# Perchlorate Free Pyrotechnic Composition and its Application in M115A2 Ground Burst Simulator and M116A1 Hand Grenade Simulator

**Gary Chen, Mark Motyka, James Wejsa**
**U.S. Army RDECOM-ARDEC, Picatinny Arsenal, NJ 07806, USA**

## ABSTRACT

A family of perchlorate-free pyrotechnic compositions for military flash-bang training rounds and non-lethal munitions have been developed and proven out. The fuel and oxidizer pre-blends of the compositions are separately prepared and loaded into the item, completely eliminating the need for dangerous manual operations. This initiative is part of DoD efforts to mitigate the potential risk to the military readiness associated with the recent EPA regulation on restricted use of perchlorate. Excessive use of perchlorate in military munitions has led to ground and surface water contamination. Perchlorate contamination in drinking water is linked to the blocking of iodide from entering the thyroid gland, and thereby interfering with production of thyroid hormone. The current fielded M115A2 Ground Burst Simulators and M116A1 Hand Grenade Simulators account for the majority of potassium perchlorate used by US Army and thus were selected as the perchlorate-free technology demonstration platform.

## INTRODUCTION

The Federal Environmental Protection Agency (EPA) has identified the perchlorate anion ($ClO_4^-$) as a ground and surface water contaminant due to its high solubility, persistence, and potential effects on human health. Perchlorate exposure has the potential of interfering with iodide absorption by the thyroid gland. A preliminary estimate of the current DOD ordnance inventory indicates that over 250 different munitions types contain perchlorates. These ordnances utilize ammonium perchlorate (AP) in rocket and missile propellants and potassium perchlorate (KP) in pyrotechnic simulator, delay, incendiary, illumination, gas generation, and tracer compositions. High levels of perchlorates were recently found in the ground water of the Aberdeen Proving Ground (APG)/FTX Ordnance Center and School. Perchlorates were also detected in some drinking water systems around the country. The excessive pechlotate levels at Aberdeen were mainly attributed to the potassium perchlotate used in the flash charge of M115A2 Ground Burst Simulators and the M116A1 Hand Grenade Simulators. In February 2005, the EPA followed the NRC (National Research Council) recommendation and established an official reference dose (Drinking Water Equivalent Level) of 24.5 ppb, a daily human exposure level that is not expected to cause adverse health effects. As part of DoD efforts to mitigate the excessive use of perchlorate in munitions systems, the ARDEC Pyrotechnic Research and Technology Branch initiated a product improvement program in 2004 to develop and prove-out a perchlorate-free flash bang composition for use in M115A2 and M116A1 simulators.

## FORMULATION DEVELOPMENT

### Identification of Potential Fuel/Oxidizer Systems

Various organic and metallic fuels as well as nitrate-base oxidizers were identified as potential ingredients for perchlorate-free formulations. The toxic or halogen-containing oxidizers (barium nitrate, Teflon, etc.) were not considered due to environmental issues. The NASA Glenn Research Center Chemical Equilibrium with Applications (CEA) Computational Program was initially used to calculate the flame temperature, gas/liquid fractions and fuel/oxidizer ratio of each formulation candidate. The results suggest that aluminum / nitrate and magnesium / nitrate systems would provide the highest visual brightness based on the calculated flame temperatures. Concerns with powdered magnesium's history of hydrogen out-gassing in the presence of moisture and high unit cost led to the selection of the aluminum fuel system as the best perchlorate-free candidate to go-forward.

The selection of the type of nitrate for the oxidizer system was mainly based on the level of hygroscopicity of each material under various environments. Vulnerability to moisture is considered detrimental to the long term storage stability of most pyrotechnic compositions. Hygroscopicity tests were conducted on dried samples of potassium nitrate, sodium nitrate, and strontium nitrate at both 75% and 90% relative humidity under ambient temperature. The moisture absorption data, collected over 2000 hours, for these nitrates in reference to potassium perchlorate were plotted in Figures 1 and 2. As shown, the potassium nitrate had the greatest moisture resistance under both conditions followed by strontium nitrate. In contrast, sodium nitrate absorbed a significantly higher percent of moisture at both humidity levels and thus was not considered for further study.

**Fuel Level and Type**

A 50-cc closed bomb was used to generate the combustion product's pressure-time correlations for each potential formulation in order to predict ballistic behavior. Initial studies focused on the peak pressure, rise time and ignitibility of aluminum / potassium nitrate (Al/KN) and aluminum / strontium nitrate (Al/SrN) compositions at various fuel/oxidizer ratios. In this effort, each sample composition was prepared with 9 micron X-65 spherical aluminum powder, 9-10 micron nitrate, 5% sulfur and 1% boric acid. A small amount of sulfur was added to facilitate ignition and increase quickness. The boric acid was used as a neutralizer to enhance the storage stability of the mix. The results show that the aluminum fuel level at 40% yielded the best performance in quickness and peak pressure for both oxidizer systems.

