Elimination of Perchlorate Oxidizers from Pyrotechnic Flare Compositions

WP-1280

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14. ABSTRACT

Owing to the health threat of perchlorate contamination of groundwater, we have re-formulated pyrotechnic compositions used in spectrally balanced decoy flares, as well as in red, green, and yellow signal flares so as to remove the perchlorate ingredient while still maintaining performance characteristics that meet or exceed those of the in-service devices. The perchlorate-free decoy flare composition chosen for scale-up was successful in matching the spectral ratio and infrared emission intensity of the older of two types of spectrally balanced flares. Chemical equilibrium computations have shown that it should also be possible to formulate a successful organic-fueled, perchlorate-free substitute for the newer of the two types of flares. We have also conducted extensive laboratory and prototype scale testing of perchlorate-free red flare compositions. Prototype scale tests revealed a degradative aging problem with the hygroscopic calcium nitrate ingredient. We then selected a slightly modified red composition that we are performance and ignition sensitivity testing, prior to proceeding with formulation qualification, final type qualification

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and Techeval testing under ESTCP funding. Based on the results of extensive laboratory scale testing, we have also selected optimized perchlorate-free green and yellow signal flare compositions that have performed at least as well as the in-service perchlorate-containing compositions and are being recommended for scale-up to the Mk 141 Green and Mk 144 Yellow Marine Smoke and Illumination Signals (MSIS's). We are seeking cooperative funding between ESTCP and individual service sponsors to perform similar qualification and Techeval testing on these green and yellow flare compositions.

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List of Acronyms

ALEX	Ultrafine Electro-Exploded Aluminum - high surface area fuel ingredient due to its average ~200 nm particle size.
ALNC	Aluminum Nanocomposite laminate - micrometer sized particles consisting of alternating nanoscale layers of aluminum and plastic laminate material.
CP	Candlepower - luminous intensity expressed in candelas (cd), where the candela is defined as, 1 cd = 1 lumen /steradian^{-1}.
DSC	A thermal analysis technique known as Differential Scanning Calorimetry
DTA	A thermal analysis technique known as Differential Thermal Analysis
GAP	Glycidyl Azide Polymer used as a curable binder in some of the spectrally balanced decoy flare compositions. It is usually cured using Hexamethylene Diisocyanate, also known commercially as N-100 curative.
GSF,RSF, YSF	Local designation to classify perchlorate-free Green, Red, and Yellow Signal Flare compositions, respectively. Typically followed by a unique alphanumeric designation, for example, composition GSF-1E.
I. C. I.	International Commission on Illumination – developed the standard Chromaticity Diagram in 1931 that is used to determine dominant wavelength and color purity of pyrotechnic emission.
LWIR	Longer Wavelength Infrared band routinely monitored in decoy flare performance tests.
MA	Mechanical Alloying technology used by Professor Edward Dreizin's research group to produce high energy mechanical alloy fuels
MPERC	Materials, Processes, and Equipment Review Committee – Crane's local safety board in charge of approving requests for scale-up of new pyrotechnic compositions.
MSIS	Marine Smoke and Illumination Signals in the Navy inventory. They come in red, green and yellow versions.
NJIT	New Jersey Institute of Technology – our academic partner in this SERDP project. Professor Edward Dreizin's research group is part of the NJIT Mechanical Engineering Department..
PMDA	Pyromellitic Dianhydride organic fuel used in some spectrally balanced decoy flare compositions. Figure 5 shows a structural formula of this molecule.
ppb	Parts per billion
SEM	Scanning Electron Microscopy – provides micron scale images of pyrotechnic fuel and oxidizer ingredient as well as pyrotechnic compositions
STANAG	Multinational STANdardization Agreement.
SWIR	Shorter Wavelength Infrared band routinely monitored in decoy flare performance tests.
TGA	A thermal analysis technique known as Thermogravimetric Analysis. Sample weight is measured as a sample is heated at a pre-determined rate.

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We also wish to acknowledge the efforts of our academic partners at the New Jersey Institute of Technology, Professor Edward L. Dreizin, Dr. Mirko Schoenitz, and other members of their research group, for the high-energy mechanical alloys they have produced and delivered to us. These alloys were evaluated as high energy fuels in a number of our perchlorate-free red and green signal flares, as well as in our spectrally balanced decoy flares.

We also wish to thank Dr. John Maassen, Branch Manager of the Environmental and Chemical Science Branch, Pyrotechnic Development Division, Ordnance Engineering Department, for his oversight and encouragement of the project, as well as Mr. Kory Boyd and Mr. Tom Clements of the Pyrotechnics, Demolition, and Small Caliber Branch, Ammunition Engineering Division, for their interest in our perchlorate-free signal flare compositions, for their very helpful information on the in-service signal flare compositions and devices, and for their help in the initial prototype scale mixing and pressing operations of the perchlorate-free red compositions. We also thank them for their willingness to become involved with us in the qualification and techeval testing of the perchlorate-free Mk 124 red flares under ESTCP funding.

We thank Mr. Charles Ash and Mr. Harold Downham of the Pyrotechnics, Plastics and Packaging Branch, Pyrotechnic Development Division, for their help in manufacturing the prototype scale perchlorate-free Mk 124 red signal flares at the Building 198 Prototype Production Facility. Similarly we thank Dr. Eric Hillenbrand, Mr. Alan Fritch, Mr. Terry Chastain, and Mr. Chris Anderson of the Missile Effectiveness Branch, Pyrotechnic Development Division, for the performance testing of the spectrally balanced decoy flares and the red, green, and yellow signal flares at the Crane Photometric Tunnel. We are also grateful to Mr. Cabot Faultless and Mr. Brian Beatty of the Explosive Sciences Branch, Test and Evaluation Division, for their ignition sensitivity testing of our perchlorate-free compositions to impact, rotary friction, and electrostatic stimuli.

Finally, helpful discussions with a number of coworkers are acknowledged. This included discussions regarding the required attributes of spectrally balanced decoy flares with Mr. Steve Norris and Mr. Doug Stark of the Countermeasure Devices Branch, Pyrotechnic Development Division, discussions regarding the safety attributes of our developmental decoy and signal flares with Dr. Bill Hubble and the other members of Crane's Materials Processes and Equipment Review Committee (MPERC), as well as discussions with Crane's Senior Scientist for Pyrotechnics, Dr. Bernard E. Douda, particularly regarding the development of the yellow signal flares and the spectrally balanced decoy flares.

Executive Summary

The majority of in-service red, green and yellow signal flares, as well as spectrally balanced decoy flare compositions contain varying weight percentages of environmentally objectionable perchlorate-type oxidizers. Residual perchlorates from these devices may be absorbed into groundwater and require remediation. Ground water contamination by perchlorates has been found to be a serious health problem. The perchlorates are known to inhibit iodine uptake by the thyroid gland, thus lowering the level of thyroid hormone in the body.[1,2] This can lead to permanent neurological damage, particularly in fetuses and the newborn. Accordingly, the U. S. Environmental Protection Agency set a tentative perchlorate concentration action level of 24.5 parts per billion (ppb) in drinking water. This is the level of contamination at or above which it is deemed necessary to remediate a contaminated site. However, many individual states think this level is too high and have accordingly enacted substantially lower action levels. In order to avoid future ground water contamination by perchlorate, we have been engaged in an attempt to formulate, test, and qualify perchlorate-free versions of these compositions.

The objective of this project is to identify feasible approaches for reformulating colored signal flare and spectrally balanced decoy flare compositions to eliminate perchlorate oxidizers while still providing equal or enhanced performance when compared with in-service (or developmental) perchlorate-containing flare devices.

There are currently two types of perchlorate-containing spectrally balanced flares, an older type that contains metallic fuel and is currently in-service, and a newer type that contains organic fuel and is currently in development. The newer type produces a significantly higher spectral ratio of the intensity in a routinely-monitored longer wavelength infrared (LWIR) band to that in a routinely-monitored shorter wavelength infrared (SWIR) band. Accordingly, the acceptance criteria of the new perchlorate-free spectrally balanced decoy flare compositions consist of their ability to produce equal or higher spectral ratios of the radiant intensity in the two normally monitored infrared bands as the perchlorate-containing flares. For high speed/high signature fighter type aircraft, the spectral ratio of the newer type of flare is considered essential for optimum self-protection against the most sophisticated infrared guided missile threats. For lower speed/lower signature platforms such as helicopters, the older type may still be adequate. For the signal flares, the acceptance criteria of the perchlorate-free compositions consists of their having burn time, luminous intensity, dominant wavelength and color purity that equal or exceed the performance of the in-service perchlorate-containing compositions, as explained in the individual flare performance specifications.

Owing to the chemical complexities involved, this project could not be accomplished merely by removing the undesirable perchlorate oxidizer and substituting another less reactive oxidizer, such as a nitrate, in its place. Because the perchlorates are among the most energetic and reactive oxidizers used in pyrotechnics, higher energy and/or higher surface area (ultrafine particle size) fuels are needed to make up for this energy shortfall in their absence. That is why we have evaluated a number of ultrafine fuels as well as high-energy mechanical alloy fuels produced by our academic partner, Professor Edward L. Dreizin and his research group at the New Jersey Institute of Technology (NJIT). Also, because the most efficient emitting species, barium monochloride (BaCl) for the green and yellow flares, and strontium monochloride (SrCl)

for the red flares, require a chlorine-donating ingredient, we have included ingredients such as polyvinyl chloride.

A number of perchlorate-free spectrally balanced decoy compositions with only boron and metallic fuels were investigated during the earlier years of the project. Unfortunately, none of them were able to produce spectral ratios comparable to those produced by even the older of the two types of spectrally balanced flares. We then investigated perchlorate-free compositions with a combination of metallic and organic fuels. Here, we were successful in matching the spectral ratio and radiant intensity produced by the older in-service type of spectrally balanced flares. However, we were unable to match the substantially higher spectral ratio produced by the newer type of flare. While slightly more expensive than the in-service flare composition, the new perchlorate-free compositions were still reasonably priced in terms of their true "cradle to grave" cost. We designated the best-performing composition as our primary scale-up candidate and the two other compositions that approached the performance of the older type of decoy flare as our secondary scale-up candidates. Although, we have not yet tested them in the laboratory, we have also used NASA Lewis Chemical Equilibrium modeling to predict the adiabatic combustion temperatures and detailed product distributions of a number of perchlorate-free compositions containing solely organic fuels. When we made a direct substitution of potassium perchlorate with potassium nitrate in the type of composition used in the newer type of flare, we observed a rather precipitous drop in the predicted plume temperature, from about 2550 ^{o}K to 1500 ^{o}K. By judicious choice of fuel to oxidizer ratios and additive ingredients, we were able to recover some of the lost temperature with a composition with a predicted adiabatic flame temperature of approximately 2000 ^{o}K. Furthermore, it is predicted to produce comparable mole fractions of products that are strong emitters in the sought after long wavelength infrared (LWIR) region of the spectrum when compared with the newer type of flare. Again, these compositions should be only slightly more expensive than the in-service compositions, and actually have a lower "cradle to grave" cost. We are currently seeking cooperative funding for continued development and testing of these perchlorate-free spectrally balanced decoy flares from ESTCP and Navy and Army program offices.

We have done the most work on the red flares during the course of the project. Testing of numerous early perchlorate-free compositions led to the identification and performance testing with both laboratory and prototype size form factors of the three perchlorate-free red flare compositions designated RSF-2A, RSF-2B, and RSF-2C. This has included the successful completion of the 87-day storage stability (accelerated aging) tests of the three compositions at 70 ^{o}C. The ignition temperature of the aged compositions did not change significantly, and no evidence for the production of degradation products such as magnesium hydroxide, calcium nitrite or strontium nitrite was observed on the simultaneous DTA/TGA thermograms. Also compatibility studies were successfully performed on the three compositions. It was verified that there was no detectable incompatibility between each of the three new perchlorate-free compositions and either the IM-6 ignition composition or the Starter Slurry composition. With these accelerated aging and compatibility tests successfully completed, our local MPERC safety board permitted us to produce and test these three perchlorate-free compositions in the 24-gram Mk 124 Mod 0 red flare form factor. They were performance tested in June 2006 along with the in-service Mk 124 Mod 0 red flares for comparison purposes. The results indicated that none of the RSF-2A and RSF-2B and only a minority of the RSF-2C flares were able to match the

performance specification of the in-service Mk 124 flares. In an attempt to achieve better performance RSF-2C' flares with smaller Granulation 15 magnesium fuel and with a 1% by weight palmitic acid coating on the hygroscopic calcium nitrate ingredient were tested during September 2006. The luminous intensities increased somewhat, but not enough to ensure the consistent production of the 3500 candela luminous intensity in the Mk 124 flare performance specification. There was also an apparent incompatibility between the palmitic acid coating and the epoxy binder ingredient that caused a rather drastic decrease in the cure time of the epoxy. This is a definite safety issue during the press consolidation and flare candle push out operations. Accordingly, it was decided that even the RSF-2C composition was not acceptable for further performance and qualification testing

Since the composition used in the Army's M158 Ground Illumination Signal, Red Star Cluster contains only magnesium, strontium nitrate, polyvinyl chloride and epoxy binder, and *no perchlorate or calcium nitrate* oxidizers, a close variant of this composition is also being evaluated for use as a perchlorate-free Mk 124 red flare. It is designated as the RSF-4 composition. Its burn rate was measured during November 2006 and found to be only slightly slower than that of the in-service Mk 124 composition. Its cost should be roughly comparable to that of the in-service Mk 124 composition. The performance characteristics were just measured in a December 2006 test of laboratory scale flare pellets and found to compare very favorably with the in-service Mk 124 composition. In fact, the average luminous intensity of the RSF-4 composition was approximately 55% higher than that of the Mk 124 composition (3120 cd versus 2020 cd). In light of the favorable performance test results of this RSF-4 composition, we plan to perform Mk 124 red flare prototype scale performance testing on this composition, and then proceed to conduct the requisite formulation qualification, final type qualification, and techeval testing under ESTCP funding.

