M485A2 155-mm illumination candles with RAM illumination composition were subjected to standard testing procedures along with standard mix-muller candles. All three RAM candles performed similarly to their mix-muller counterparts and demonstrated that RAM is a viable alternative to mix-muller mixers. Furthermore, projected benefits of a production-scale RAM process may result in significant increases to overall throughput, labor cost reduction of 61-96%, and a reduction in acetone used for cleanup operations by over 99%.

6.2 IMPLICATIONS FOR FUTURE RESEARCH/IMPLEMENTATION

Future process development needs to investigate the effect of solvent as a process aide on the resulting mechanical properties of the flare. This is important as the artillery and mortar-fired illumination rounds experience some of the highest accelerations and spin rates of all fielded pyrotechnic flares. Alternative to using solvent as a process-aide, a number of promising lower-viscosity binder systems have been identified. Also, a solvent-less mix process that uses a cooled mixing vessel to keep the process temperature below 100 °F should be considered.

Per Appendix B:, CAAA is interested in this mixing technology, but due to current high inventory levels of the various Mortar and Artillery-Fired Illumination Projectiles, the future production schedule and interest in alternative mixing processes, is uncertain.

REFERENCES

[1] A. P. Hardt, Pyrotechnics, Post Falls: Pyrotechnica Publications, 2001.

[2] "Crane Army Ammunition Activity Brochure," Crane Army Ammunition Activity, [Online]. Available: http://www.crane.army.mil/pa/docs/CAAA_Brochure.pdf. [Accessed March 2017].

[3] Resodyn Acoustic Mixers, "I. Mixer Products & Services," [Online]. Available: http://www.resodynmixers.com/products/.

[4] Huntsman Advanced Materials Americas LLC, *Araldite GY 507 US Safety Data Sheet,* Huntsman Advanced Materials Americas LLC, 2014.

[5] Gabriel Phenoxies Inc., *Versamid 140 Safety Data Sheet,* Gabriel Phenoxies, Inc., 2016.

[6] Crane Army Ammunition Activity, "Crane Army Ammunition Activity Brochure," [Online]. Available: https://www.crane.army.mil/pa/docs/CAAA_Brochure.pdf. [Accessed September 2019].

[7] U.S. Environmental Protection Agency, "AP 42, Fifth Edition Compilation of Air Pollutant Emissions Factors, Volume 1: Stationary Point and Area Sources," U.S. Environmental Protection Agency, Research Triangle Park, NC, 1995.

[8] Global Security.org, "M485A2 - 155mm," [Online]. Available: https://www.globalsecurity.org/military/systems/munitions/m485.htm. [Accessed September 2019].

[9] U.S. Army Materiel Command, "Engineering Design Handbook - Military Pyrotechnics Series. Part One. Theory and Application," Alexandria, VA, 1967.

[10] J. A. Conkling, Chemistry of Pyrotechnics. Basic Principles and Theory, New York: CRC Press, 1985.

[11] H. Ellern, Military and Civilian Pyrotechnics, New York: Chemical Publishing Company, 1968.

[12] R. R. Nellums, B. C. Terry, B. C. Tappan, S. S. F. and L. J. Groven, "Effect of Solids Loading on Resonant Mixed Al-Bi2O3 Nanothermite Powders.," *Propell Explos Pyrot,* vol. 38, no. 5, pp. 605-610, 2013.

[13] S. L. Couguill, "Synthesis of Highly Loaded Gelled Propellants," Resodyn Corporation, Butte, MT, 2009.

[14] E. J. Miklaszewski, S. F. Son, G. L. J., J. Pret, A. P. Shaw and G. Chen, "Combustion Characteristics of Condensed Phase Reaction in Sub-Centimeter Geometries," in *38th International Pyrotechnics Seminar*, Denver, CO, 2012.

[15] E. J. Miklaszewski, J. C. Poret, A. P. Shaw, S. F. Son and L. J. Groven, "Ti/C-3Ni/Al as a Replacement Time Delay Composition," *Propellants, Explos., Pyrotech.,* vol. 39, pp. 138-147, 2013.