Various types of aluminum powder were also tested in the closed bomb to investigate their impact on the ballistic behavior of sample compositions. The evaluated candidates include spherical (X-65, X-80), flake (German Balckhead), and conventional (atomized 101Al) aluminum powders. For Al/KN system the study focused on the medium particle size oxidizer with an average of 34 microns because the fine oxidizer yielded a very low fill density of below 0.6 g/cc. For Al/SrN system, both the fine and medium size oxidizers are considered usable due to strontium nitrate's high theoretical density as demonstrated in the following samples:

| **Formulation** | **Non-vibrated Fill Density, g/cc** |
|---|---|
| 604 - Al 25µm / KN 34µm | 0.81 |
| 605 - Al 25µm / KN 9µm | 0.53 |
| 609 - Al 8µm / KN 9µm | 0.58 |
| 603 - Al 25µm / SrN 49µm | 0.96 |
| 606 - Al 25µm / SrN 10µm | 0.70 |
| 610 - Al 8µm / SrN 10µm | 0.77 |

Among the various types of powdered aluminum, it was found that the formulations 604 (Al/KN system) and 603 (Al/SrN) system performed the best. Both were formulated with 40% of 25 micron flake aluminum, 5% sulfur and 1% boric acid. The standout ballistic performance for 603/604 formulations is attributed to the flake aluminum's high surface area of approx. 9 $m^2/g$, comparing to approx.0.7 $m^2/g$ for 65X spherical aluminum. The atomized aluminum, 101Al (26 microns), also performed poorly due to low surface area.

**Sulfur Level**

Sulfur is a secondary fuel and also an excellent ignition facilitator due to its low melting point. The amount of sulfur used in the formulations will also impact the ballistic performance, which is closely related to the