Unlike several of the earlier perchlorate-free green compositions, the GSF-1E and GSF-4K compositions that had been formulated with the help of chemical equilibrium modeling and successfully performance tested at laboratory scale during December 2004, were found to compare quite favorably in terms of Candle Power luminous intensity, dominant wavelength and color purity with the in-service perchlorate-containing composition in the green Mk 117 and Mk 141 MSIS's. Also, their measured ignition sensitivity to impact, rotary friction and electrostatic stimuli were acceptable. However, during the final year of the project, optimization efforts have led to the selection of the GSF-1E1 composition as the primary scale-up candidate for the Mk 141 green flare candle. Rather than the GSF-1E fuel mixture consisting of Granulation 18 magnesium and a small percentage of the $Al_{0.5}Mg_{0.5}$ mechanical alloy from NJIT, the GSF-1E1 composition contains a fuel mixture of 33% by weight of Granulation 15 magnesium and 67% of Granulation 18 magnesium, and no mechanical alloy. This optimized GSF-1E1 scale-up composition had an almost identical burn rate as the Mk 141 in-service composition, and should offer considerable cost and electrostatic ignition sensitivity safety advantages over the GSF-1E composition. However, its ignition sensitivity characteristics still need to be measured. The actual scale-up of this GSF-1E1 composition to the 110-gram Mk 141 green candle form factor, flare fabrication, and performance testing will have to await future cooperative funding from ESTCP and/or a potential service customer such as the Navy's 2T Cog Conventional Ammunition and Night Vision Program Office, Code PEO-IWS3C/PM4 office. The successful

composition would also have to undergo formulation qualification, final type qualification, and techeval testing prior to its introduction into the service inventories.

Finally, in response to a Navy customer who is interested in replacing the perchlorate in red, green and yellow signal flares, we have recently formulated and performance tested at laboratory scale, three perchlorate-free yellow flare compositions designated YSF-1, YSF-3, and YSF-8. They contain optimized mixtures of magnesium, barium nitrate, polyvinyl chloride, sodium nitrate, and epoxy binder. The in-service perchlorate-containing yellow Mk 144 MSIS composition was tested alongside for comparison purposes. It should be noted that in addition to removing the perchlorate, sodium nitrate was substituted for the sodium oxalate ingredient in the Mk 144. This has the added advantage that the predicted yields of environmentally objectionable cyanide combustion products such as NaCN and HCN are either greatly reduced or totally eliminated. The measured performance results in terms of Candle Power luminous intensity, burn time, dominant wavelength, and color purity compared very well with the perchlorate-containing Mk 144 composition. To an observer, the perchorate-free compositions appeared slightly more yellow in color than the Mk 144 composition which was more orange in color. The YSF-8 composition with 60% Granulation 15 magnesium and 40 % Granulation 18 magnesium was chosen as the primary scale-up candidate owing to its high luminous intensity, favorable color characteristics, and a burn rate similar to the Mk 144 composition. As with the similar perchlorate-free green composition, we continue to seek cooperative funding from such sources as ESTCP and the PM4 office for scale-up to the prototype Mk 144 MSIS yellow flare form factor which is also a 110-gram yellow flare candle. Also, as with the green flare, performance testing, formulation qualification, final type qualification, and techeval testing would then need to be performed prior to the introduction of this item into the service inventories.

What is urgently needed in order to accelerate the pace of our planned transition of these perchlorate-free flare compositions into fielded devices is additional guidance in the form of an updated DOD Perchlorate Policy that would mandate the actual replacement of perchlorate-containing compositions with perchlorate-free compositions in fielded devices. Currently the policy is to initiate remediation of perchlorate-contaminated water tables when either the U.S. or the individual state Perchlorate Action Level is reached, whichever is more stringent. The U.S. action level is 24.5 ppb of perchlorate. However, the state of Massachusetts has recently set their action level over an order of magnitude lower at 2 ppb. Other states are in the process of setting intermediate action levels. Until perchlorate replacement is mandated, there will be no guarantee that remediated sites will remain perchlorate-free. Also, the individual services are reluctant to commit the relatively large sums of money that will be required to successfully develop and qualify the perchlorate-free compositions and introduce them into the inventories until mandated to do so.

Objective

The objective of this project is to identify feasible approaches for reformulating colored signal flare and spectrally balanced decoy flare compositions to eliminate perchlorate oxidizers while still providing equal or enhanced performance when compared with in-service perchlorate-containing decoy and colored signal flare devices. It responded to PPSON-02-06, "Environmentally Acceptable Pyrotechnic Formulations" by proposing to remove perchlorate oxidizers from a number of military pyrotechnic formulations. For the perchlorate-free red, green, and yellow signal flares, the performance metrics include luminous intensity, burn time, dominant wavelength and color purity. They must match or exceed the levels appearing the corresponding Mk 124 red, Mk 141 green, and Mk 144 yellow flare performance specifications. For the perchlorate-free spectrally balanced decoy flares, the performance metrics include the radiant intensity in the LWIR band and the (LWIR/SWIR) spectral ratio. In order to provide the maximum self-protection to fighter type aircraft against the most sophisticated infrared guided missile threats, they should meet or exceed the performance specifications of the newer type of organically-fueled, perchlorate-containing spectrally balanced decoy flares.

Background

Pyrotechnics are used in a variety of military applications. Two such applications are infrared decoy flares and colored signal flares. Many such pyrotechnic flare compositions contain chlorate or perchlorate oxidizers. Residual perchlorates from these devices may be absorbed into groundwater and require remediation. Ground water contamination by perchlorates has been found to be a serious health problem. Perchlorate contamination of either drinking water or foodstuffs are known to inhibit iodine uptake by the thyroid gland, thus lowering the level of thyroid hormone in the body.[1,2] This can lead to permanent neurological damage, particularly in fetuses and the newborn. Accordingly, the U. S. Environmental Protection Agency set a tentative perchlorate concentration action level of 24.5 parts per billion (ppb) in drinking water. This is the level of contamination at or above which it is deemed necessary to remediate a contaminated site. However, many states have subsequently expressed their opinion that this level is too high, especially for the at-risk populations. For example, Massachusetts has recently set their state action level at only 2 ppb of perchlorate in drinking water.[3] This is over an order of magnitude lower than the federal action level. Similarly, California has just set a draft action level of 6 ppb[4] and is currently holding public hearings on the matter. Other states are also considering perchlorate action levels that are below the federal level. The policy of the DOD, and each of its individual services, is to comply with either the federal or state perchlorate action level, whichever is more stringent.[5] In light of the aforementioned concerns, it would be of benefit to identify new alternative pyrotechnic compositions that contain no perhchlorate oxidizer and only the minimum practical level of color enhancing chlorine-containing compounds such as polyvinyl chloride (PVC). This would serve to prevent additional perchlorate contamination of drinking water sites, but of course would not remediate the presently contaminated sites.

Because perchlorate oxidizers are more reactive and energetic than other commonly used oxidizers, the "easy fix" of simple substitution of a perchlorate-free oxidizer for a perchlorate-

containing oxidizer in a pyrotechnic or propellant composition will usually not be successful in fulfilling the objective of equal or superior performance from the perchlorate-free composition. Rather, high energy and/or high surface area metallic or alloy type fuel ingredients are typically required to make up for the energy shortfall caused by switching from perchlorate to other less reactive oxidizers. This is the reason that we have teamed with our academic partner, Professor Edward Dreizin's research group at the New Jersey Institute of Technology in Newark, NJ. They have extensive experience in metallic fuel synthesis and combustion. They used Mechanical Alloying (MA) technology to produce high energy metal alloy fuels, as well as nanocomposite fuels, which we evaluated in some of our spectrally balanced decoy flare and colored signal flare compositions. Specifically, the ignition sensitivities of these high energy fuel ingredients as well as the pyrotechnic compositions made from them were measured, together with the performance parameters of the flare compositions. The results from the high energy metal alloy-containing compositions were then compared with those of compositions containing conventional, commercially available fuels and alloys. In addition, we have similarly evaluated smaller fuel particle size distributions (granulations) as well as ultrafine materials such as Electro-Exploded Aluminum (ALEX) and Aluminum Nanocomposite (ALNC) laminate in our pyrotechnic compositions. By virtue of their larger surface area, the reactivity and energy content of ultrafine material tends to be higher than that of larger particle size commercially available fuels.

Approximately twenty years ago, an early attempt was made at Crane to evaluate a boron-fueled, perchlorate-free spectrally balanced decoy flare composition. This was back when such compositions were produced by the so-called "shock gel" method which used copious quantities of acetone and hexane solvents to coat the fuel and oxidizer ingredients with Viton binder. The metal perchlorate oxidizer was straightforwardly replaced with the corresponding metal nitrate oxidizer. As expected, the performance characteristics of the flare were adversely affected.

More recently, a number of other SERDP and individual service research projects are also endeavoring to replace perchlorate oxidizers in a number of other pyrotechnic and rocket propellant compositions. At Picatinny Arsenal, the U.S. Army has already eliminated the potassium perchlorate in its M115A2 Ground Burst Simulator and M116A1 Hand Grenade Simulator used in troop training. Still other Army efforts are under way to remove the perchlorate from the M117 Booby Trap Flash Simulator, the M118 Booby Trap Illuminating Simulator, and the M119 Booby Trap Whistling Simulator pyrotechnic devices. Three current SERDP projects in the Green Energetics category are also attempting to eliminate perchlorate ingredients. Two of these, WP-1403, “Synthesis, Evaluation, and Formulation Studies in New Oxidizers as Alternatives to Ammonium Perchlorate in DOD Missile Propulsion Applications”, and WP-1404, “Robust Perchlorate-Free Propellants with Reduced Pollution”, are focusing on eliminating ammonium perchlorate from rocket propellants. A third project, WP 1424, “Alternatives for Perchlorates in Incendiary Mix and Pyrotechnic Formulations for Projectiles”, is concentrating on eliminating potassium perchlorate from flash bang pyrotechnic devices.

In order to prevent future additional perchlorate contamination of ground water sites, it is essential that all of these projects that are endeavoring to produce perchlorate-free DOD propellant and pyrotechnic devices be provided sufficient funding to reach the point that they result in successful introduction of the perchlorate-free replacement devices into the service inventories. Typically performance, formulation qualification, final type qualification, and

techeval testing are required to accomplish this introduction. However, until perchlorate-containing device replacement is mandated by DOD policy, the service program offices of the individual services tend to be reluctant to commit the necessary financial support.

Materials and Methods

High Energy Mechanical Alloy and Nanocomposite Fuels

Perchlorate oxidizers currently used in various in-service flare compositions[6] are being substituted with nitrate or other less energetic oxidizers. Because these oxidizers are less reactive and energetic than those that contain chlorine, high-energy and/or high surface area fuels are being used to make up for the loss in energy. Novel high-energy fuels have been produced by our academic partner, Professor Edward Dreizin and his research group at the New Jersey Institute of Technology (NJIT) using Mechanical Alloying (MA) technology. MA is a relatively young material processing technique originally developed by Benjamin[7] and actively exploited in materials research and technology. Figure 1 shows a conceptual diagram of a mechanical alloying reactor. It is a dry, high energy ball milling process in which an initial blend of powders is repeatedly kneaded together and re-fractured by the action of the ball-powder collisions. The process usually produces a powder in which each particle has the content similar to that of the original powder blend. The mechanisms of MA include repeated cold welding and fracturing leading to ultrafine mixing and true alloying. While detailed understanding of the MA is only being developed, the process finds numerous applications in metallurgy and materials processing because of its relative simplicity and efficiency. Recent research has shown that MA can be used, similar to rapid quenching, to produce highly metastable phases and supersaturated solid solutions[8]. NJIT has produced mechanical alloys for use in our pyrotechnic flare compositions, and have provided us with $Al_{0.5}Mg_{0.5}$ and $Al_{0.7}Mg_{0.3}$ mechanical alloys[9,10], as well as $B_{0.5}Ti_{0.5}$ and Al-SrO_2 nanocomposite materials[11,12] that have been included in candidate pyrotechnic compositions. Their earliest mechanical alloying high energy ball mill reactors worked with relatively small scale 2-gram to 10-gram batch sizes. However, recently they have successfully scaled up their high-energy ball mill mixers in which the mechanical alloys are produced. The new larger mixer is based on a planetary mill design. Up to four 50-gram batches may be processed simultaneously. A computer model useful for computing the milling dose[13] aided them in the scale-up effort. Figure 2 shows a photograph of the scaled-up planetary mill at NJIT. Figure 3 shows a Scanning Electron Microscopy (SEM) photograph and a typical particle size distribution of the $B_{0.5}Ti_{0.5}$ nanocomposite. Figure 4 shows similar photographic and particle size distribution information for the Al-Mg mechanical alloys. These are included because it was these three high energy alloys, $Al_{0.5}Mg_{0.5}$, $Al_{0.7}Mg_{0.3}$ and $B_{0.5}Ti_{0.5}$, that were included in some of our perchlorate-free spectrally balanced decoy flare compositions. Similarly, the $Al_{0.5}Mg_{0.5}$ mechanical alloy was included in some of our perchlorate-free red and green signal flare compositions.