[16] E. J. Miklaszewski, A. P. Shaw, J. C. Poret, S. F. Son and L. J. Groven, "Performance and Aging of Mn/MnO2 as an Environmentally Friendly Energetic Time Delay Composition," *ACS Sustainable Chem. Eng.,* vol. 2, pp. 1312-1317, 2014.

[17] LA Container Inc., "LA Container Home Page," [Online]. Available: http://www.lacontainer.com/. [Accessed 2018].

[18] Miller-Stephenson Chemical Company, Inc., "Two-Part Epoxy Adhesive Kit," 2015.

[19] C. Peletski, *NAVSEAINST 8020.5C: Qualification and Final (TYPE) Qualification Procedures for Navy Explosives,* Arlington, VA, 2000.

[20] *MIL-STD-1751A: Department of Defense Test Method Standard, Safety and Performance Tests for the Qualification of Explosives (High Explosives,Propellants and Pyrotechnics),* 2001.

[21] Resodyn Corp., "PowerPoint Slides on Industrial Applications of Resonant Acoustic® Mixing," 5th Annual Technical Interchange, Butte, MT, 2015.

[22] Resodyn Corp., "PowerPoint Slides on RAM Process Scale-up of Mixing Pastes," 7th Annual Technical Interchange, Butte, MT, 2017.

[23] C. Campbell, "SERDP WP-1240: Twin Screw Extruder Production of MTTP Decoy Flares," ATK Thiokol, Inc., 2005.

APPENDIX A: LIST OF SCIENTIFIC/TECHNICAL PUBLICATIONS

Presentations:

Miklaszewski, E. J., Yamamoto, C. M., Shaw, A. P., Mullins, M. L., Dunham, J. T. (2017). *Safer Resonant Acoustic Manufacturing for High Volume Pyrotechnics (WP-2631)*. Poster at 2018 SERDP & ESTCP Symposium, Washington, DC.

Miklaszewski, E. J., Dunham, J. T., Yamamoto, C. Y., Shaw, A. P., Gilbert, R. A., Mullins, M. L., (2018). *Effect of Epoxy on Processing, Mechanical Properties and Performance of Pyrotechnic Compositions*. Poster at 2018 SERDP & ESTCP Symposium, Washington, DC.

Miklaszewski, E. J.; Yamamoto, C. Y.; Dunham, J. T.; Shaw, A. P.; Gilbert, R. A.; Poret, J. C., "Safer Resonant Acoustic Mixing Methods for High-Volume Production of Pyrotechnics", 43rd International Pyrotechnics (IPS) Symposium, Fort Collins, CO, July 8, 2018.

Miklaszewski, E. J. (2017). Overview of NSWC Crane RAM Projects and RAM5 Facility. 3rd RAM Operation and Safety Forum, Phoenix, AZ.

Miklaszewski, E. J., Dunham, J. T., Yamamoto, C. M., Shaw, A. P., Gilbert, R. A., Mullins, M. L., (2017). Effect of Epoxy on Processing, Mechanical Properties and Performance of Pyrotechnic Compositions. Poster at 2017 SERDP & ESTCP Symposium, Washington, DC.

Nelson, A. (2017). Resonant Acoustic Mixing (RAM) Focus Area US Summary. 43rd Meeting of TTCP WPN TP-4. Fort Walton Beach, FL.

Miklaszewski, E. J. (2017). Overview of NSWC Crane RAM Projects and Facilities. 2nd RAM Operation and Safety Forum, Picatinny Arsenal, NJ.

Miklaszewski, A. (2016). Overview of NSEC Crane RAM Projects and Facilities. 42nd Meeting of TTCP WPN TP-4. Porton Down, UK.

Conference Proceedings:

Miklaszewski, E. J., Dunham, J. T., Yamamoto, C. M., Shaw, A. P., Gilbert, R. A., Mullins, M. L., (2018). *Effect of Epoxy on Processing, Mechanical Properties and Performance of Pyrotechnic Compositions*. Poster at 2018 SERDP & ESTCP Symposium, Washington, DC.

