EXECUTIVE SUMMARY

Safer Resonant Acoustic Manufacturing for High Volume Pyrotechnics

SERDP Project WP-2631

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ACRONYMS AND ABBREVIATIONS

$	United States Dollar
°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
cP	Centipoise
ESD	Electro-static discharge
J	Joules
kg	Kilograms
L	Liter
lbs.	Pounds
Mg	Magnesium
mj	Milljoules
$NaNO_3$	Sodium Nitrate
NSWC	Crane Naval Surface Warfare Center, Crane Division
RAM	Resonant acoustic mixing
RDECOM	U.S. Army's Research, Development, and Engineering Command
s	seconds
SERDP	Strategic Environmental Research and Development Program
wt. %	Weight percent

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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 the Armaments Center.

1.0 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**) (Hardt, 2001). 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 of 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 and occupational health risks as well as significant toxic solvent waste streams.

Figure 1. Illumination Candles

Illumination candles enhance the warfighter's capability to operate at night (CAAA Brochure 2017).

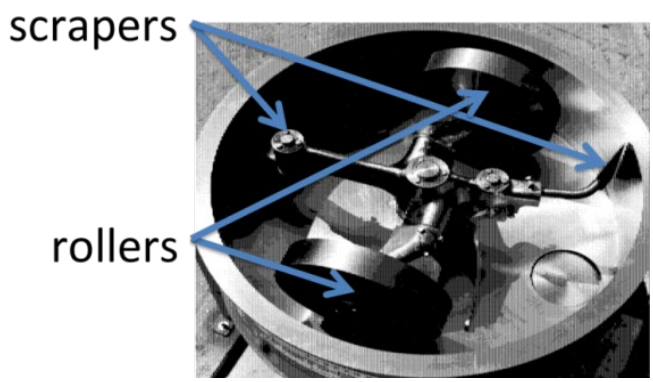

Figure 2. Example of a Mix-Muller Mixer

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. 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 (Resodyn Acoustic Mixers, 2020). 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 Different Batch Sizes

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)

(Resodyn Acoustic Mixers, 2020).

2.0 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 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 from cleaning large mixing hardware.

3.0 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 two 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 the Naval Surface Warfare Center, Crane Division (NSWC Crane). This pilot-scale manufacturing demonstration will be examined with the advisement of CAAA which is the sole U.S. 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.

4.0 RESULTS AND DISCUSSION

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). (Huntsman Advanced Materials Americas LLC, 2014; Gabriel Phenoxies Inc., 2016).

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 one-step, two-step, and three-step process, each with their own mix routine, order of addition, and pros/cons from a technical perspective. The development of these processes also utilizes 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 three-step RAM process 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.