From the SEM photographs of these three high energy fuels, it is seen that they are comprised of micron scale particles. The size range is from a few microns to as large as approximately 100 microns. However, as noted on Figure 4, the mechanical alloy particles are chemically homogeneous to at least the 100 nanometer level. That is, they are composed of alloy particles

Synthesis of Metastable Materials: Mechanical Alloying

Ball milling: dry, high energy process: initial blend of powders is repeatedly kneaded together and re-fractured by the action of ball-powder collisions

> products far from equilibrium and with high degrees of
- supersaturation
- mechanical stress

> allows control of particle size

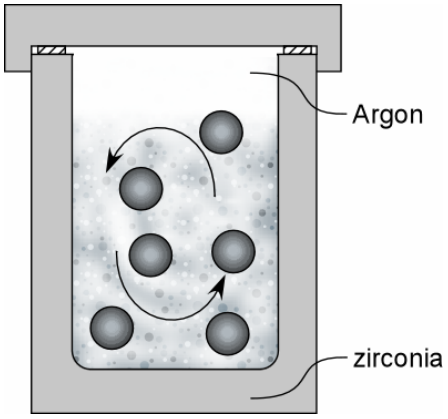
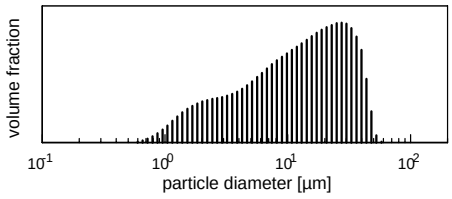
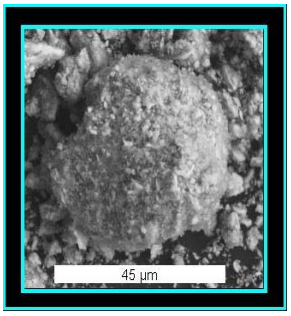


Figure 1. Conceptual Diagram of Mechanical Alloying Reactor

Figure 2. NJIT Scaled-up Planetary Mixer

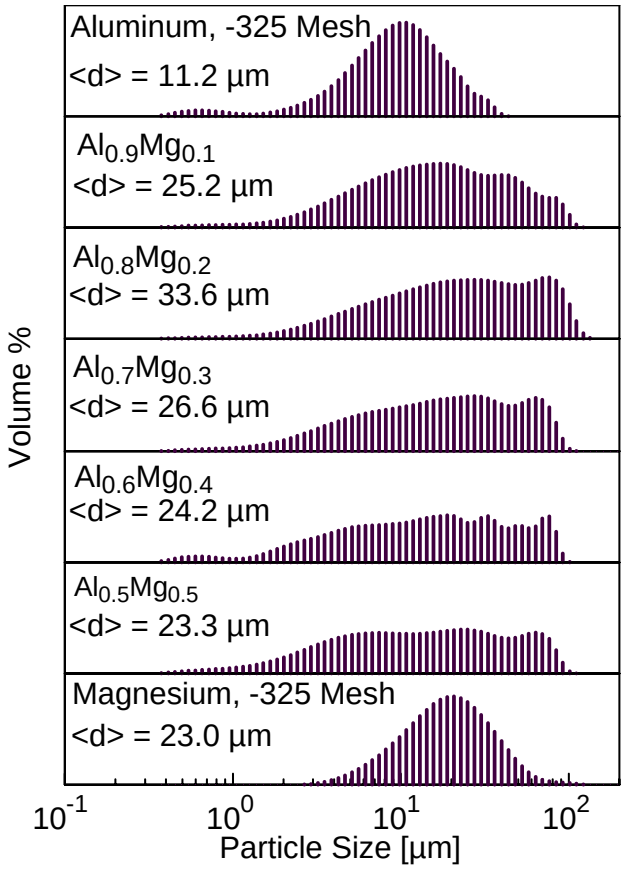
▪ $B_{0.5}Ti_{0.5}$ *Mechanical Alloy*





This mechanical alloy is produced using the Arrested Reactive Milling (ARM) technique

Figure 3. NJIT Particle Size Distribution and SEM Photograph of $B_{0.5}Ti_{0.5}$ Nanocomposite



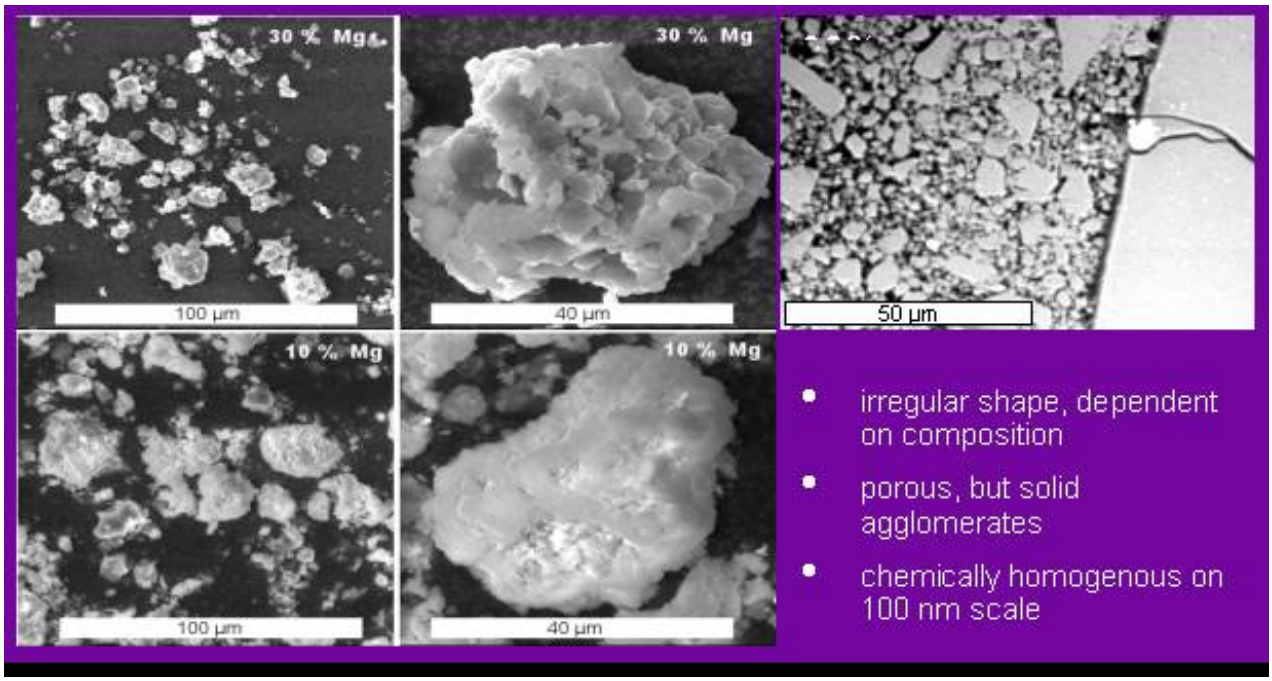


Figure 4. NJIT Particle Size Distribution and Scanning Electron Micrograph Plots of Aluminum-Magnesium Mechanical Alloys

rather than agglomerated clusters of the constituent metal starting material (elemental magnesium and aluminum particles). This is further illustrated in Figure 5 which shows X-ray spectra of the original blend of magnesium and aluminum particles (labeled "Al Mg blend") before the mechanical alloying operation as well as of the various Al-Mg mechanical alloys that were produced in the high energy ball mill. It is observed that when the magnesium content of the alloy rises above 30%, all of the X-ray peaks attributable to the component magnesium and aluminum starting materials are absent, and the $Al_{12}Mg_{17}$ mechanical alloy peaks are present.

Once these high energy metal alloys have been synthesized, they can be expected to undergo a somewhat more complex oxidation mechanism than elemental pyrotechnic fuel ingredients. This is illustrated by Professor Dreizin's postulated mechanism for Al-Mg mechanical alloys shown in Figure 6. Specifically, the mechanical alloys react in an oxidative environment to produce ultrafine metal droplets, the hot combustion gases necessary to disperse them, and ultimately metal oxide combustion products. This is true whether the oxidizing environment is provided by an oxygen gas flow as in the NJIT reactor, or by a chemical oxidizer such as nitrate or perchlorate in one of Crane's pyrotechnic compositions.

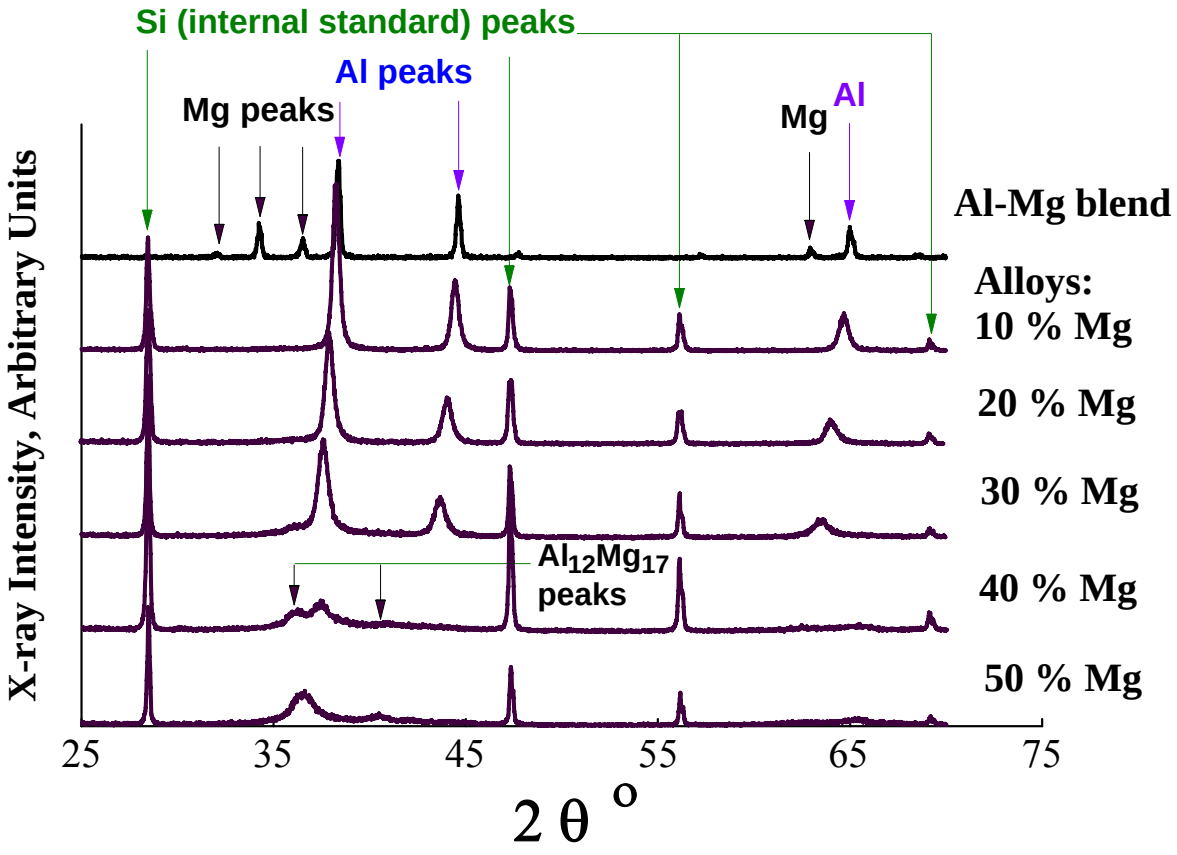


Figure 5. X-ray spectra of Al-Mg powder blend, and Al-Mg mechanical alloys.

Mechanical Alloys react to produce ultrafine reactive metal droplets, the hot combustion gases needed to disperse them, and metal oxides

Al-Mg alloys:

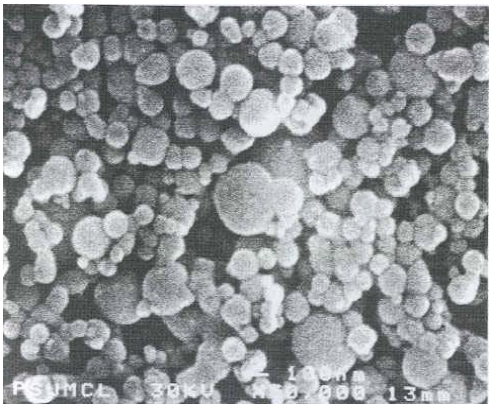
- preparation: Mg (0-30%) + Al → Al - Mg(0-30%)
- ignition/phase change: Al - Mg(30%) + O_2 → [Al + $Al_{12}Mg_{17}$ + Mg] + O_2
- combustion: [Al + $Al_{12}Mg_{17}$ + Mg] + O_2 → Al_2O_3 + Al_2MgO_4 +MgO

Key: metastable solid solution (MSS) nanoparticles

Figure 6. Combustion Mechanism for NJIT's Al-Mg Mechanical Alloys

High Energy Ultrafine Fuels and Organic Fuels

Other energetic fuels used in these new perchlorate-free pyrotechnic compositions included various particle size distributions (or granulations) of magnesium, sub-micron amorphous boron, copper, Ultafine Electro-Exploded Aluminum (also known as ALEX), and an organic fuel known as pyromellitic dianhydride (PMDA). A typical SEM photograph of ALEX is shown in Figure 7. A structural formula for PMDA is shown in Figure 8.