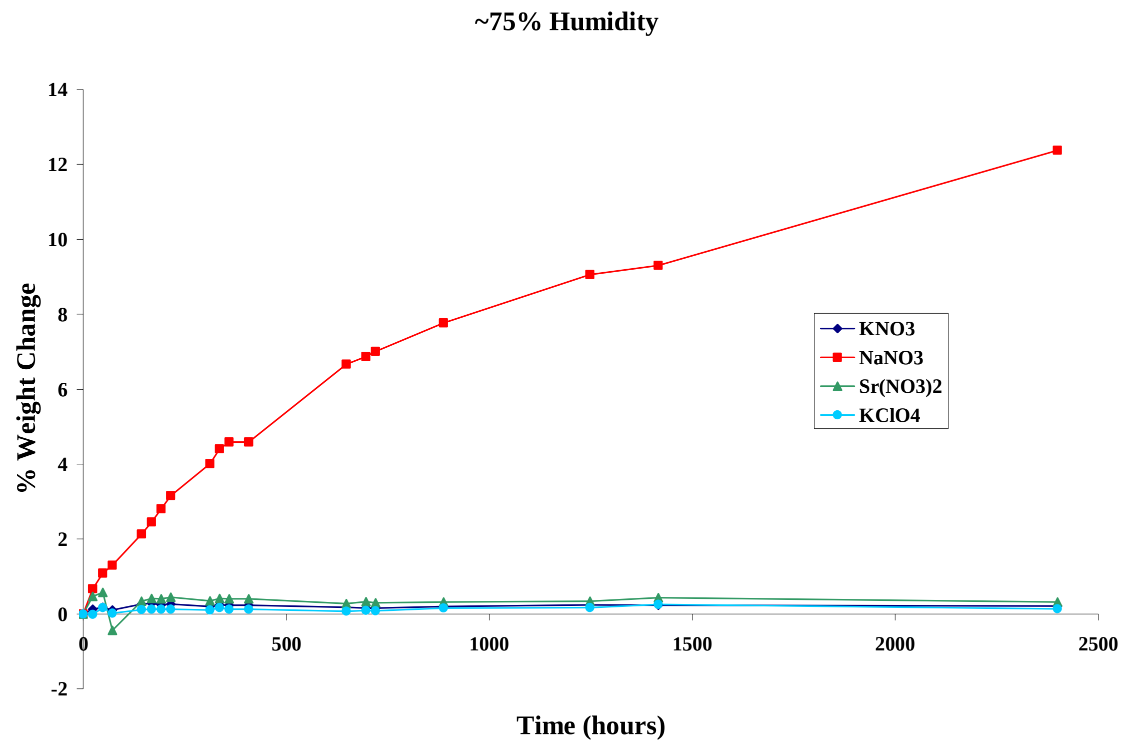


**Figure 1: Moisture absorption for oxidizers at 75% relative humidity**

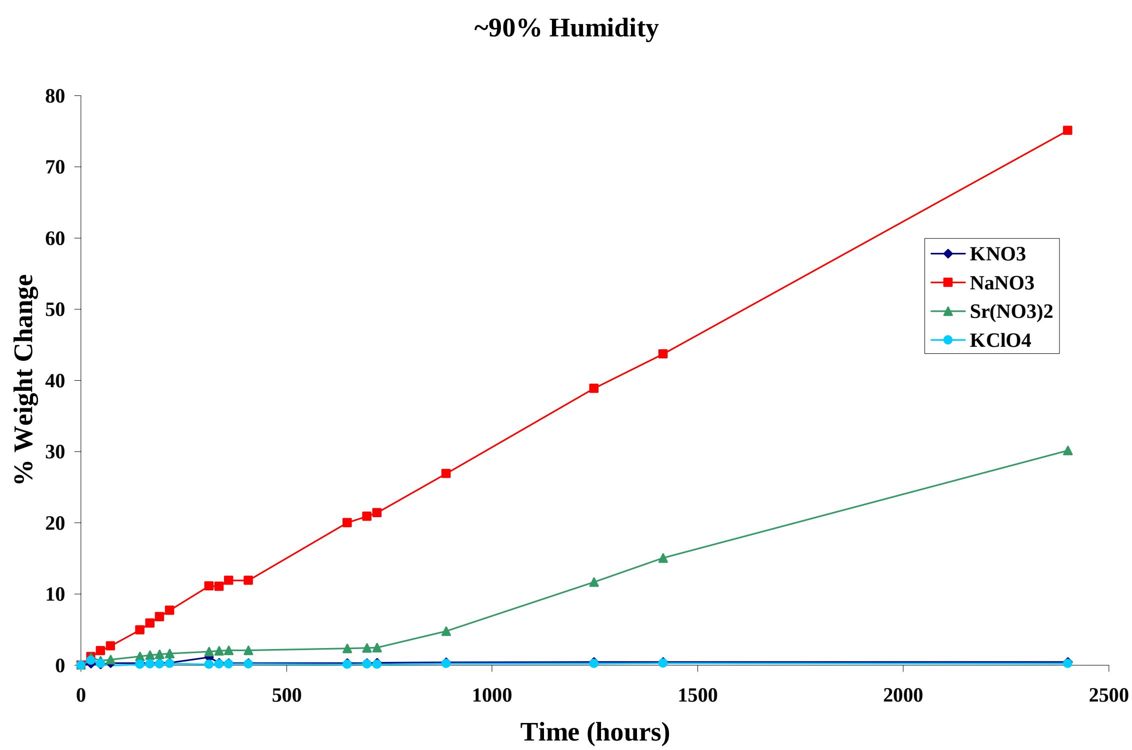


**Figure 2: Moisture absorption for oxidizers at 90% relative humidity**

system's sound intensity and photometric output. Previous closed bomb testing indicates that Al-KN system without sulfur had ignition and low peak pressure problems. As a result, the optimal sulfur level was investigated for the Al/KN and Al/SrN systems using the 34 micron nitrate. Closed bomb data show that the formulations utilizing 5% to 10% sulfur burned smoothly with a quick rise time.

A separate study was setup as a prototype platform to determine the optimal sulfur level for the Al/KN system with regard to sound level and photometric output. 13 grams of mix was loaded into 20-gage shotgun cartridges and initiated with a percussion primer. Results showed that the best sound level and photometric output was achieved when using mixes with a sulfur content of 5-15%. For this study the fuel level was set at 50% with atomized 101Al aluminum.

### Variation of Flash Charge Weight

Study was conducted with a 50 CC closed bomb to determine the sample sizes of Al/KN and Al/SrN compositions that would generate an equivalent pressure to 0.5 grams of the current M115A2 / M116A1 flash charge (aluminum / potassium perchlorate) designated as 473B (standard). Results showed that 0.75 to 0.875 grams of 604 composition is required to achieve an equivalent level. The 603 composition yielded somewhat lower peak pressure than the 604 composition at equivalent sample weights. This suggested that the 603 requires a higher sample amount in order to provide a similar peak pressure as 473B. Figure 3 contains the closed bomb pressure-time traces for Al/KN and Al/SrN systems in reference to the standard.

### Anti-caking and Processing Agent

Pyrotechnic dry mixes have a tendency of caking during loading, assembly and storage, especially in high humidity conditions. The mixes were also prone to adhere to the walls of processing equipment. To prevent this problem an anti-caking and processing aid, Cab-O-Sil (Grade M5), was selected for use in the composition 604. Two levels of M5 (0.25% and 0.5%) were used in a closed bomb study for comparison with the baseline 604 composition without any anti-caking agent. It was found that M5 not only reduced the dry mixing time but also increased the peak pressure of the 604 composition by 20% and 25% respectively for 0.25% and 0.5% Cab-O-Sil. The pressure traces of these tests can be seen in Figure 4.

## MANUFACTURING PROCESS DEVELOPMENT

### Full Up Hardware Assembly

All parts on the M115A2 and M116A1 were glued together using an epoxy of EPON 828 and Epikure 3125 in a 2:1 ratio respectively. For M115A2 the pre-assembled whistle tube, composition and quick match were epoxied into the top sleeve. Next, the inner tube that holds the flash-bang charge was epoxied into the top sleeve. This preassembly was then placed into a 140°F oven for at least one hour to accelerate the epoxy curing. The charge mix was loaded after the epoxy had fully cured and the end cap and bottom sleeve were epoxied in place. The final assembly was placed back into the oven to complete curing. The safety match and igniter came preassembled and glued to the top disk for the M116A1. The ignition assembly and inner tube were epoxied into the top sleeve and the bottom disk was epoxied into the bottom sleeve. The ends of the M116A1 round were filled with epoxy to strengthen them. The two halves of the M116A1 were then placed into the oven to shorten the curing time. Once the epoxy had fully cured the charge mix was loaded into the top half of the round and the bottom half was epoxied on. The final assembly was then placed back into the oven.

### Two Part Loading and In-Round Mixing

The ability to mix the developed perchlorate-free formulations in round at the selected charge weight was studied. A two part loading and mixing method was used. The first part consists of the blended primary fuel aluminum powder and secondary fuel sulfur.