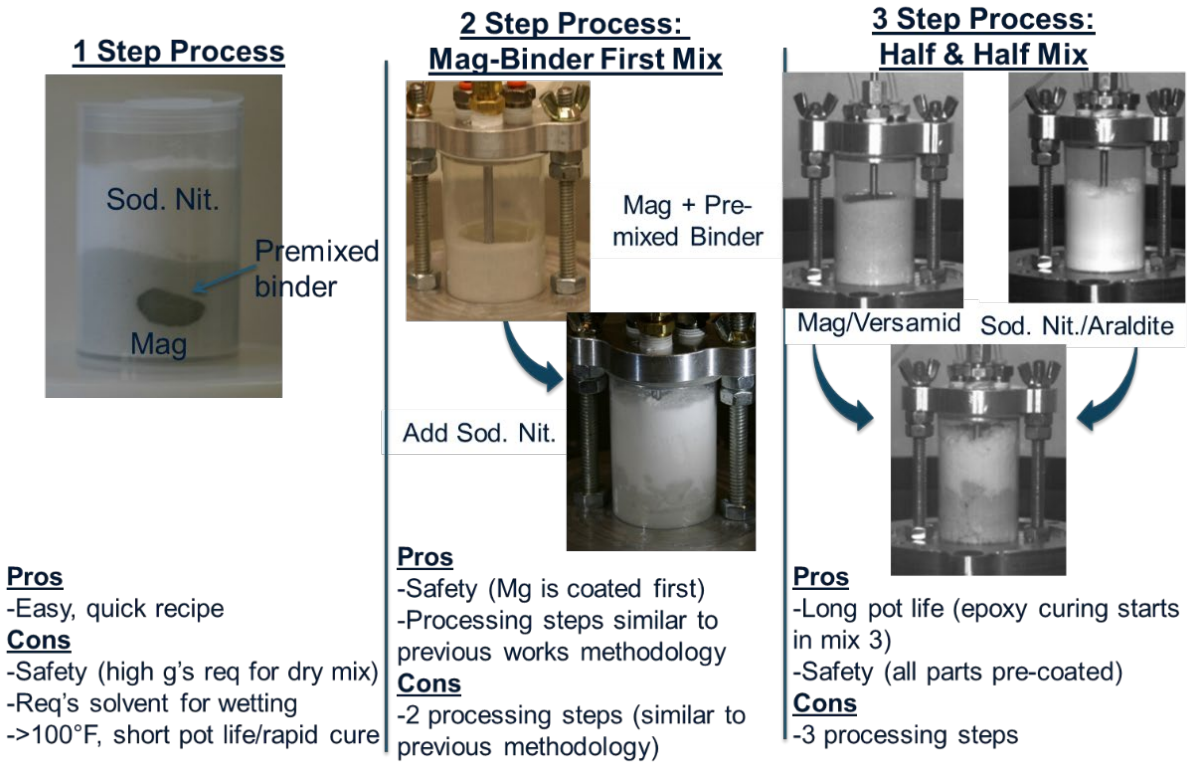

Figure 4. Overview of Successful Resonant Mixing Methodologies for Epoxy-Based Pyrotechnics

Table 1 shows the impact sensitivity of illumination composition prepared on a Resodyn via the previously described one-step, two-step, and three-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 the 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.

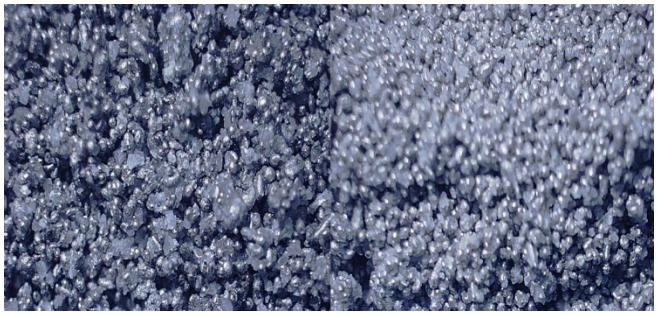

Figure 5. Microscopic Images of the Baseline Illumination Composition

These images were 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 produce 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.

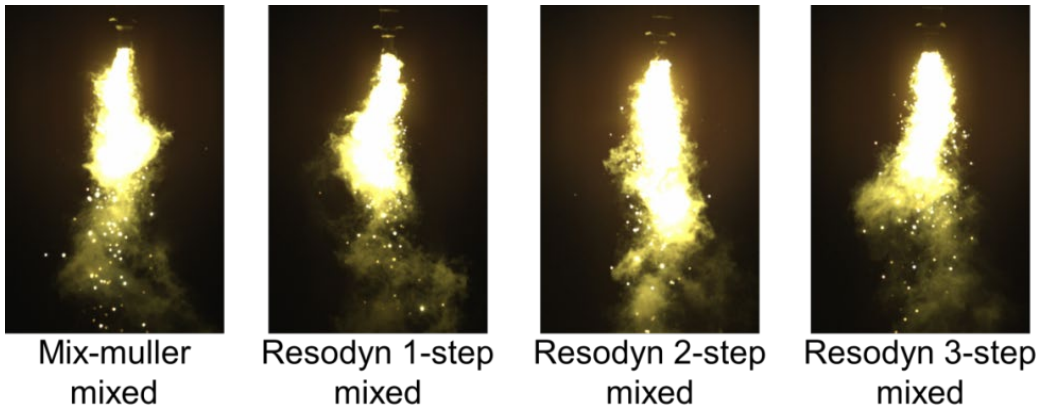

Figure 6. Images of Performance Testing of the Baseline Illumination Compositions

These images were produced by various mixing methods.