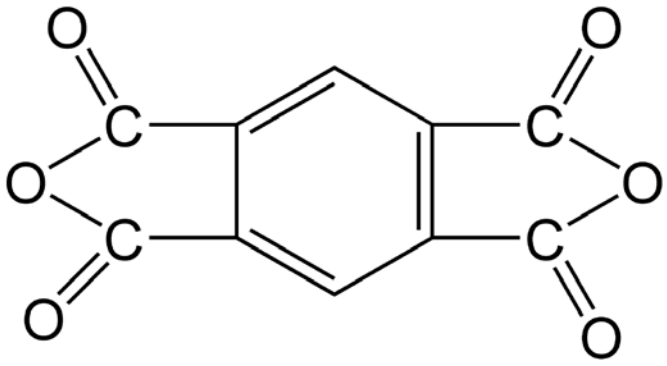


Figure 7.Electro-Exploded Aluminum Figure 8. Structural Formula of Pyromellitic Dianhydride

Potential Problem Areas with High Energy Fuels

It is noted that all of these high energy fuels, whether they are mechanical alloys or ultrafine metals, may potentially have two disadvantages that must be evaluated as they are being considered for incorporation into pyrotechnic compositions. The first is the general tendency toward increased ignition sensitivity to impact, friction, and electrostatic stimuli, when compared

with the more conventional micron size elemental fuels. The second is drastically higher current ingredient costs compared to the conventional elemental fuels inasmuch as they are still research and development type materials. As synthesis methods are perfected, batch sizes are scaled up, and customer demand for the new products increases, the general trend is for the price per pound to decrease. However, they will still be more expensive than the constituent elemental fuels, by factors ranging anywhere from about 2 to 10. Unfortunately, the ignition sensitivity is *not* expected to decrease during the scale-up process unless additional proactive steps are taken as part of the synthetic pathway. For example, we have found that the dangerously high sensitivities of the high energy fuels that we have been using usually decrease somewhat if separate binder pre-coating steps are performed on the fuels prior to their incorporation into our pyrotechnic compositions. Binders evaluated for this purpose included viton, which is a copolymer of vinylidene difluoride and hexafluoropropylene, and the Epon 813/Versamid 140 curable epoxy binder system. More information will be provided regarding the measured ignition sensitivities of coated and uncoated high energy fuels as well as the pyrotechnic compositions made from them in the results section of this report. With the ever-increasing emphasis being placed on the safety of propellants and pyrotechnics, it is critically important that the new perchlorate-free compositions developed in this project have acceptable ignition sensitivities so that the probability of their accidental initiation during manufacture, storage, or use aboard military aircraft, helicopters or ships is minimized. Therefore, successful passage of the tests required for formulation qualification as well as final type qualification would be extremely difficult, if not impossible, for a perchlorate-free composition that is more ignition sensitive than the corresponding perchlorate-containing in-service composition it is intended to replace.

Two general types of pyrotechnic flare compositions were studied during this project with the objective of replacing the objectionable perchlorate ingredient. They consisted of red, green and yellow colored signal flares and spectrally balanced infrared decoy flare compositions.

Technical Approach for Spectrally Balanced Decoy Flares

There are two different types of perchlorate-containing spectrally balanced decoy flares. The older of the two types contains boron fuel and is currently in service inventories. The newer of the two types is still in the developmental stage and it contains organic type fuels. The newer type of flare has been able to achieve significantly higher spectral ratios of the sought after radiation intensity in a longer wavelength infrared band to that in a shorter wavelength infrared band than the older type of spectrally balanced flare. However, only the older type of flare was in the test and evaluation stage at the inception of this project in 2002. Therefore, our initial objective was to equal or exceed the spectral ratio of the older type of flare, as well as its emission intensity in the longer wavelength band. We were aided in composition selection by the predictions obtained from the NASA Lewis Chemical Equilibrium computer code that predicts adiabatic combustion temperature and detailed combustion product distribution.[14] Since recent conversations with Crane's Countermeasure Devices Branch and their Navy sponsor led us to the conclusion that it will be necessary for the perchlorate-free spectrally balanced composition to match or exceed the performance of the newer type of spectrally balanced decoy flares, our revised goal is to equal or exceed the spectral ratio and the long wavelength emission intensity of the newer of the two types of flares. This is because the highest possible spectral

ratio will be required in order to provide adequate self-protection to typical high speed/high signature military fighter/attack aircraft from infrared-guided missile threats. It is likely that such high ratios may only be produced by organic as opposed to metallic fuels. Therefore, the NASA Lewis Chemical Equilibrium program has continued to be used to simulate perchlorate-free spectrally balanced compositions with only organic fuels.[14]

Our initial strategy for the spectrally balanced decoy flares had been to substitute potassium nitrate for the objectionable perchlorate oxidizer and to use various fuel additives in addition to the boron fuel. The $Al_{0.5}Mg_{0.5}$, $Al_{0.7}Mg_{0.3}$ and $B_{0.5}Ti_{0.5}$ mechanical alloys from NJIT, ultrafine aluminum (ALEX), aluminum nanocomposite (ALNC), and various combinations thereof were included in the earliest perchorate-free spectrally balanced compositions. Other parameters that were systematically varied included fuel to oxidizer ratio, and weight fraction of the high energy glycidyl azide polymer (GAP) binder. The next group of spectrally balanced compositions contained *both* similar combinations of metal fuels as well as organic fuels rich in carbon and oxygen such as PMDA. These were described in the 2005 Annual Report as well as in the 2005 Symposium poster. While these compositions were very successful in emulating the older of the two types of spectrally balanced flares, they still fell short of the performance of the newer type of flares. At this point the NASA Lewis program was used to see if a perchlorate-free composition with only organic fuel could perform as well as the newer type of flare.

Technical Approach for Red, Green and Yellow Signal Flares

Colored signal flares have also been investigated. Both red and green in-service signals use potassium perchlorate as a source for chlorine, along with PVC or another chlorine donor for color-enhancement purposes.[6] Chlorine in these compositions combines with strontium or barium to form chlorides of these species that produce emission in the appropriate visible bands to give these flares their red and green colors. Yellow flares require a sodium containing oxidizer such as sodium nitrate or sodium oxalate for the production of the intense sodium D-line at 589 nm in the orange region, as well as additional ingredients for the production of green emitters such as BaCl and BaOH in order to make the flare appear yellow as opposed to orange. For these perchlorate-free recompositions, alternate methods for generating these or other color producing species will be necessary. Figure 9 shows the general reaction pathways undergone by both in-service perhclorate-containing flare compositions, as well as by the perchlorate-free compositions proposed as their replacements.

Our earliest attempts to reformulate the red signal flares at laboratory scale involved two separate approaches. The first approach resulted in the "RSF-1" type compositions that contained magnesium and/or mechanical alloy fuels, strontium nitrate oxidizer, and polytetrafluoroethylene (Teflon) as the color enhancer. It was hoped that this completely chlorine-free type of composition would produce the SrF intermediate species that has emission bands in the red region of the spectrum, in close proximity to those of the more traditional SrCl emitting species. This strategy led to disappointing results with washed out (whitish) red flames.

The second approach resulted in the "RSF-2" type compositions, which were also completely chlorine-free, and contained a combination of magnesium and $Al_{0.5}Mg_{0.5}$ mechanical alloy, and both calcium nitrate and the more traditional strontium nitrate as oxidizers. This approach

Examples of Red Colored Signal Flare Compositions:

$Mg + Sr(NO_3)_2 + KClO_4$ + PVC + Epoxy Binder →
MgO + SrOH/SrCl + HCl + Other Products (Existing Mk 66 MSIS)

Mg + Mg/Al Alloy + $Ca(NO_3)_2 + Sr(NO_3)_2$ + Epoxy Binder →
$MgO + Al_2O_3$ + CaO/CaOH + SrO/SrOH + Other Products
or
$Mg + Sr(NO_3)_2$ + PVC + Epoxy Binder →
MgO + SrOH/SrCl + HCl + Other Products (Proposed)

Examples of Green Signal Flare Compositions:

Mg + Cu + $KClO_4$ + Ba $(NO_3)_2$ + PVC + Binder,etc. →
BaOH + BaCl + HCl + Other Products (Existing Mk 141 MSIS)

Mg + Cu + B + Mg-Al Alloy + $Ba(NO_3)_2$ + PVC + Binder, etc →
$BO_2 + B_2O_3$ + BaOH + BaCl + HCl + Other Products (Proposed)

Examples of Yellow Signal Flare Compositions**:**

Mg + $KClO_4$ + $Ba(NO_3)_2$ + $Na_2C_2O_4$ + PVC + Binder,etc. →
Na* + BaCl + BaOH + HCl + NaCN + Other Products (Existing Mk 144 MSIS)

Mg + $Ba(NO_3)_2$ + $NaNO_3$ + PVC + Binder, etc →
Na* + BaCl + BaOH + HCl + Other Products (YSF-8 Yellow Candidate)

Figure 9. General Reaction Pathways for Existing and Perchlorate-Free Red, Green and Yellow Signal Flare Compositions

appeared far more promising, producing brilliant red-orange flare plumes whose luminous intensities matched or exceeded those of our initial internal standard, the in-service Mk 66 Ground Illumination Signal, Red composition. Our subsequent approach involved the optimization of this composition into the RSF-2A, RSF-2B, and RSF-2C compositions that were tested extensively. Eventually Crane's local safety board, the Materials Processes and Equipment Review Committee (MPERC), approved the laboratory to prototype scale-up process to the 24-gram Mk 124 Mod 0 Marine Smoke and Illumination Signal (MSIS) red candle after having settled a number of issues related to ignition sensitivity, ingredient and composition compatibility, and storage stability. This Mk 124 MSIS device was chosen based upon the large number of these types of devices in the service inventories. Only after prototype scale performance testing of these perchlorate-free Mk 124 prototype candles did it become apparent that absorption of atmospheric water vapor by the hygroscopic calcium nitrate ingredient was causing degradative aging of the composition prior to testing. All of the RSF-2A and RSF-2B composition flares fell short of the luminous intensity specified in the Mk 124 flare performance specification (3500 candela). Some of the RSF-2C composition flares were just barely able to

meet the luminous intensity specification, but the intensities varied widely and the majority fell short of the specification.

Our initial approach to remedy this problem was to switch from the coarser Granulation 18 magnesium to the finer Granulation 15 magnesium and to use calcium nitrate that had been pre-coated with a small amount of palmitic acid. While these changes did produce an increase in luminous intensity, it was not of sufficient magnitude to ensure the consistent achievement of the 3500 candela luminous intensity in the flare performance specification. Our final and successful approach was to choose the composition used in an in-service Army red flare, the M158 Ground Illumination Signal, Red Star Cluster, and to modify this composition by replacing the Type I 30/50 mesh magnesium (MIL-P-14067) with an optimized mixture of Type III Granulations 15, 17 and 18 magnesium (MIL-M-382) that produced as close a burn rate as possible as the Mk 124 red flare, and to use a more modern Epon 813/Versamid 140 epoxy binder system to replace the former less desirable Laminac/Lupersol DDM binder system. This optimized composition contains neither calcium nitrate nor potassium perchlorate. Besides the magnesium fuel and epoxy binder, it contains only the traditional strontium nitrate oxidizer and polyvinyl chloride color enhancer.

Our efforts aimed at identifying a perchlorate-free green signal flare composition at laboratory scale began by removing the potassium perchlorate from the composition used in the Mk 117 (and Mk 141) Green MSIS that we hoped to replace in the service inventories. We continued to use the Granulation 18 magnesium fuel, and also included Al-Mg mechanical alloy fuels in some of the compositions. We also added sub-micron amorphous boron fuel in the hope of producing additional emission in the green region of the spectrum from various boron oxide intermediate species. The traditional barium nitrate oxidizer continued to be used, but potassium nitrate was added to replace the potassium perchlorate that had been removed. Some compositions continued to use polyvinyl chloride as a color enhancer to obtain the BaCl green-emitting intermediate species, while others used Teflon in the hope of producing a similar green emitting species, BaF. These early GSF-1, GSF-2, GSF-3, and GSF-4 series of compositions were evaluated in performance test series in November 2003 and April 2004. They all resulted in compositions that tended to have faster than desired burn rates, as well as flare plumes that looked washed out (whitish) when compared with the vivid green colors produced by the Mk 117 MSIS flare composition. It was determined that the relatively high weight percentages of the sub-micron boron fuel and the potassium nitrate oxidizer were primarily responsible for these excessively fast burn rates and washed out flames. At this point, use was made of the aforementioned NASA Lewis Chemical Equilibrium code[14] to optimize these perchlorate-free green compositions. This led to the formulation and testing of three optimized compositions GSF-1E, GSF-4D, and GSF-4K in December 2004. Of these three, the GSF-1E was the most successful in attaining or exceeding the Candle Power luminous intensity, the dominant wavelength and color purity given in the flare performance specification for the perchlorate-containing Mk 117 Green MSIS flare composition. Like the Mk 117 composition it contains Granulation 18 magnesium and copper fuels, barium nitrate oxidizer, polyvinyl chloride color enhancer, and epoxy binder. Unlike the Mk 117 composition, the perchlorate oxidizer had been removed and been replaced with additional barium nitrate. Also, a small weight percentage of the $Al_{0.5}Mg_{0.5}$ mechanical alloy has been substituted for a corresponding weight percentage of magnesium. Our final approach to optimization was to use a similar weight percentage of the

finer Granulation 15 magnesium in place of the electrostatically ignition sensitive mechanical alloy in composition GSF-1E1. Since this composition also seems to also have very similar performance characteristics as the in-service Mk 117 composition, it is our final choice of the composition for which we will request MPERC permission for scale-up to the prototype scale 110-gram green flare used in the Mk 117 MSIS, and its product improvement the Mk 141 Green MSIS which uses the same flare composition.