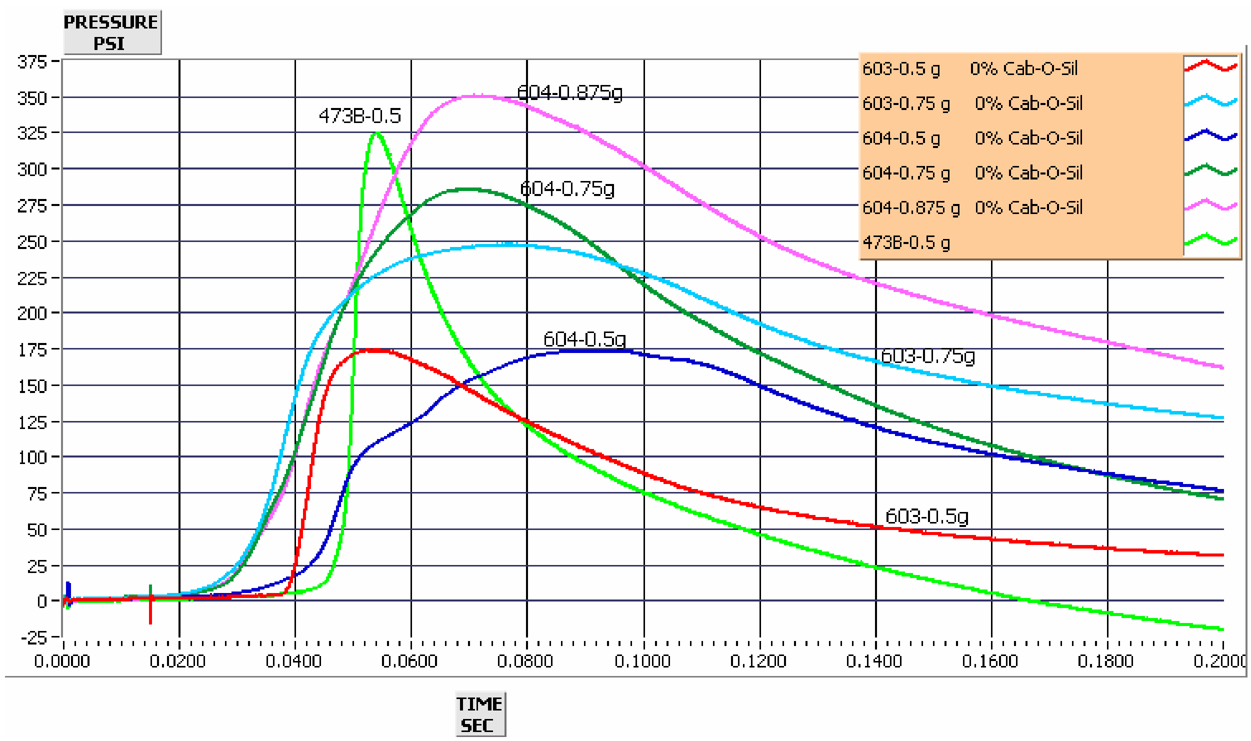


**Figure 3: Pressure profiles of Al/KN and Al/SrN systems at various charge weights**

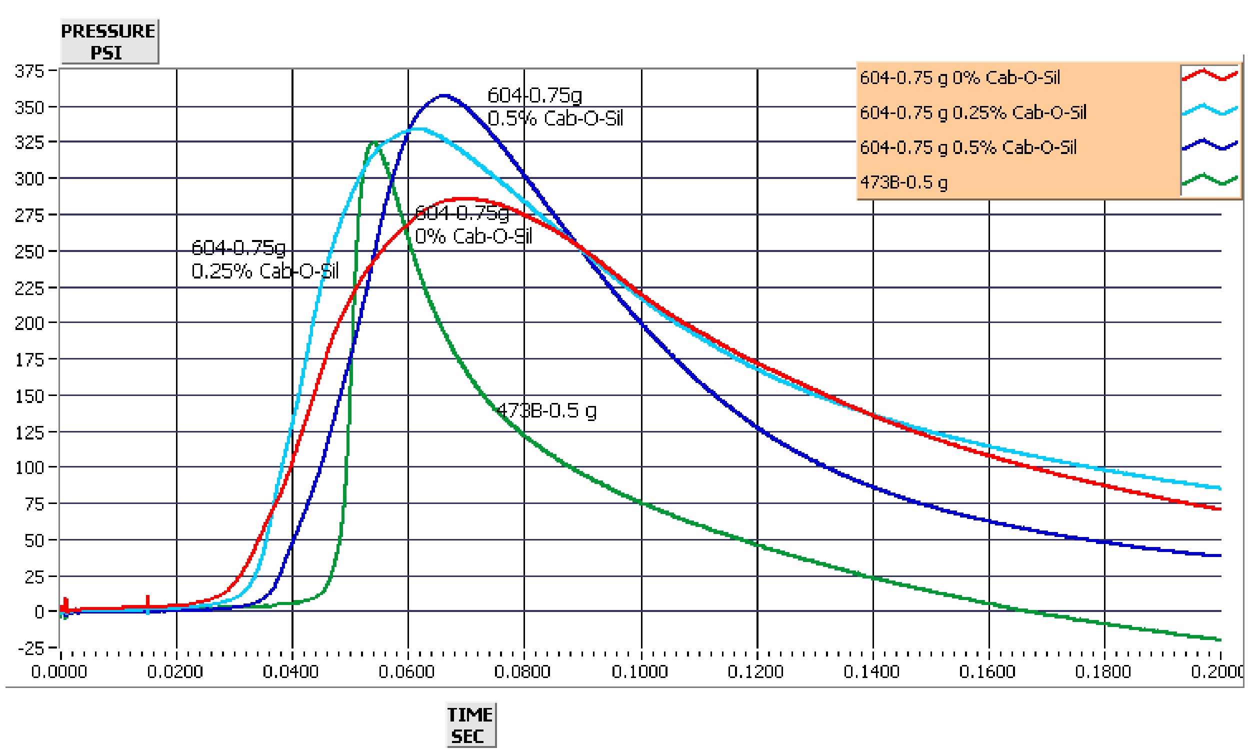


**Figure 4: Pressure profiles of Al/KN system showing the effect of Cab-O-Sil**

The second part consists of nitrate oxidizer, Cab-O-Sil (M5), and boric acid. The oxidizer was pre-dried and screened before blending with Cab-O-Sil and boric acid. The fuel pre-blend was loaded into the charge container first followed by the oxidizer pre-blend on the top. The round was fully assembled, sealed, and mixed for an hour.

To assist the observation of mixing progress, two sizes of clear polycarbonate tubes were made that have the same length and inner diameter as the inner tubes of the M115A2 and M116A1. The powders were loaded into the round and the ends were taped over. The full rounds were placed in foam holders. These holders kept the rounds at a ~30$^{o}$ angle while tumbling. Figure 5 is an example of the clear tube model. Figure 6 shows the mixing device with eight rounds loaded.

**Figure 5: Clear polycarbonate tube model for mixing study**

**Figure 6: Tumbling machine**

Table 1 on the following page shows the various 604-based configurations (4 each for the M115A2 and M116A1) that were tested in the mixing study as well as the observations made.

The rounds were tumbled for 15 minutes then the machine was stopped to check the condition of the mixing. After the first 15 minutes of mixing, the formulations with Cab-O-Sil appeared to be visually well mixed where as separation could still be observed in the other two