Patents (application submitted, pending examination):

Yamamoto, C. M., Miklaszewski, E. J., Mullins, M. L., Shaw, A. P. (2018), THREE PART MIXING PROCESS FOR ENERGETIC MATERIALS AND EPOXY BINDER. US Patent 20190270683A1 (2019).

APPENDIX B: OTHER SUPPORTING MATERIALS

Other supporting materials:

1. Letter of support from CAAA
2. Patent application

Placeholder for letter of support from CAAA

To whom it may concern:

As a part of SERDP project WP-2631, on April 25, 2019 Crane Army Ammunition Activity (CAAA) participated in the demonstration of the resonant acoustic mixing (RAM) of illumination composition for use in the Mortar and Artillery-Fired Illumination Projectiles family of candles. The Magnesium/Sodium Nitrate/Epoxy pyrotechnic material was RAM mixed at NSWC Crane facilities and delivered to CAAA where approximately 16 lbs of pyrotechnic material was successfully pressed into 3 M485A2, 155mm Artillery-Fired Illumination Projectile candles. The material appeared homogeneous, with equal or better pot life, and pressed well using our production tooling. In comparison to the currently used mixed muller, the RAM mixer has several safety advantages and also mixes these types of compositions faster. These candles were functioned at the NSWC Crane lot acceptance testing facility and passed.

CAAA is interested in the technology and shared these results with our customer. However due to current high inventory levels of the various Mortar and Artillery-Fired Illumination Projectiles, the future production schedule of these items is uncertain. CAAA representatives will be traveling to Resodyn in September 2019 to gain more first-hand knowledge of this mixer technology and will continue to share with our customer.

Leslie Thompson

Leslie Thompson

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Manufacturing & Engineering Directorate

Crane Army Ammunition Activity

Placeholder for Patent Application

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(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2019/0270683 A1**

Yamamoto et al. (43) **Pub. Date: Sep. 5, 2019**

(54) **THREE PART MIXING PROCESS FOR ENERGETIC MATERIALS AND EPOXY BINDER**

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(21) Appl. No.: **16/290,200**

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Related U.S. Application Data

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Publication Classification

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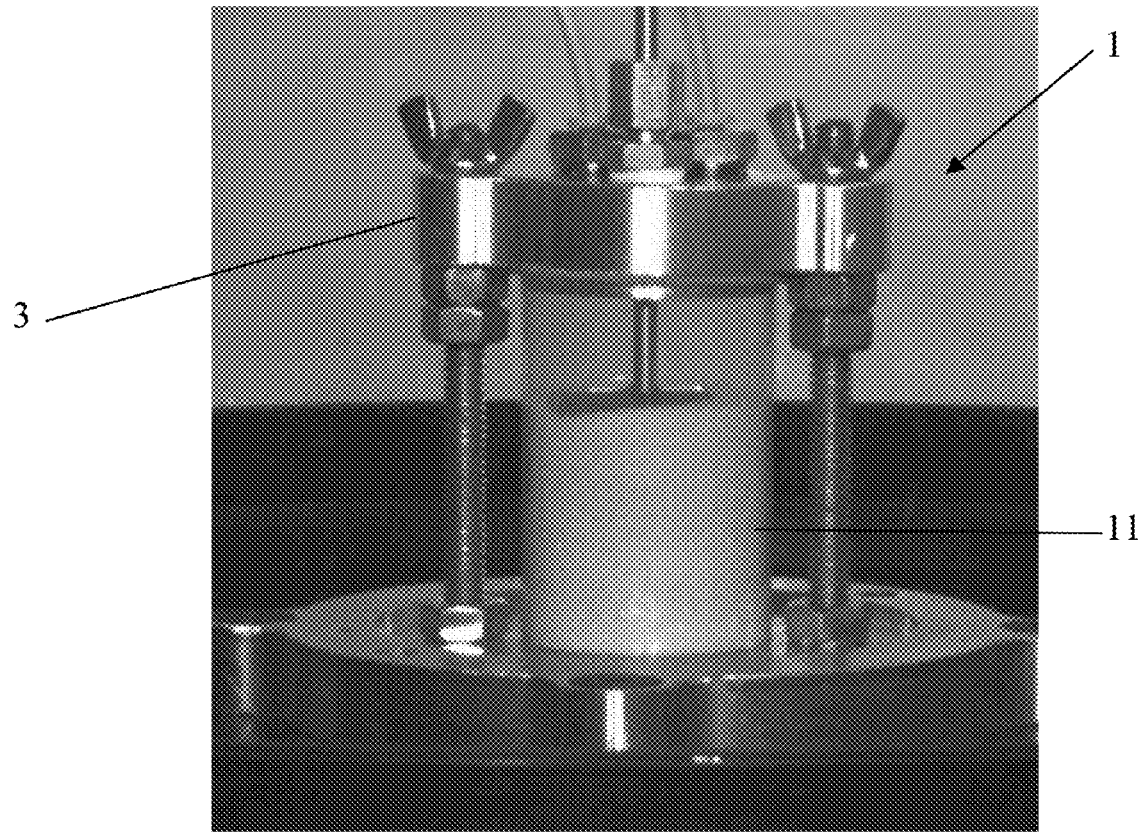
C06B 21/00 (2006.01)