Also, in response to a February 2006 request from a potential Navy customer, we have used the NASA Lewis Chemical Equilibrium code[14] to similarly formulate a perchlorate-free yellow signal flare composition that would perform as well as the perchlorate-containing Mk 118 and Mk 144 Product Improvement Yellow MSIS's. Owing to the chemical similarities of the green and yellow flare compositions, our approach has been to once again remove the potassium perchlorate and replace it with additional barium nitrate. Also, we substituted sodium nitrate oxidizer for the sodium oxalate that provides the orange/yellow color in the Mk 118 flare. This was done because the computer predictions indicated that we could either drastically reduce or eliminate the environmentally objectionable cyanide combustion products such as HCN and NaCN by eliminating the oxalate ingredient. A total of eight perchlorate-free compositions containing magnesium, sodium nitrate, barium nitrate, polyvinyl chloride and epoxy binder were simulated and the three most promising, YSF-1, YSF-3, and YSF-8 were performance tested. A YSF-8 variant with an optimized combination of Granulation 15 and Granulation 18 magnesium was found to have a very similar burn rate as the Mk 118 composition, as well as to produce equal or superior luminous intensity, dominant wavelength and color purity. Hence, it will be the composition recommended to the MPERC safety board for scale-up to the 110-gram prototype scale yellow flare in the Mk 118 MSIS and similar Mk 144 Yellow Product Improvement MSIS.

When the successful perchlorate-free pyrotechnic compositions developed under this program are introduced into the service inventories, the potential need for remediation of newly introduced perchlorate in the environment from these items will be eliminated. Rather, efforts can concentrate solely on the clean up of previous perchlorate releases. There will also be a slight reduction in the total atmospheric burden of HCl imparted by the current family of chlorine-containing pyrotechnic devices. Furthermore, the identification of new high-energy metal/alloy fuels in this project should benefit the energetics community as a whole, as these fuels may have uses in other pyrotechnic or propellant applications.

Preparation of compositions

All compositions have been mixed by hand. Initially, 10-gram mixes were prepared to obtain ignition sensitivity data to impact, rotary friction, and electrostatic stimuli. Compositions deemed to have acceptable sensitivities were then prepared as 45-gram mixes, from which three 15-gram pellets were pressed for performance testing. The oxidizers and the magnesium and boron fuels were dried at >100 ^{o}C prior to use. The solid ingredients were sequentially added to the GAP/N-100 binder system (spectrally balanced flares) or to the Epon 813/Versamid 140 epoxy binder system (colored signal flares). The compositions were mixed thoroughly after the addition of each ingredient. The order in which the fuels, additives, and oxidizers were added was also varied. The compositions were mixed until no clumps of oxidizer were visible, and the

mixture appeared homogeneous. Owing to the low levels of the epoxy binder ingredient (typically 5% by weight), small amounts of acetone were sometimes added to the mix as a processing aid. However, acetone was always allowed to completely evaporate before the mixture was pressed into pellets. Acetone was not added to the mixtures containing higher weight percentages of the GAP/N-100 binder system.

As during the previous years of this project, all mixing and curing continued to be performed in a temperature and humidity controlled laboratory. As a consequence, any minor humidity fluctuations did not seem to cause any water absorption or pellet discoloration problems during preparation of the compositions. No crumbly or discolored pellets were observed. However, the baseline spectrally balanced perchlorate-containing mixtures with its GAP/N-100 binder still appeared more gooey and moist than the other spectrally balanced mixtures, and as a consequence continued to be tamp cured in the special three-chambered split-half aluminum mold, rather than being press consolidated at 6000 PSI (2650 lbs dead load) for 45 seconds dwell time like all of the other spectrally balanced pellets. This was done to prevent them from loosing their cylindrical shape during the curing process at 60^0C. While increment lines indicative of where sequential portions of the composition had been tamped into each mold were visible around the sides of some of the cured pellets, all of the pellets burned in stable fashion. None of the pellets deflagrated during burn testing. Therefore, true inverse burn rates (seconds/inch) could be calculated for all pellets. All of the signal flare mixtures with epoxy binder tended to be relatively dry, so it was not necessary to employ the special three chamber split molds during the curing process of any of the signal flares. After pressing at 4200 PSI (1900 lbs dead load) for 15 seconds dwell time, the signal flare pellets were allowed to cure for 48 – 72 hours at 60^oC in the laboratory oven.

The cured pellets were then prepared for linear burn rate testing. The sides and bottom of the pellets were inhibited to force them to burn in a linear fashion down the longitudinal axis. Miller Stephenson Model 907 two-part epoxy was used to inhibit the pellets. Pellets for testing in the radiometric test facility were attached to a special mounting block that attached to the test fixture in test tunnel.

A small bead of Magnesium-Teflon-Viton (MTV) ignition slurry was applied to the top of all of the spectrally balanced pellets. For the colored signal flare pellets, approximately one gram of IM-6 ignition composition was pressed at the top of the candle and then the MTV ignition slurry bead was applied to the top of the IM-6 portion of the candle. An electric match was taped to the top of each pellet for ignition. Figure 10 has been included to show the laboratory press and press tooling, together with a pyrotechnic pellet prepared for burn testing at the radiometric test facility.

Composition pressed into 15 gram ¾" diameter pellets. Sides of pellets inhibited to burn linearly. Ignition slurry and electric match or firecracker fuse attached to top of pellet for performance testing.

Figure 10. Laboratory Pellet Press and Flare Pellet Prepared for Radiometric Testing

The perchlorate-free prototype scale 24-gram Mk 124 Mod 0 red candles were prepared in our Prototype Production Facility (Building 198). Up to 450-gram batches of each composition were mixed remotely in an interlock-equipped mixing cell using a Hobart 10-quart mixer. The Epon 813 and Versamid 140 binder components were first weighed, mixed together by hand, and then added to the mixing bowl. The $Al_{0.5}Mg_{0.5}$ mechanical alloy (RSF-2A) or commercial magnalium (RSF-2C) was then added to the bowl and mixed, followed by the magnesium fuel. The remaining strontium nitrate, calcium nitrate, and asphaltum ingredients were then pre-blended and passed three times through a No. 30 Standard Sieve. They were then added to the bowl and mixed. Between the additions of each ingredient(s), the sides of the mixing bowl were wiped down using a non-sparking rubber spatula in order to ensure a uniform mix.

The press consolidation of each flare pellet was accomplished with a 5-Ton Hannifan Hydraulic Press. A certified Lexan shield was in place between the press and the operator. The procedure involved placing a fish paper tube (ID=1.20-inch) into the press tooling. Approximately 2.5 grams of IM-6 Ignition Composition was poured into the press tooling and leveled. This was followed by approximately 21 grams of perchlorate-free flare composition which was also leveled. Finally, approximately 2.5 grams of inert fireclay composition were added and leveled. Press consolidation at 6000 P.S.I. was then performed for a minimum of 5 seconds dwell time. Once removed from the press, the candle was inverted so that the fireclay layer was at the bottom and the IM-6 layer was at the top. A Starter Slurry solution consisting of 50% ignition mix and 50% acetone was then used to coat the top (IM-6) portion of the candle to aid in pellet ignition. In order to minimize exposure to atmospheric water vapor, the fish paper tubes are heated to

>100 ^{o}C and then pre-coated with a mixture of Epon 813 and Versamid 140 binder ingredients and allowed to cure before the candle pressing operation. The pressed candles were then cured at 60 ^{o}C for a minimum of 48 hours and placed in sealed M20A1 ammunition containers along with one or more bags of desiccant for storage prior to performance testing.

Testing of Compositions

Ignition Sensitivity Tests:
Crane's Explosive Sciences Branch performed ignition sensitivity tests in accordance with MIL-STD-1751[15] on 10-gram mixtures of representative perchlorate-free spectrally balanced decoy flare and red, green and yellow signal flare compositions, and on samples of some of the more sensitive fuel additives by themselves. This data was collected to determine the potential risks of unplanned ignition for the compositions and fuel ingredients during manufacturing, storage and handling operations. The impact, rotary friction, and electrostatic ignition sensitivities were measured. Impact sensitivities were determined by doing a 25-sample Bruceton test using an apparatus where a weight is dropped on a sample from a series of fixed heights. The friction sensitivity was measured using a rotary friction apparatus with a test sample size of 10 trials. Electrostatic sensitivity was determined to be the highest energy corresponding to a given voltage and capacitance, at which 20 consecutive samples do not fire. Based upon Crane's Classification Criteria, samples were rated as having dangerous, high, moderate, low, or very low sensitivity to each of the three types of ignition stimuli. (Summaries of this sensitivity data will be presented in Tables 5, 6, and 18.)

Accelerated Aging – Storage Stability Tests:
Such tests have become an MPERC requirement when scaling pyrotechnic compositions from the laboratory to the concept/prototype scale. Here the requirement is to prepare the pyrotechnic composition and submit it for initial thermal analysis using either a Differential Scanning Calorimeter (DSC) or a Simultaneous Thermogravimetric Analyzer (TGA)/Differential Thermal Analyzer (DTA). The composition is then split into two sealed samples. The first sample is subjected to accelerated aging for a minimum of 85 days at 70 ^{o}C. The second sample is maintained at ambient temperature over the same period. The storage at elevated temperature is designed to simulate approximately 5 years of ambient storage, and assumes that the degradative aging rate approximately doubles for each 10 ^{o}C increase in storage temperature. When the storage stability test has been completed, both the aged and ambient samples are subjected to another thermal analysis. In order for the composition to pass this accelerated aging test, there must be no significant change in the ignition temperature of the composition, and there should be no changes in the general ignition behavior of the composition. Furthermore, detectable evidence for the production of degradative aging products (such as magnesium hydroxide) should not appear on the thermogram of the aged sample. This type of accelerated aging test has been performed on selected red, green and yellow signal flare compositions studied during this project.

Compatibility Tests:
Whenever a developmental pyrotechnic composition is going to be in contact with other pyrotechnic compositions (such as an ignition composition) or with any other potentially reactive materials in the overall device, thermal analysis-based chemical compatibility tests are mandated

prior to scale-up and formulation qualification. These requirements are given in *Chemical Compatibility of Ammunition Components with Explosives (Non-Nuclear Applications)*, *STANAG 4147* (Edition 2) dated 5 June 2001.[16] The compatibility metric used in the STANAG 4147 thermal analysis procedure is the presence and magnitude of a shift in the thermal event associated with the decomposition/ignition of the energetic material. That is, if the decomposition/ignition peak of an energetic is shifted to a 20 degree lower temperature in the mixture, then the components of the mixture are *not* chemically compatible. In contrast, if the decomposition/ignition peak is shifted to ≤ 4 degrees lower temperature, then the materials are chemically compatible. Intermediate temperature shifts require additional testing. For compatibility tests that we performed for our perchlorate-free red and green signal flare compositions in contact with ignition and starter slurry compositions, we again used a simultaneous TGA/DTA thermal analysis method with the mandated relatively slow heating rate of 2 ^{o}C/minute.

Performance Tests:
Performance testing was conducted at laboratory scale on 15-gram pellets of composition. Typically, three pellets were tested per 45-gram batch of composition. Performance testing was also conducted on the 24-gram prototype scale perhclorate-free Mk 124 red flares. Radiometric testing was conducted at Crane's Photometric Tunnel Test Facility where radiometric measurements in two infrared bands of interest, burn times, and video coverage were obtained for all spectrally balanced decoy compositions. For the red, green and yellow signal flare compositions, luminous intensity, color purity and dominant wavelength measurements were performed using a Candle Power head and a Hunter Tri-Stimulus Colorimeter with reference to the standard I. C. I. Chromaticity Diagram. Burn times and the pellet lengths were used to compute linear burn times (seconds/inch) for the pellets. The average linear burn time for the pellets of each composition was then computed. Video coverage was obtained for all flares, and digital color photographs of some of the burning red, green and yellow flares of the in-service and candidate compositions were also obtained. Comparison of the test data from the candidate compositions with the in-service perchlorate-containing comparison standard compositions enabled us to judge whether or not they achieved the performance criteria required for scale-up.

Results and Accomplishments

Introduction

The perchlorate-free spectrally balanced decoy flare and red, green and yellow signal flare compositions discussed in the Materials and Methods section have been thoroughly evaluated alongside the corresponding perchorate-containing in-service compositions for comparison purposes during the course of this project. The tests results are described in this section

Spectrally Balanced Decoy Flares

All of the perchlorate-free spectrally balanced compositions mixed and tested at laboratory scale from the inception of the project in 2002 through January 2005 contained only boron and metal type fuels. While all but a few of the compositions included boron, various other metals and alloys were added to the composition. This included various combinations of ultrafine Electro-Exploded Aluminum (ALEX), Aluminum Nanocompostie (ALNC), and the $Al_{0.5}Mg_{0.5}$, $Al_{0.7}Mg_{0.3}$, and $B_{0.5}Ti_{0.5}$ mechanical alloys produced by Professor Dreizin's research group at the New Jersey Institute of Technology. In most cases the environmentally objectionable potassium perchlorate was replaced by potassium nitrate as the sole oxidizer. However, in one test series in mid-2004, varying weight percentages of iron (III) oxide (Fe_2O_3) were added as a second oxidizer. Table 1 has been included to give an overview of the results obtained from these earlier metal-fueled compositions. It is seen that all of them were unsuccessful in their attempt to equal or exceed the infrared spectral ratio produced by the perchlorate-containing SB-43 baseline composition which was a surrogate for the composition used in the older of the two types of in-service spectrally balanced decoy flares. This spectral ratio is obtained from the ratio of the emission intensity in the longer of the two routinely monitored infrared spectral band to that obtained from the shorter of the two routinely monitored infrared spectral band. In most cases, the total integrated energy and the average intensity in the longer wavelength band was measured to be higher than that obtained from the SB-43 baseline composition. However, it is considered essential that the spectral ratio be as high as possible in order to provide adequate self-protection to typical high signature fighter aircraft from the most sophisticated infrared-guided missile threats. It is noted that the NASA Lewis Chemical Equilibrium program[14] was used to optimize the proportions of the ingredients in the compositions that were tested during January 2005 so that the maximum yield of combustion products that emit in the LWIR region would be obtained.. Indeed one of the compositions in that series, SB-61, consisting of boron, $B_{0.5}Ti_{0.5}$ and ALEX fuels, achieved the highest spectral ratio of any of the metallic fueled compositions. However, even it fell significantly below the ratio achieved by the SB-43 baseline composition.