mixes. The rounds were placed back in the machine and tumbled for another 45 minutes. After mixing for a full hour, seven of the eight rounds appeared to be visually well mixed. Non-mixed powder could still be seen in the M115 round with 70 grams of 604 without Cab-O-Sil. Results were photographed in Figures 7-14.

## FULL -UP SYSTEM PROVE OUT

### Formulation Definition

Two candidate formulations 603 and 604 defined below were selected for M115A2/M116A1 full-up system prove-out. The particle sizes are at 50% point using a laser diffraction instrument. The aluminum powder is a German Blackhead version.

| | wt % |
|---|---|
| Aluminum<br>Mil-A-512 Type 1, Grade B | 40.0 |
| Oxidizer<br>Strontium Nitrate<br>Mil-S- 20322B, Grade A<br>-or-<br>Potassium Nitrate<br>Mil-P156B, Class 3 | 53.5 |
| Sulfur<br>Mil-S-487, Grade C | 5.0 |
| Boric Acid<br>Commercial Grade | 1.0 |
| Cab-O-Sil<br>M5 Grade | 0.5 |

**Table 1: Mixing study matrix and observations**

| Number | Contents | Observations | |
|---|---|---|---|
| | | 15 minutes | 60 minutes |
| 1 | 70 gm 604 | Not well mixed | Some white still visible |
| 2 | 50 gm 604 | Some white still visible | Visually well mixed |
| 3 | 70 gm 604 w/ 0.25% Cab-O-Sil | Visually well mixed | Visually well mixed |
| 4 | 70 gm 604 w/ 0.5% Cab-O-Sil | Visually well mixed | Visually well mixed |
| 5 | 33 gm 604 | Not well mixed | Visually well mixed |
| 6 | 25 gm 604 | Not well mixed | Visually well mixed |
| 7 | 33 gm 604 w/ 0.25% Cab-O-Sil | Visually well mixed | Visually well mixed |
| 8 | 33 gm 604 w/ 0.5% Cab-O-Sil | Visually well mixed | Visually well mixed |