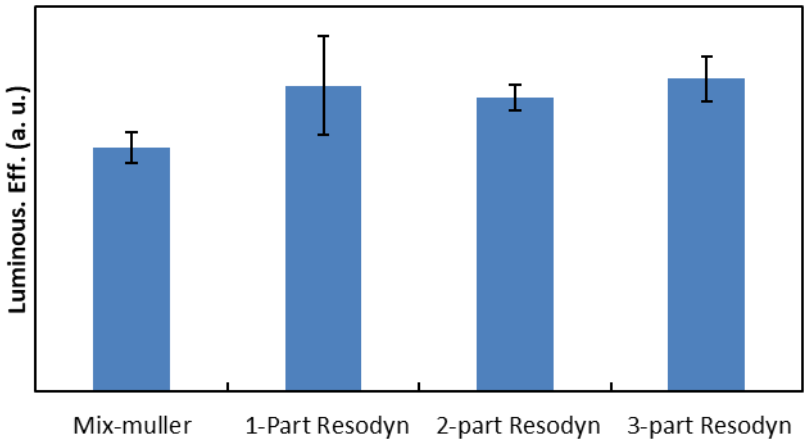

Figure 7. Relative Luminous Efficiency of the Baseline Illumination Compositions Produced by Various Mixing Methods

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 the warfighter's capability to operate at night and compliment the capabilities of night vision equipment (CAAA Brochure 2017). 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 (EPA, 1995).

Figure 8. M485A2 Projectile and Illumination Candle

Projectile on left and Illumination Candle on right. (Global Security.org, 2020)

In preparation for consolidation into the M485A2 155-mm Illumination Round hardware, nine one-kg batches of illumination composition was prepared using the two-step RAM process, as previously described (*see* full report for additional details). Two CAAA engineers that 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, the RAM composition was 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 one and a half hours; five 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 nine 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

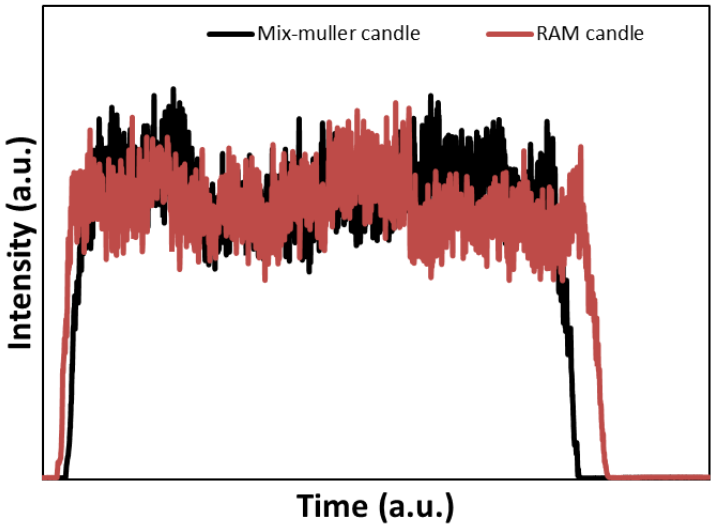

Figure 11. Comparison of Arbitrary Intensity Plot for Mix-Muller and RAM Candles

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, one to two 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 an 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 eight 125 lb. batches. A RAM 5/RAM55 could produce similar amounts of composition in five and one and a half 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.

4.4 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 $Mg/NaNO_3$/Epoxy illumination compositions. These methodologies include a one-step, two-step, and three-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 three-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 (two-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%.

5.0 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.

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