By this time in the program, the second newer type of spectrally balanced decoy flare had entered into developmental testing. Like the older type of flare, the new type also contained the objectionable potassium perchlorate oxidizer. However, unlike the older type of flare, it used an exclusively organic-fueled composition.[17] The newer type of flare had a significantly higher spectral ratio than its predecessor and rapidly became much more favorably regarded than the older flare, especially for the self-protection of high speed/high signature fighter/attack aircraft against the most sophisticated infrared-guided missile threats. It was at this point in 2005 that we began the use of an organic fuel, pyromellitic dianhydride (PMDA) in our perchlorate-free spectrally balanced compositions. The initial effort involved adding it as an *additional* fuel to the metallic fuels present in the older compositions. This effort was in response to an April 2005 SERDP In Process Review (IPR) Action Item requesting a plan for increasing the spectral ratio. As before, the NASA Lewis Chemical Equilibrium Program was used to optimize the ingredient mass fractions in the composition so that maximized yields of combustion products that emit in

Table 1. Measured Performance Characteristics of Metal-Fueled Perchlorate-Free Compositions

Mixture[a]	**Fuel/Oxid. Ratio**	**Burn Time, s/in**	**Band Intensity, LWIR**	**Spectral Ratio**	**Scale-up**
B/$KClO_4$/(Baseline)	2.21	BL	BL	BL	-
B/KNO_3		~BL	>BL	<<BL	No
B/ALNC/KNO_3	6.49	>BL	>>BL	<<BL	No
B/$Al_{0.5}Mg_{0.5}$/KNO_3	3.55	>>BL	>>BL	<<BL	No
B/$Al_{0.5}Mg_{0.5}$/KNO_3	4.97	>BL	>>BL	<<BL	No
B/$Al_{0.7}Mg_{0.3}$/KNO_3	4.93	>>BL	>>BL	<<BL	No
B/ALEX/KNO_3	4.73	>BL	>>BL	<<BL	No
$Al_{0.5}Mg_{0.5}$/ALEX/KNO_3	3.27	>BL	>>BL	<BL	No
$Al_{0.5}Mg_{0.5}$/ALEX/KNO_3/25Fe_2O_3	3.30	>BL	>>BL	<BL	No
$Al_{0.5}Mg_{0.5}$/ALEX/KNO_3/50Fe_2O_3	3.29	>BL	>>BL	<<BL	No
$Al_{0.5}Mg_{0.5}$/ALEX/KNO_3/75Fe_2O_3	3.31	>>BL	>>BL	<<BL	No
$Al_{0.5}Mg_{0.5}$/KNO_3	4.28	>>BL	>BL	<<BL	No
B/$B_{0.5}Ti_{0.5}$/KNO_3	7.74	~BL	>>BL	<<BL	No
$B_{0.5}Ti_{0.5}$/ALEX/KNO_3	4.54	>BL	>>BL	<BL	No
$B_{0.5}Ti_{0.5}$/ALEX/KNO_3/25Fe_2O_3	4.51	>BL	>>BL	<BL	No
$B_{0.5}Ti_{0.5}$/ALEX/$KNO_3$50Fe_2O_3	4.58	>BL	>>BL	<<BL	No
$B_{0.5}Ti_{0.5}$/ALEX/KNO_3/75Fe_2O_3	4.70	>BL	>>BL	<<BL	No
$B_{0.5}Ti_{0.5}$/ALEX/KNO_3	2.83	>>BL	>BL	<BL	No
Jan. 2005 – Optimized					
$Al_{0.5}Mg_{0.5}$/ALEX/KNO_3	2.29	>>BL	>BL	<BL	No
$B_{0.5}Ti_{0.5}$/ALEX/KNO_3	2.55	>BL	>BL	<BL	No
B/ $B_{0.5}Ti_{0.5}$/ALEX/KNO_3	2.72	>BL	>BL	<BL	No[b]

[a]All compositions used energetic GAP/Hexamethylene Diisocyanate Curable Binder System
[b]This composition came the closest to the spectral ratio of the baseline composition, but it was still significantly lower.

the desirable LWIR spectral band would be obtained. Table 2 has been included to similarly summarize the results of this Metal + Organic Fuel test series of July 2005. It is seen that 3 of the 6 compositions tested were very successful in their ability to match or exceed the spectral ratio of the SB-43 composition which is very similar to the composition used in the older of the two types of in-service flares. Accordingly, the B/ALEX/PMDA/KNO_3 with the 1.19 fuel to oxidizer ratio, with its nearly equal LWIR band intensity and its slightly superior spectral ratio was chosen as the primary scale-up candidate. The same composition with the 1.56 fuel to oxidizer ratio, as well as the composition with B/ $B_{0.5}Ti_{0.5}$/ALEX/KNO_3 and a 2.46 fuel to oxidizer ratio were chosen as secondary scale-up candidates.

Table 2. Measured Performance Characteristics of Metal/PMDA-Fueled Perchlorate-Free Compositions – July 2005 Test Series

Mixture	Fuel/Oxid. Ratio	Burn Time,s/in	Band Intensity LWIR	Spectral Ratio	Scale-up
B/$KClO_4$ (Baseline)	2.21	BL	BL	BL	-
B/$B_{0.5}Ti_{0.5}$/ALEX/PMDA/KNO_3	2.46	>BL	<BL	=BL	Yes-2
B/ALEX/PMDA/KNO_3	1.56	>BL	<BL	>BL	Yes-2
B/ALEX/PMDA/KNO_3	1.19	>BL	=BL	>BL	Yes-1
ALEX/PMDA/KNO_3	143	>BL	<BL	<BL	No
B/ALEX/PMDA/KNO_3	1.58	>BL	<BL	<BL	No
B/ALEX/PMDA/KNO_3	1.87	>BL	<BL	<BL	No

BL – Baseline Value
Yes-1 - Primary Scale-up Candidate
Yes-2 – Secondary Scale-up Candidates

Obviously these three Metal/PMDA-fueled perchlorate-free compositions performed very well in these static tests when compared with the older of the two types of in-service spectrally balanced decoy flares. However, the newer of the two types of spectrally balanced decoy flares has a much higher spectral ratio than the older type. Therefore, they are also significantly higher than the new perchlorate-free candidate compositions. As discussed previously, this shortfall will limit their usefulness for the self-protection of high signature/high speed fighter/attack aircraft. However, the older of the two types of flares, as well as these 3 new perchlorate-free flare compositions may still have considerable usefulness in protecting lower signature/lower speed aircraft such as helicopters.

Figure 11 has been included to show representative emission intensity versus time plots in the SWIR and the LWIR spectral bands for the perchlorate-containing SB-43 standard composition and the PMDA-61-7 composition which is our primary scale-up candidate composition. It is observed that the burn time of the perchlorate-free composition is somewhat longer than the standard composition, but that its magnitude of the emission intensity in the LWIR band is within 10-15% of that of the standard composition. The spectral ratio as a function of burn time is similarly plotted in Figure 12. It is observed that the perchlorate-free PMDA-61-7 composition slightly exceeds that of the standard perchlorate-containing SB-43 composition.

In our search for a perchlorate-free spectrally balanced composition with a higher spectral ratio closer to that produced by the newer of the two types of spectrally balanced decoy flares, we have been using NASA Lewis Chemical Equilibrium[14] calculations to evaluate a number of perchlorate-free compositions that like the newer in-service compositions contain solely organic fuels. When the potassium perchlorate oxidizer was straightforwardly replaced by potassium nitrate, the predicted adiabatic combustion temperature was observed to plummet from approximately 2550 ^{o}K to approximately 1500 ^{o}K. Such a precipitous drop in temperature would certainly be expected to result in an unacceptable decrease in the burn rate and emission intensity of the composition. That is why it was necessary to systematically vary a number of

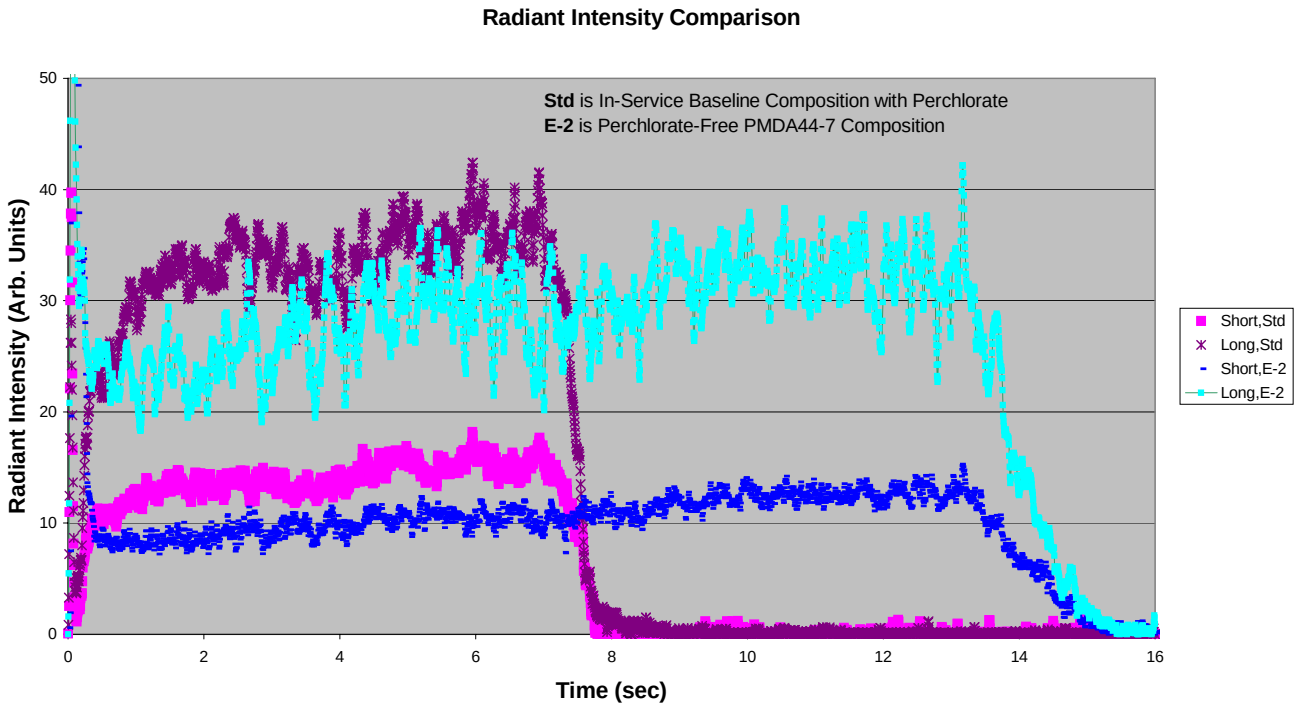


Figure 11. Emission Intensity versus Time Plots for the Short and Long Wavelength Bands for the Primary Perchlorate-Free Scale up Candidate Composition (PMDA-61-7) and the SB-43 Perchlorate-Containing Standard Composition

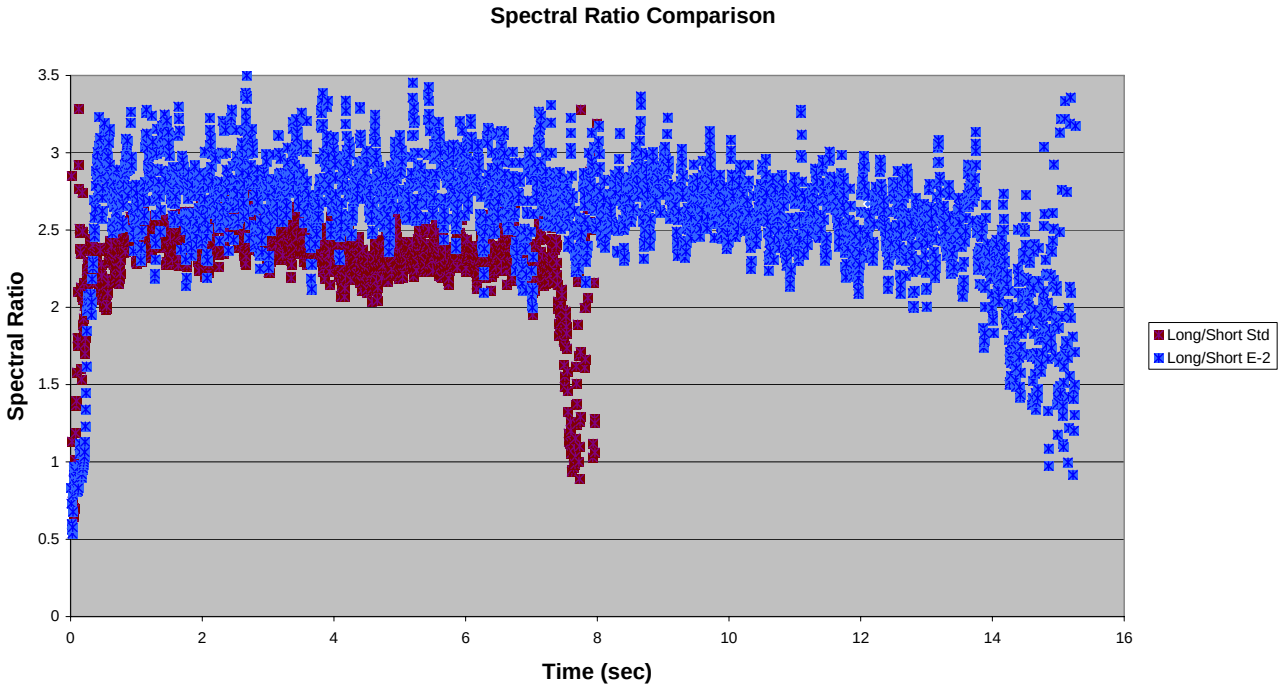


Figure 12. LWIR/SWIR Spectral Ratio versus Time Plots for the Perchlorate-Free PMDA-61-7 Composition and the Perchlorate-Containing SB-43 Standard Composition

other parameters such as fuel to oxidizer ratios, weight percentages of miscellaneous additives, etc. After this was done, it was possible to attain predicted adiabatic combustion temperatures as high as 1984 ^{o}K. Furthermore, it was also possible to obtain predicted yields of combustion products which produce the desired LWIR emission which compare favorably with the product yields predicted for the corresponding perchlorate-containing compositions. However, these compositions have not yet been prepared at laboratory scale and subjected to performance testing. It is hoped that such an investigation can eventually be cooperatively funded by ESTCP and interested Navy and/or Army activities.