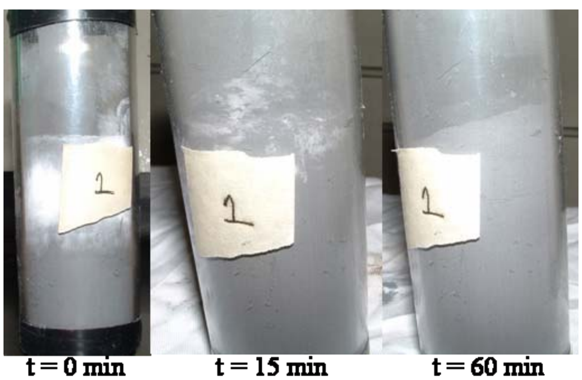

**Figure 7: M115A2 70g 604**

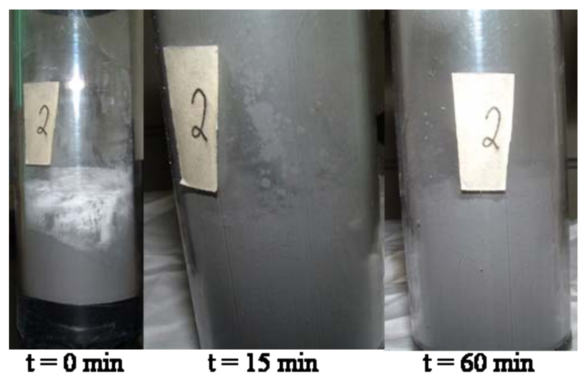

**Figure 8: M115A2 50g 604**

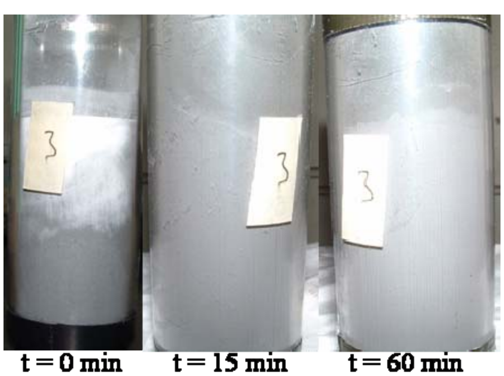

**Figure 9: M115A2 70g 604 w/ 0.25% Cab-O-Sil**

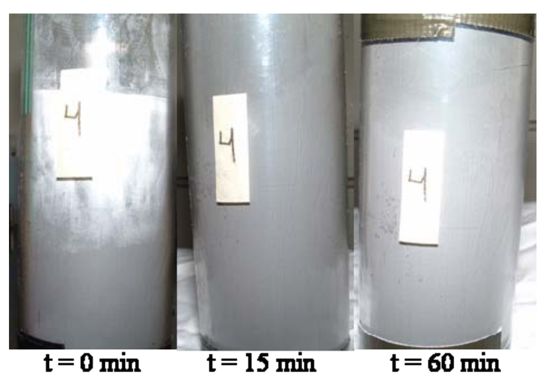

**Figure 10: M115A2 70g 604 w/ 0.5% Cab-O-Sil**

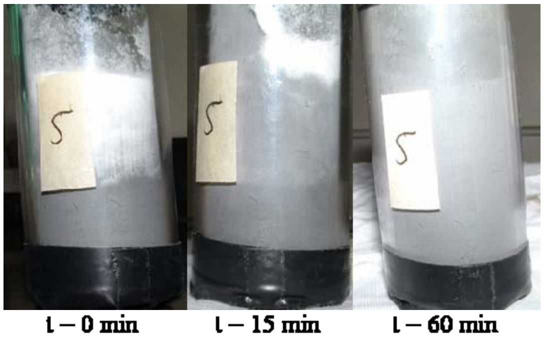


**Figure 11: M116A1 33g 604**

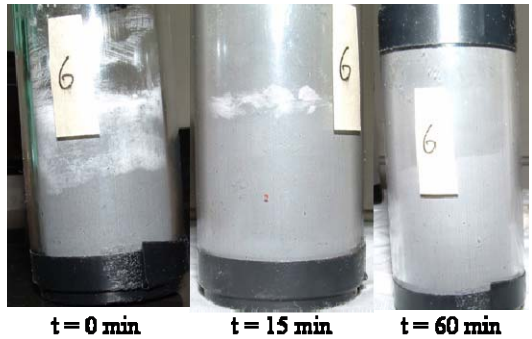


**Figure 12: M116A1 25g 604**

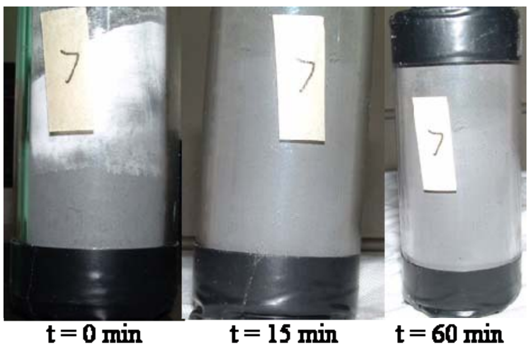


**Figure 13: M116A1 33g 604 w/ 0.25% Cab-O-Sil**

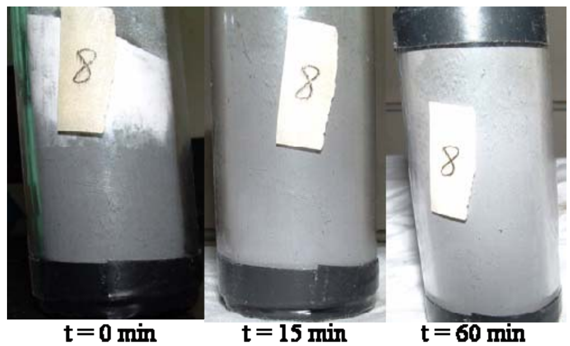


**Figure 14: M116A1 33g 604 w/ 0.5% Cab-O-Sil**

**Sound and Photometric Output Performance**

Mixes were pre-blended and dried prior to loading into the system hardware. For each formulation two different charge weights were loaded: 60 and 70 grams for the M115A2 Simulator and 30 and 33 grams for the M116A1 Simulator. The charge weights were determined from the closed bomb study. The standards contain 40 grams 473B for the M115A2 and 20 grams 473B for the M116A1. The test matrix is summarized in Table 2.