(52) **U.S. Cl.**
CPC ***C06B 21/0008*** (2013.01)

(57) **ABSTRACT**

The present invention relates to methods of preparing pre-mixed compositions that can be combined to form pyrotechnic compositions. In exemplary embodiments, a binder ingredient is premixed with the pyrotechnic fuels and can also include other pyrotechnic additives and processing aides. Other binder ingredients can be premixed with the pyrotechnic oxidizers and can also include other pyrotechnic additives and processing aides. The resulting mixtures are not explosive and are therefore easier to store and much safer to handle. These pre-mixed mixtures can be stored in bulk until needed and rapidly combined to achieve final composition.



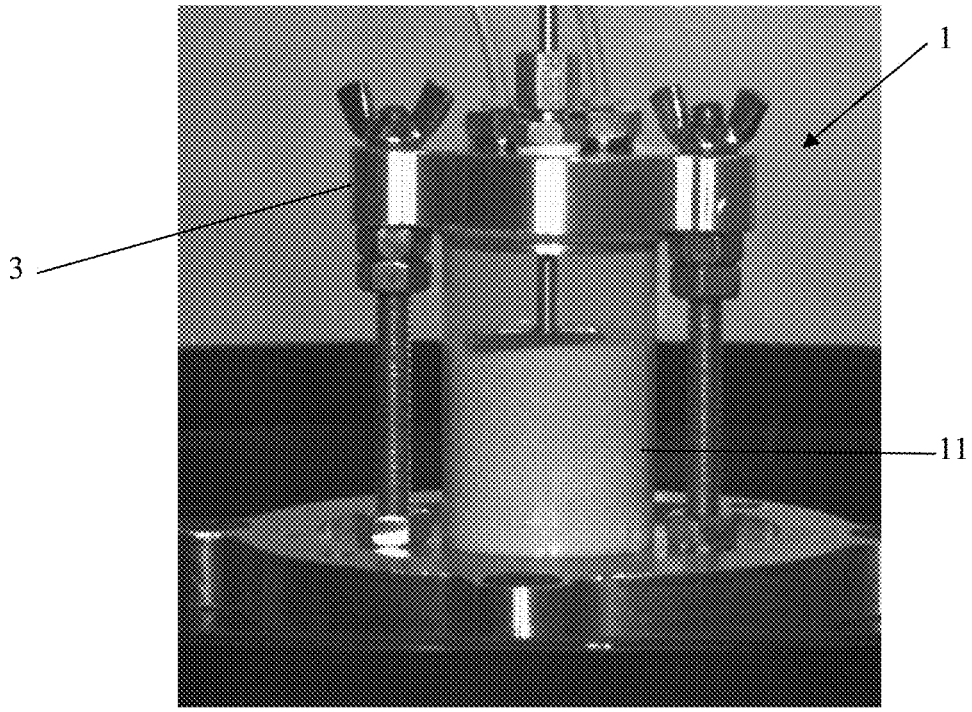


Fig. 1

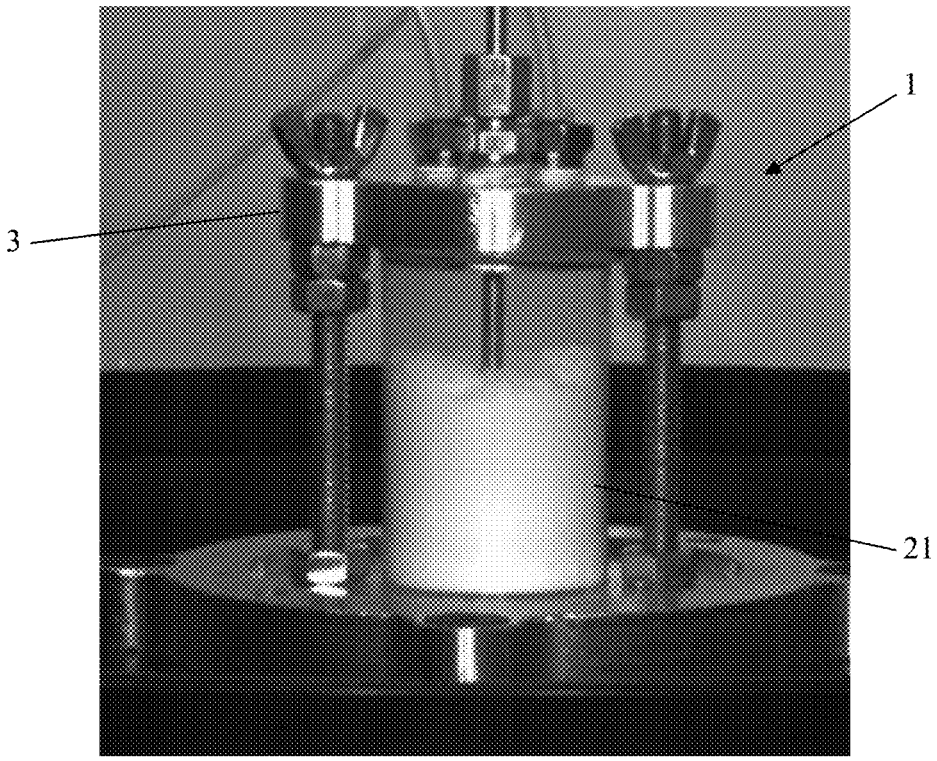


Fig. 2

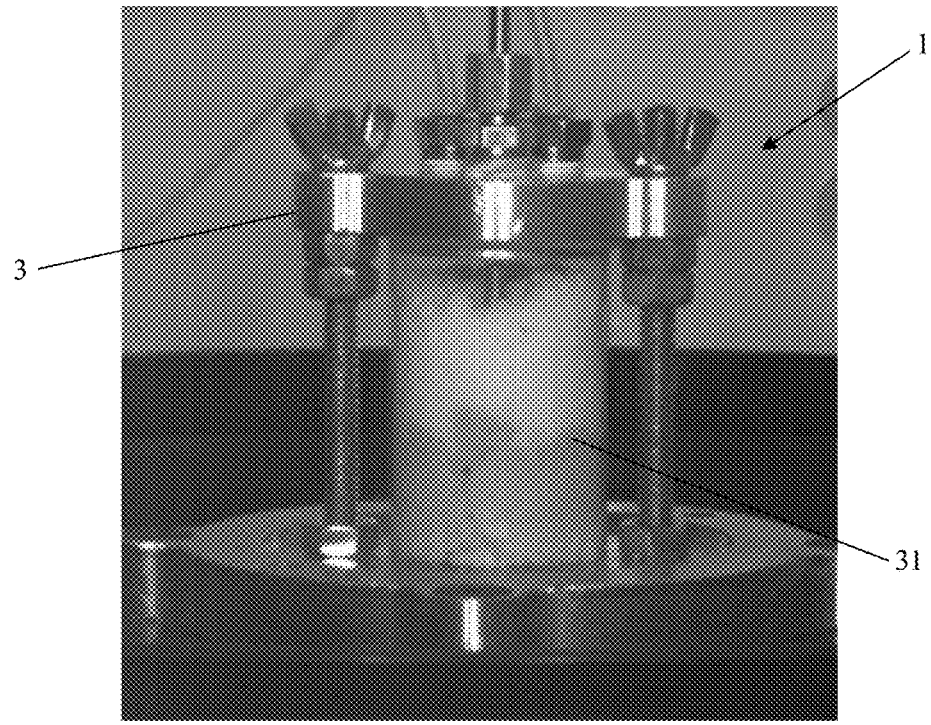


Fig. 3

THREE PART MIXING PROCESS FOR ENERGETIC MATERIALS AND EPOXY BINDER

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority to U.S. Provisional Patent Application Ser. No. 62/636,932, filed Mar. 1, 2018, entitled "THREE PART MIXING PROCESS FOR ENERGETIC MATERIALS AND EPOXY BINDER," the disclosure of which is expressly incorporated by reference herein.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] The invention described herein includes contributions by one or more employees of the Department of the Navy made in performance of official duties and may be manufactured, used and licensed by or for the United States Government for any governmental purpose without