Red Signal Flare Compositions

Table 3 has been included to summarize the performance tests of the earliest two test series in November 2003 and April 2004 in which we evaluated two general approaches to formulate perchlorate-free red flares. Specifically the RSF-1 series explored using a combination of strontium nitrate and potassium nitrate oxidizers and either polytetrafluoroethylene (Teflon) to produce red-emitting species such as SrF (strontium monofluoride), or polyvinyl chloride to produce the SrCl (strontium monochloride) red emitter. The RSF-2 series utilized strontium nitrate and anhydrous calcium nitrate as oxidizers and *no* halogen-containing color enhancing ingredients. Rather the presumed red/orange emitters were SrOH (strontium hydroxide) and CaOH (calcium hydroxide). Both composition types had combinations of magnesium and $Al_{0.5}Mg_{0.5}$ and $Al_{0.7}Mg_{0.3}$ mechanical alloy fuels.

In general, the RSF-1 composition produced very disappointing results. The Candle Power luminous intensities were much lower than the RSF-2 type compositions and the in-service Mk 66 composition. Also, the dominant wavelength was approximately 576 nm which is in the yellow rather than the red region of the spectrum. The color purity was also considerably lower than that of the Mk 66 composition. The RSF-1A and RSF-1B compositions had higher weight percentages of strontium nitrate and lower weight percentages of potassium nitrate and polyvinyl chloride in lieu of the teflon ingredient. This led to an improvement in the dominant wavelength and color purity, but the luminous intensities remained disappointingly low.

These early compositions were followed by three optimized compositions, RSF-2A, RSF-2B, and RSF-2C in the April 2004 test series. The RSF-2 and RSF-2A compositions both contained the $Al_{0.5}Mg_{0.5}$ mechanical alloy, with the RSF-2A composition containing a lower weight percentage of the mechanical alloy. The RSF-2B composition contained only magnesium fuel, and the RSF-2C composition contained commercial magnalium alloy (Al-Mg) in addition to the magnesium. The RSF-2 series of compositions appeared to perform much better. It is observed that the RSF-2C composition produced the highest luminous intensity by a quite substantial amount. Also, the dominant wavelengths and color purities of the RSF-2 series of compositions were quite favorable, and the flares produced brilliant red plumes that compared well with those of the in-service composition to a visual observer. Therefore, the RSF-2A, RSF-2B, and RSF-2C compositions were selected for scale-up. Because of the large number of Mk 124 Mod 0 Marine Smoke and Illumination Signals (MSIS), Red in service inventories, the 24-gram red signal flare in this device was selected as the prototype scale form factor. This flare contains Granulation 15 magnesium fuel, potassium perchlorate and strontium nitrate oxidizers, polyvinyl chloride color enhancer, and asphaltum as the non-curable binder. Its performance specifications have been

Table 3. Performance of Standard and Developmental Red Signal Compositions during November 2003 and April 2004 Tests

Composition	Pellet No.	Burn Time (sec)	Average Candle-power, CP	Dominant Wavelength nm	Color Purity %	Fuel make-up	Scale-up?
Mk 66 Red	B-2	>47	257	608	81	Mg	
	B-3	54	293	604	82		
	B-1	>51	277	604	71.5		
	B-2	>51	207	611	82		
	B-3	46	343	608	80		
RSF-1	P-1	27	147	575	77	$Al_{0.5}Mg_{0.5}$	N
	P-2	36	116	562	79	MA+	
	P-3	34	131	570	78	Mg	
RSF-1A	M-1	47	144	608	84.5	Magnalium	N
	M-2	>50	110	605	87	+Mg	
	M-3	47	145	605.5	88		
RSF-1B	N-1	10*	169	608	90	$Al_{0.7}Mg_{0.3}$	N
	N-2	>51	61	604	82	MA+	
	N-3	48	97	608	87	Mg	
RSF-2	Q-1	24	663	605	90	$Al_{0.5}Mg_{0.5}$	Y
	Q-2	28	518	604	88	MA+	
	Q-3	25	752	604.5	88	Mg	
	I-1	34	757	610	90		
	I-2	33	838	608	90		
	I-3	33	906	611	92		
RSF-2A	J-1	42	823	609	90	$Al_{0.5}Mg_{0.5}$	Y
	J-2	39	873	609	88	MA+	
	J-3	38	909	610	91	Mg	
RSF-2B	K-1	>51	454	608	92	Mg	Y
	K-2	>50	505	611	84		
	K-3	>52	561	610	90		
RSF-2C	L-1	33	1698	608	91.5	Magnalium	Y
	L-2	29	1505	608	92	+	
	L-3	30	1874	610	90	Mg	

* Pellet N-1 extinguished prematurely and could not be re-ignited. Pellets N-2 and N-3 burned normally.

listed in Table 4. (The specifications for the flare candles in the green and the yellow MSIS devices from which we also hope to eliminate the perchlorate are also listed in Table 4.) Permission for laboratory to prototype scale-up of the three perchlorate-free red compositions was requested subsequent to this April 2004 testing. Prior to receiving final approval for scale-up, it was necessary for us to provide significant additional data regarding issues such as the hygroscopic nature of the calcium nitrate ingredient, and the compatibility of each of the three flare compositions with the IM-6 ignition composition, as well as with the Starter Slurry composition. This was necessary because both of these compositions are in contact with flare composition in the Mk 124 red flare. Also, as for all new compositions undergoing scale-up, it was necessary for us to provide ignition sensitivity to impact, rotary friction and electrostatic

Table 4. Summary of Flare Performance Specifications

Flare Description	Burn Time (sec)	Candle Power (cd)[19]	Dominant Wavelength (nm)	Minimum Color Purity
Mk 124, Red, MSIS	16-23	3,500	>600	88%
Mk 141, Green, MSIS	>20	12,000	500-570	35% under 560 nm
Mk 144, Yellow, MSIS	>20	15,000	575-593	77%

stimuli for each of the three red compositions at both laboratory and concept scale, and an 85-day storage stability (accelerated aging) test had to be performed for each composition.

The results of the laboratory and prototype scale ignition sensitivity tests are presented in Tables 5 and 6, respectively. It is observed that the impact sensitivities of all three of the laboratory

Table 5. Ignition Sensitivity Results for Prototype Scale Mixes, RSF-2A, RSF-2B, RSF-2C

Sample	Impact Sensitivity		Friction Sensitivity			Electrostatic Sensitivity
	50% fire		Energy (ft-lb)		Response	Maximum No Fire Energy (Joules)
	Height (cm)	Energy (J)	Average	Lowest		
RDX Class5 - Standard	81.55	15.98	2031.61	518.94	20% Fired	0.180
RSF-2A	92.64	18.16	587.75	223.82	90% Fired	0.125
RSF-2B	155.99	30.57	640.82	213.13	80% Fired	0.180
RSF-2C	164.10	32.16	313.12	167.86	100% Fired	0.080

Dangerous High Moderate Low Very Low

Table 6. Ignition Sensitivity Results for Laboratory Scale Mixes RSF-2A, RSF-2B, RSF-2C and Fuel Ingredients:

Sample	Impact Sensitivity		Friction Sensitivity			Electrostatic Sensitivity
	50% fire		Energy (ft-lb)		Response	Maximum No Fire Energy (Joules)
	Height (cm)	Energy (J)	Average	Lowest		
RDX Class5 - Standard	49.84	9.77	1162.81	916.93	No Response	0.151
RSF-2A	178.40	34.97	1438.90	242.60	60% Fired	0.180
RSF-2B	178.40	34.97	2402.24	391.08	30% Fired	0.151
RSF-2C	178.40	34.97	2887.05	585.58	40% Fired	0.151
Fuels						
$Mg_{0.5}Al_{0.5}$	159.00	31.17	N/A	997.11	N/A	0.002
$Mg_{0.5}Al_{0.5}$/Viton	178.40	34.97	2364.97	59.17	20% Fired	0.450
$Mg_{0.5}Al_{0.5}$ /17.9% Epoxy	178.40	34.97	1399.48	357.11	10% Fired	0.450
$Mg_{0.5}Al_{0.5}$ /52.1%Epoxy	178.40	34.97	1520.94	1357.91	0% Fired	0.180
Magnalium-200	178.40	34.97	1928.03	950.44	30%Fired	1.250
Magnesium GR18	178.40	34.97	1847.21	371.29	60% Fired	18.000

scale mixtures were in the very low sensitivity range. However the measured sensitivities of the prototype scale mixes were moderate for RSF-2A, low for RSF-2B, and very low for RSF-2C. While these changes for the RSF-2A and RSF-2B compositions were not anticipated, it should be emphasized that all sensitivity measurements in question were moderate or lower. While the lowest rotary friction results show similar moderate sensitivity results for the RSF-2A and RSF-2B laboratory and prototype samples, the prototype RSF-2C sample exhibited moderate sensitivity while the laboratory RSF-2C sample exhibited low sensitivity. Both the laboratory and prototype scale samples of all three compositions exhibited electrostatic sensitivity measurements in the highly sensitive category, which is not uncommon for pyrotechnic flare compositions such as these. Since the Standard Operating Procedure (SOP) for the manufacturing of these prototype scale mixes and flare pellets incorporates all of the necessary safeguards and engineering controls, the MPERC board gave their permission for the press consolidation of the prototype scale mixtures of the RSF-2A, RSF-2B, and RSF-2C flare compositions.

We determined that there was no compatibility issue between the two types of binder, viton and epoxy. However, we also determined that either the epoxy or the Viton could mitigate the dangerously high electrostatic ignition sensitivity of the $Al_{0.5}Mg_{0.5}$ mechanical alloy. This sensitivity data for both pre-coated and uncoated mechanical alloy is shown in the "Fuels" section of Table 6. This data prompted the MPERC to recommend that during scale-up to the Mk 124 Mod 0 form factor we perform the pre-coating simply by adding the uncoated $Al_{0.5}Mg_{0.5}$ as the first ingredient to the Epon 813/Versamid 140 binder system which results in pre-coating it before any of the additional ingredients are added to the mixture.

We also used a simultaneous TGA/DTA thermal analysis technique to verify that there was no incompatibility between each of the three candidate red compositions and both the IM-6 ignition composition, and the starter slurry composition, which are used in the flare candle to aid in ignition. Both binary and ternary combinations of the red flare, the ignition, and the starter compositions were examined. As described in the Materials and Method Section, these tests were performed using the thermal analysis procedures described in *Chemical Compatibility of Ammunition Components with Explosives (Non-Nuclear Applications)*, *STANAG 4147* (Edition 2) dated 5 June 2001.[16]

Initially, samples of the IM-6, the Starter Slurry, and each of the red signal flare compositions were run separately and then a roughly equal mixture by weight of the three components were subjected to simultaneous TGA and DTA thermal analysis measurements using a heating rate of 2 ^{o}C/minute in the Perkin Elmer Simultaneous Thermal Analyzer with nitrogen carrier gas. None of the three red flare compositions were found to undergo a lower temperature ignition exotherm when the IM-6 and the starter slurry compositions were present.