Each sample group was tested at ambient temperature. Cold testing was conducted for 70 gram and 33 gram groups only. The sound and the light measurement systems were placed approximately 50 feet from the samples to satisfy geometric requirements and to protect the measurement systems from the shockwave produced by the energetic rounds. The peak sound intensity was measured with a Bruel & Kjaer 2238 Mediator sound meter equipped with a 0.25 inch microphone (rated to 170 dB). Prior to sound level measurements, the sound meter was calibrated with a Bruel & Kjaer type 4231 sound calibrator. In these measurements, only the peak sound intensity level was measured for each round. The luminous flux emitted from each round was measured with a photometric based light measurement system. A calibrated International Light Silicon photo detector, with a matched photometric filter, was used to measure the

**Table 2: Perchlorate free full-up system prove out test matrix**

| **M115A2** | | | | | |
|---|---|---|---|---|---|
| | Std. | 604 | 604 | 603 | 603 |
| | | 60g | 70g | 60g | 70g |
| Ambient | 5 | 5 | 5 | 5 | 5 |
| Cold, -65F | | | 5 | | 5 |
| **M116A1** | | | | | |
| | Std. | 604 | 604 | 603 | 603 |
| | | 30g | 33g | 30g | 33g |
| Ambient | 5 | 5 | 5 | 5 | 5 |
| Cold, -65F | | | 5 | | 5 |

**Table 3: Summary of visible light output and sound intensity measurements**

| M115A2 | | | | | |
|---|---|---|---|---|---|
| Average of 5 rounds | Std. | 604-60g | 604-70g | | 603-60g |
| | Ambient | Ambient | Ambient | Cold | Ambient |
| Integrated photopic output (Cd*sec) | 1.20E+05 | 9.88E+04 | 1.59E+05 | 1.16E+05 | 2.87E+05 |
| Peak photometric output (Cd) | 3.32E+07 | 8.85E+06 | 1.09E+07 | 8.74E+06 | 2.03E+07 |
| Sound intensity (dB) @ 50ft | 155.8 | 149.1 | 150.4 | 149.1 | 147.1 |
| **M116A1** | | | | | |
| Average of 5 rounds | Std. | 604-30g | 604-33g | | 603-30g |
| | Ambient | Ambient | Ambient | Cold | Ambient |
| Integrated photopic output (Cd*sec) | 6.35E+04 | 5.03E+04 | 6.81E+04 | 6.61E+04 | 1.55E+05 |
| Peak photometric output (Cd) | 3.32E+07 | 8.67E+06 | 5.92E+06 | 5.97E+06 | 1.41E+07 |
| Sound intensity (dB) @ 50ft | 151.6 | 150.9 | 148.5 | 146.8 | 144.8 |

visible light generated by the rounds. The current produced by the silicon photo detector was converted to a voltage with an Ithaco model 1211 current pre-amplifier. Depending on the brightness of the rounds, the amplifier gain used in these measurements ranged from $10^{-3}$ A/V to $10^{-5}$ A/V. The voltage versus time data was collected with both an oscilloscope and a Labview™ based computer data acquisition system. Post experiment analysis consisted of calculating the peak luminous flux, the integrated flux, rise time to peak flux, and the pulse duration. These quantities were calculated for each sample with an algorithm written with the Labview™ programming language.

Test results show that the integrated photometric output for the groups with 60 gram (M115A2) and 30 gram (M116A1) 604 mix are approximatly 20% below that of the standard group. This suggests a higher amount of 604 charge is required to match the standard performance, as confirmed by the data for the groups with 70 gram and 33 gram 604 charge weights. It was also found that the groups with 60 gram and 30 gram 603 had over twice amount of integrated visual output and somewhat lower sound intensity than the standard. The data for 70 gram and 33 gram 603 groups are not available. In summary, the 604 outperformed the 603 in sound intensity while underperformed in photometric output. Test results are summarized in Table 3.

**Fragmentation**

Another finding from the system prove-out was that a minimum of 60 gram (M115A2) and 30 gram (M116A1) of 603 or 604 mix were required to fragment the flash charge cardboard housing bodies and sleeves into a few large pieces. Fragmentation was improved by increasing the amount of flash charge in the system as demonstrated in the sample groups with 70 gram and 33 gram 604 mix. In general, the 604 performed slightly better than the 603 at the same charge weight with respect to the fragmentation. The fragmented pieces from each test group were collected in plastic bags and photographed for comparison in Figures 15, 16, and 17.