payment of any royalties thereon. This invention (Navy Case 200,433) is assigned to the United States Government and is available for licensing for commercial purposes. Licensing and technical inquiries may be directed to the Technology Transfer Office, Naval Surface Warfare Center Crane, email: Cran_CTO@navy.mil.

FIELD OF THE INVENTION

[0003] The present invention relates to a mixing process of a multi-part binder-based pyrotechnic composition using two pre-mixed compositions.

BACKGROUND AND SUMMARY OF THE INVENTION

[0004] The present invention relates to a mixing process of a multi-part binder-based pyrotechnic composition for safe pre-mixing and storage of less hazardous, partially processed multi-part binder based pyrotechnics.

[0005] Typically, a number of pyrotechnic ingredients (e.g., fuel, oxidizer, binder, additives) will be subsequently added to a mixing bowl until a homogeneous mixture is obtained. The binder is often composed of a resin and a curing agent and sometimes one or more modifying ingredients. In many pyrotechnic mixing processes, the binder ingredients are pre-blended and added to the mixer as a single component. In other cases, the binder ingredients can be added individually but often early in the process, to give the binder time to coat all of the other pyrotechnic ingredients or to coat the most sensitive material first. Most often, the binder is premixed and added to the fuel first to coat it and make it less sensitive then the other ingredients are added one at a time each being coated. If the energetic mix was blended beforehand without the binder, it could be hazardous and problematic to store. To this point, once the resin and curing agent portions of the binder come into contact, the overall process becomes time-limited because the cross-linking polymeric chemistry has a finite time before it cures and hardens. Furthermore, the curing process will ideally take place in the items form factor to provide mechanical strength to the end-item. Therefore, the mixed pyrotechnic composition has a limited "pot life" where all subsequent processing steps (e.g., granulation, extrusion, multi-step pressing) must be completed in a relatively short time frame; sometimes as short as a few hours. As such, if one does not process a batch of multi-part binder based pyrotechnic into its form factor within that timeframe, one may have to dispose of the remaining composition at significant cost or risk making suspect-quality end-items.

[0006] According to an illustrative embodiment of the present disclosure, mixing allows for safe pre-mixing and storage of less hazardous, partially processed multi-part binder based pyrotechnics. Two pre-mixtures can be combined on an as-needed basis and the final processing step can occur significantly faster than a conventional mixing process since the binder ingredients have already been dispersed in the previous pre-mixing steps. As such, when the two parts of the pre-mixed materials are combined, the final composition can be rapidly generated and post-processed on an as-needed basis.

[0007] According to a further illustrative embodiment of the present disclosure, one of the binder ingredients (e.g., resin or curing agent) is premixed with the pyrotechnic fuels and can also include other pyrotechnic additives and processing aides. The resulting mixtures are not explosive and are therefore easier to store and much safer to handle. The other binder ingredients (e.g., resin or curing agent) can be premixed with the pyrotechnic oxidizers and can also include other pyrotechnic additives and processing aides. The resulting mixtures are not explosive and are therefore easier to store and much safer to handle. These pre-mixed mixtures can be stored in bulk until needed and rapidly combined to achieve final composition.

[0008] Additional features and advantages of the present invention will become apparent to those skilled in the art upon consideration of the following detailed description of the illustrative embodiment exemplifying the best mode of carrying out the invention as presently perceived.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The detailed description of the drawings particularly refers to the accompanying figures in which:

[0010] FIG. **1** shows an exemplary apparatus for creating an exemplary first pre-mixed composition.

[0011] FIG. **2** shows an exemplary apparatus for creating an exemplary second pre-mixed composition.

[0012] FIG. **3** shows an exemplary apparatus for creating a pyrotechnic composition by combining a first and second pre-mixed composition.

DETAILED DESCRIPTION OF THE DRAWINGS

[0013] The embodiments of the invention described herein are not intended to be exhaustive or to limit the invention to precise forms disclosed. Rather, the embodiments selected for description have been chosen to enable one skilled in the art to practice the invention.

[0014] FIG. **1** shows an exemplary apparatus **1** for creating an exemplary first pre-mixed composition **11**. Fuel (e.g., magnesium, aluminum, sucrose) can added to a first container, then a binder curing agent (e.g., Versamid 140) and an optional process aide (e.g., acetone) can be added into a second container and mixed thoroughly until the binder curing agent is dissolved to create a first mixture, then the first mixture can be poured on top of the fuel and placed in a mixer **3** (e.g., a mix-muller mixer, a Resonant Acoustic Mixer (RAM), etc.). In at least some embodiments, processing aides can be preferred when the combination of fuel and

curing agents do not mix well. A processing aide (e.g., acetone, polyethylene glycol) can prevent clumping and help mix the fuel and curing agents evenly, and can be beneficial for certain types of mixers (e.g., RAM). Highly viscous binder curing agents (e.g., Versamid 140) mix better with metallic, higher density, low hydroscosity materials, and high surface area, so highly viscous binder curing agents are well suited to be mixed with metallic fuels (e.g, magnesium, aluminum, copper, etc.). The first mixture and fuel can be mixed for various durations (e.g., 2 minutes) and mixing speeds (e.g., 65 G of acceleration), and, in at least some embodiments, under a vacuum setting (e.g., 22 inches of vacuum) dependent on mixing location (e.g., elevation). The resulting mixture is a first pre-mixed composition which can be safely stored for longer than the shelf life of a pyrotechnic composition.

[0015] FIG. **2** shows an exemplary apparatus **1** for creating an exemplary second pre-mixed composition **21**. An oxidizer (e.g., sodium nitrate, iron oxide, potassium chlorate, etc.) can be added to a third container, a binder resin (e.g., Araldite 507) can be added on top, and then a processing aide (e.g., acetone, polyethylene glycol) can added on top to create a second mixture. The second mixture can be placed in a mixer **3** and can be mixed for various durations (e.g., 1 minute) and mixing speeds (e.g., at 95 G's of acceleration, then reduced to 65 G of acceleration), and, in at least some embodiments, under a vacuum setting (e.g., 22 inches of vacuum). The resulting mixture is a second pre-mixed composition **21** which can be safely stored for longer than the shelf life of a pyrotechnic composition. Other additives (e.g, asphaltum, carbon black, etc.) can be added to the second mixture.