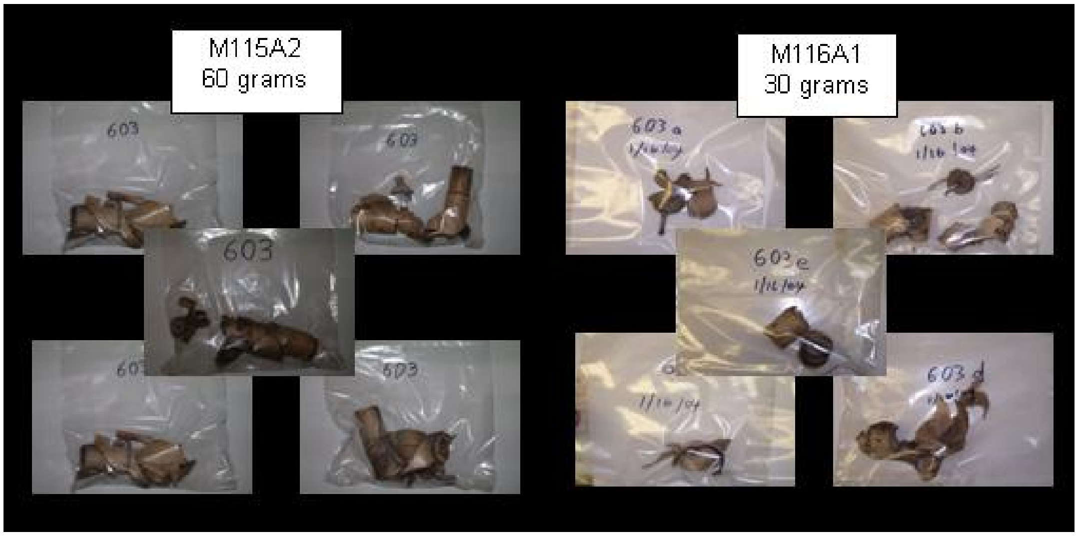


**Figure 15: Fragmented housing bodies for 603 mix in M115A2 and M116A1**


**Figure 16: Fragmented housing bodies for 604 mix in M115A2**

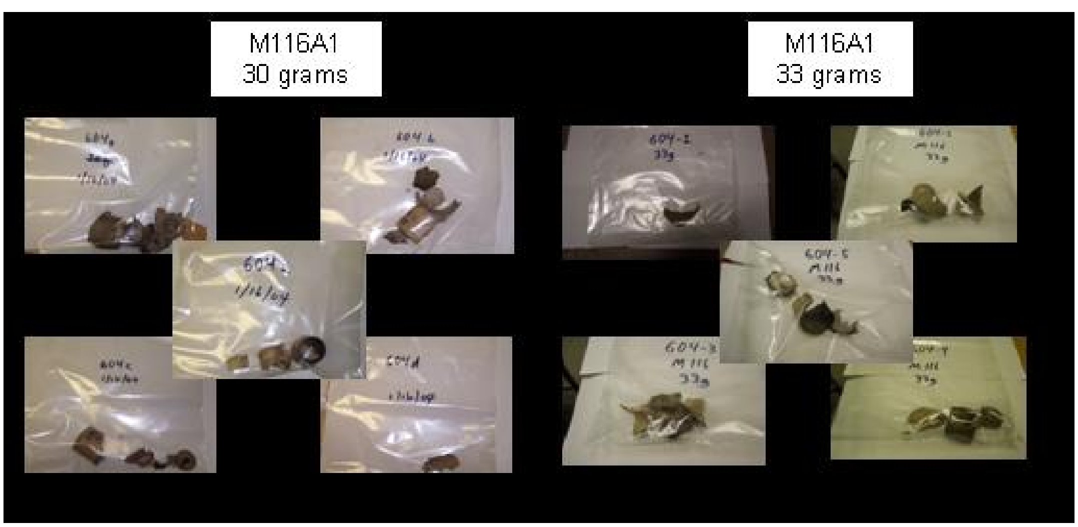


**Figure 17: Fragmented housing bodies for 604 mix in M116A1**

## CONCLUSION

Two perchlorate-free flash compositions have been developed and proven out. The formulation consists of a high surface area flake aluminum as the primary fuel, sulfur as the secondary fuel, and potassium nitrate or strontium nitrate as the oxidizer. Low levels of boric acid and silicon dioxide were added to improve the product storage shelf life, processing, and mixture homogeneity. The fuel/oxidizer ratios and particle sizes were optimized through a parametric study, using the NASA CEA computer program to simulate the thermal properties and a 50 cc closed bomb model to determine the ballistics of each formulation. In an effort to completely eliminate the need for dangerous manual operations, a two part (fuel and oxidizer pre-blends) in-round loading and mixing method was developed to manufacture the perchlorate-free M115A2 and M116A1 Simulators. The fuel pre-blend consists of flake aluminum and a small amount of sulfur as initiation facilitator. The potassium nitrate or strontium nitrate was mixed with Cab-O-Sil and boric acid to form a free-flowing oxidizer pre-blend. The fuel and oxidizer pre-blends were then separately loaded into the item for final system assembly and mixing in a tumbler.

A clear polycarbonate tube with a similar system configuration was used to optimize the critical powder mixing parameters, such as mixing time, homogeneity, fill volume, etc. During the system prove-out, various sample groups were fabricated and tested to correlate the amount of flash charge with the sound level, photometric output, and fragmentation level. It was determined that 60-70 grams of 604 or 603 mix for M115A2 and 30-33 grams of 604 or 603 mix for M116A1 were required to achieve satisfactory fragmentation and sound level performance. It was also found that the Al/SrN 603 formulation yielded over twice amount of the photometric output of the Al/KN 604 system and the existing perchlorate counterpart. The 604 formulation was considered the best perchlorate-free candidate based on the overall performance, material cost, and storage stability.

## REFERENCES


[1] Chen, G.; Motyka, M.; Poret, J.; "Perchlorate Free Flash Band Compositions and Method Making Same for Pyrotechnic Training Rounds," Patent Application Serial No. 10/907206, 24 March, 2005.

[2] Parker Bodine, S.; "Memorandum: Assessment Guidance for Perchlorate," United States Environmental Protection Agency, 26 January 2006.

[3] Shidlovshy, A. A.; Principles of Pyrotechnics, 1964.

[4] Conkling, J. A.; Chemistry of Pyrotechnics, Marcel Dekker, Inc., New York, 1985.