[0016] In at least some embodiments, different combinations of fuel, oxidizer, binder curing agent, and binder resin can be used. The fuel and oxidizer should always be kept in separate pre-mixed compositions. Binder curing agents and binder resins should be kept in separate pre-mixed compositions to prevent premature hardening of the compositions. Additives generally have a tendency to act as either a fuel or an oxidizer, and it is preferred to add additives to the mixture matching their tendencies (e.g., oxidizer additives added to the oxidizer) to minimize potential for energetic reactions. For example, graphite tends to act as a fuel, and can be included as an additive in the first pre-mixed composition. By keeping fuel and oxidizer separate as well as curing agent and resin separate, there are two primary permutations of pre-mixed compositions: (1) fuel+curing agent and oxidizer+resin; and (2) fuel+resin and oxidizer+curing agent. Viscous curing agents (e.g., Versamid 140) can be effectively mixed with coarse oxidizers.

[0017] The proportion of fuel to oxidizer will be set based on the desired pyrotechnic composition. The amount of binder ingredients required will be based on the selected fuel and oxidizer. Exemplary methods can use predetermined proportions of each ingredient typically used to prepare selected pyrotechnic combinations without varying the amount of binder required to evenly mix with other ingredients (e.g., fuel, oxidizer). By coating the fuel with binder ingredients, the fuel becomes far less likely to oxidize during storage, even when exposed to air. As such, a pre-mixed composition including fuel can be stored for long periods of time without needing to vacuum seal the pre-mixed composition. Mixing compatibility between binder ingredients and either fuel or oxidizer will depend on the type of mixer selected. For example, RAM mixers are more likely to cause clumping when adding a viscous curing agent to a fuel, whereas mix-muller mixers will be comparatively easier.

[0018] FIG. **3** shows an exemplary apparatus **1** for creating a pyrotechnic composition **31** by combining a first and second pre-mixed composition. In most pyrotechnic compositions, the ratio of first to second pre-mixed composition can be very important. To ensure that the proper amounts of pre-mixed compositions are added, any processing aides used in either composition can be evaporated from the compositions prior to storing the compositions or before mixing the compositions together. In some embodiments, if the amount of processing aide (e.g., percent by weight) is known in both pre-mixed compositions, then the compositions can be mixed without removing (e.g., evaporating) the processing aide. The first and second pre-mixed compositions can then be combined and mixed with mixer **3** to create a pyrotechnic composition.

[0019] This method can be utilized using a variety of mixers such as bowl, mix-muller, twin-screw extrusion or resonant acoustic mixing. The concept of separate mixing and holding can potentially be used for many different applications, the illumination flare just happened to be the flare of choice however, this method is adaptable to colored flares, IR flares, and any other pyrotechnic with a multi-part binder system.

[0020] Although the invention has been described in detail with reference to certain preferred embodiments, variations and modifications exist within the spirit and scope of the invention as described and defined in the following claims.

1. A method of preparing pyrotechnic compositions.

2. A method of preparing pre-mixed compositions.

3. A method of selecting pre-mixed composition ingredients.

4. A method of preparing pyrotechnic compositions comprising:

selecting first and second pre-mixed composition ingredients comprising:

selecting a desired pyrotechnic composition;

identifying component ingredients of the pyrotechnic composition including at least one fuel, at least one oxidizer, at least one binder curing agent, and at least one binder resin;

mixing a first ingredient combination comprising the least one fuel and the at least one binder curing agent;

mixing a second ingredient combination comprising the least one oxidizer and the at least one binder resin, wherein the first and second ingredient combinations form a first combination pair;

mixing a third ingredient combination comprising the least one fuel and the at least one binder resin;

mixing a fourth ingredient combination comprising the least one oxidizer and the at least one binder curing agent, wherein the third and fourth ingredient combinations form a second combination pair;

determining a least difficult mixing combination between the first and second combination pairs;

selecting the first and second pre-mixed composition ingredients comprising the least difficult mixing combination;

preparing the first and second pre-mixed compositions comprising:

preparing the first pre-mixed composition comprising mixing the first pre-mixed composition ingredients at a first predetermined mixing setting;

preparing the second pre-mixed composition comprising mixing the second pre-mixed composition ingredients at a second predetermined mixing setting;

preparing pyrotechnic compositions comprising:

mixing the first and second pre-mixed compositions at a third predetermined mixing setting.

* * * * *