Subsequently, at the request of the MPERC, a binary combination of RSF-2A and IM-6 compositions, as well as a binary combination of RSF-2A and Starter Slurry compositions were similarly studied by DTA and TGA thermal analysis. Tables 7 and 8 have been included to summarize the results of these tests. They clearly show that RSF-2A is compatible with both the IM-6 and the Starter Slurry inasmuch as the mixtures underwent the ignition exotherm at slightly higher rather than lower temperatures than did the RSF-2A composition by itself. These results

Table 7. Ignition Temperatures of RSF-2A/IM-6 from DTA and TGA Data

Material	Peak Temperature Associated with Ignition (^{0}C)	Peak Temperature Shift (^{0}C)
IM-6	350	---
RSF-2A	351	---
IM-6 / RSF 2A	360	+10

Table 8. Ignition Temperatures of RSF-2A/Starter Slurry from DTA and TGA Data

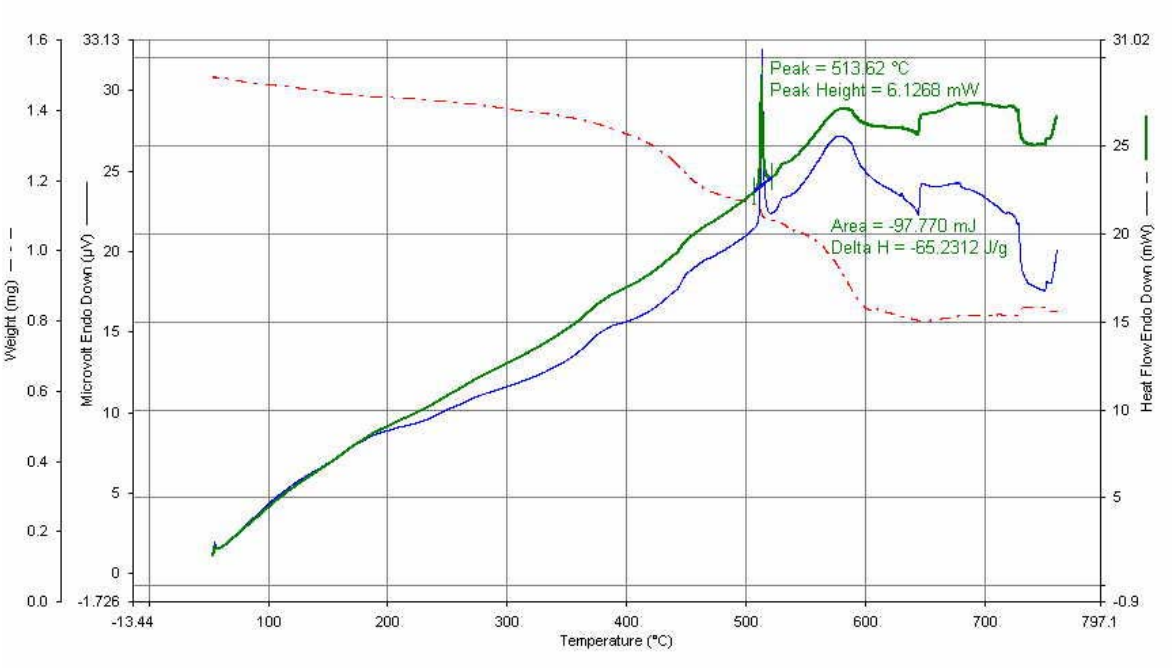
Material	Peak Temperature Associated with Ignition (^{0}C)	Peak Temperature Shift (^{0}C)
Ignition Starter Slurry	405	---
RSF-2A	351	---
Starter Slurry /RSF 2A	367	+16

were sufficient to convince the MPERC of the compatibility of three red compositions with both the IM-6 and the Starter Slurry Compositions.

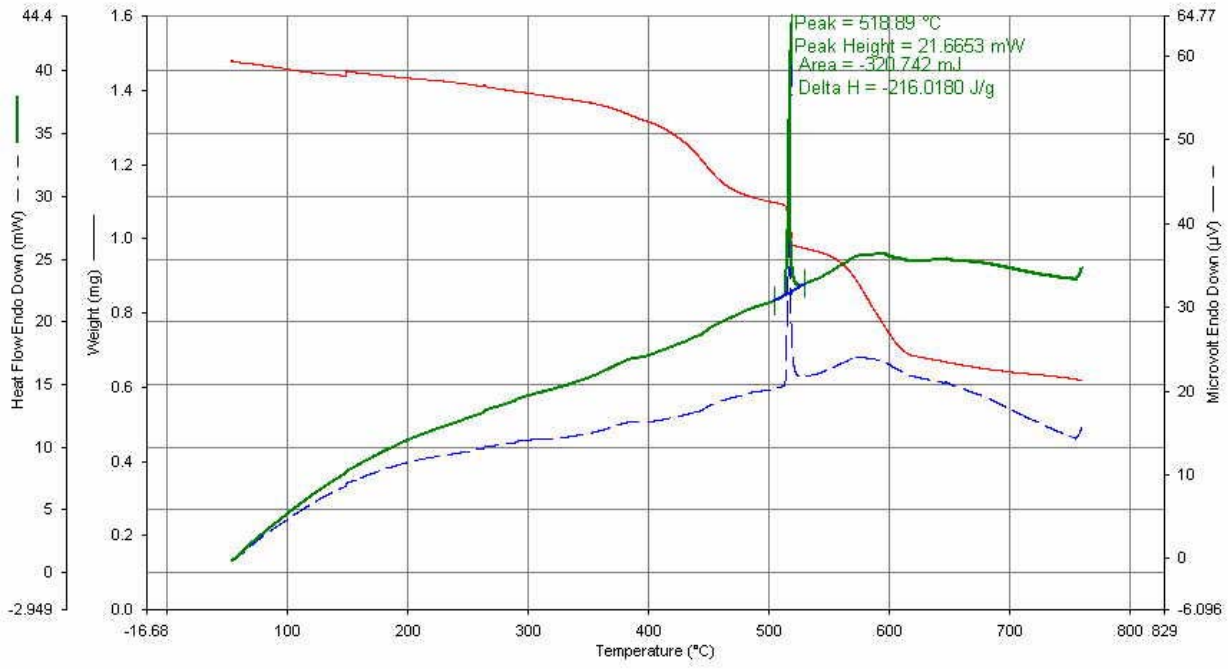
We also did storage stability (accelerated aging) studies on the RSF-2A, RSF-2B, and RSF-2C perchlorate-free compositions, as well as the in-service perchlorate-containing red Mk 66 composition. Such studies are an MPERC requirement for the scale-up of all new compositions. Each composition is placed into two sealed containers. One container is subjected to a minimum of 85 days of storage at 70 ^{o}C, while the other is kept at ambient temperature over the same time period. The elevated temperature is meant to simulate a five-year storage period at ambient temperature, assuming a doubling of the degradation reaction rate with each 10 ^{o}C rise in temperature.

Upon the completion of the 85-day storage stability study, simultaneous TGA/DTA thermal analysis run were performed on both the aged and the ambient samples of each composition. The resulting thermograms were then examined for any evidence of a significant change in the ignition temperature of each composition, or any other change in the general ignition behavior. Also, the thermograms were inspected for any evidence for the production of degradation products such as magnesium hydroxide ($Mg(OH)_2$), strontium nitrite ($Sr(NO_2)_2$ or calcium nitrite ($Ca(NO_2)_2$.

The ignition temperatures for the RSF-2A, RSF-2B, and RSF-2C compositions in Table 9 were determined using simultaneous DTA/DSC/TGA thermal analysis of sealed samples that had been aged for 87 days at 70 ^{o}C, as well as similar control samples that had been held at ambient conditions over the same period. Also included are an aged and a control sample of the in-service perchlorate-containing Mk 66 red composition for comparison purposes. Failure criteria for these storage stability tests are a significant change in either the ignition temperature or the ignitability of the aged sample as compared with the control sample. It is observed from Table 9 that there were no significant changes in the ignition temperature for the aged compositions. Furthermore, the actual simultaneous thermograms revealed no general changes in the ignitability or ignition behavior of the compositions upon aging. Also, they showed no evidence for the production of degradative aging products such as magnesium hydroxide, strontium nitrite or calcium nitrite according to reactions (1) and (2) below. Figure 10 is included to show the



(a) Unaged sample of 1.50 mg of RSF-2A composition with exotherm at 514 °C



(b) RSF-2A 1.49 mg sample aged 87 days at 70 °C with exotherm at 519 °C

Figure 13. Comparison of Simultaneous TGA/DTA Thermograms of Unaged and Aged (87 days at 70 °C) Samples of RSF-2A Composition

Table 9. Decompositon Exotherm Temperatures from Simultaneous DSC/DTA/TGA Thermograms of Aged and Unaged Perchlorate-Free Compositions

Composition	Aged at 70 °C Temperature, °C	Unaged Temperature, °C
RSF-2A	514	519
RSF-2B	518	518
RSF-2C	517	523
Mk 66 Red Std	489	485
GSF-1E	523	523
GSF-4K	483	482
Mk 117 Green Std	494	490

thermograms obtained from the control (un-aged) and aged samples of the RSF-2A composition. Although not shown, the corresponding thermograms obtained from the RSF-2B, RSF-2C and Mk 66 compositions were very similar.

It should be emphasized that these samples were in sealed containers during the accelerated aging period. This sealing effectively precludes additional water vapor from the ambient environment from interacting with the sample. However, if any of the ingredients in the composition (such as the hygroscopic calcium nitrate) has absorbed any ambient water vapor and converted it to waters of hydration (i.e. calcium nitrate tetrahydrate) during the mixing and curing operations, then it will be available for degradative aging of the composition during the storage stability tests. For magnesium/alkaline nitrate type flares such as these, the following degradative aging reactions can occur [18,19]:

$$Mg + 2\ H_2O = Mg(OH)_2 + H_2 \quad (1)$$

$$4\ Mg + Ca(NO_3)_2 .. 2\ H_2O + Sr(NO_3)_2 \ldots 2\ H_2O = 4\ Mg(OH)_2 + Ca(NO_2)_2 + Sr(NO_2)_2 \quad (2)$$

It is known that if the magnesium hydroxide degradation product is present in detectable quantities, it undergoes an endothermic decomposition reaction in the 350 ° - 400 °C temperature range as shown in reaction (3) below,[18]

$$Mg(OH)_2 = MgO + H_2O \quad (3)$$

Since no detectable decomposition endotherms attributable to the decomposition of magnesium hydroxide were observed in Figure 10, or in the corresponding thermograms for the RSF-2B and RSF-2C compositions, it may be concluded that it was *not* being formed as a detectable degradative aging product in reactions (1) and (2) during the storage stability sealed sample tests. By comparison, an earlier study[18] was easily able to detect the endotherm peaks when its magnesium/teflon/viton samples had undergone as little as 10% degradation to the magnesium hydroxide product. However, these storage stability test results do not necessarily imply that these compositions will not degrade if either the calcium nitrate ingredient or the red flare compositions made from it are not sealed off from moisture in the ambient environment during the manufacturing, storage and testing operations. Indeed, some of the laboratory and prototype scale performance test data that will be discussed shortly seem to suggest that degradative aging

may in fact have been occurring at some point before the flares were burned during the performance tests.

With all of the concerns of the MPERC having been successfully addressed, permission was granted for laboratory to prototype scale-up. Each prototype scale batch from which Mk 124 Mod 0 red flare pellets were pressed consisted of 450 grams of composition. Since these are curable compositions, the candles were pressed immediately upon completion of the mixing operation. The mixing and pressing of the RSF-2B composition took place on 22 May, the RSF-2C composition on 23 May, and the RSF-2A composition on 24 May 2006. 21 Candles each were pressed from the RSF-2A and RSF-2B compositions, and 20 candles were pressed from the RSF-2C composition.

These 62 candles were performance tested along side 10 in-service perchlorate-containing Mk 124 Mod 0 composition red candles used as comparison standards. The testing was carried out at the Crane Photometric Tunnel on 7 and 8 June 2006.

Table 10 shows the averaged results obtained from groups of 10 (or 11) RSF-2A, RSF-2B, and RSF-2C flares that were burned on each of the two days of testing.

Table 10. Averaged Performance Test Results of Standard Mk 124 and Perchlorate-Free Prototype Scale Red Signal Flare Compositions

June 7 Tests:

Flare	#Averaged	Dominant Wavelength, nm	%Color Purity	Candle Power, cd^{20}	Burn Time, sec
Mk 124 Std	4	612	88.4	4080	16
RSF-2A	11	614	72.4	1350	25
RSF-2B	11	619	60.4	990	26
RSF-2C	10	614	76.6	1900	24

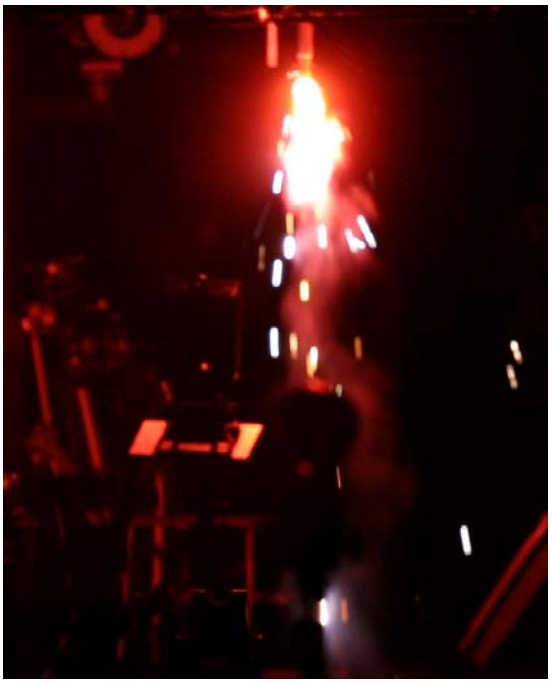
June 8 Tests:

Flare	#Averaged	Dominant Wavelength, nm	%Color Purity	Candle Power, cd^{20}	Burn Time, sec
Mk 124 Std	6	610	90.4	4030	16
RSF-2A	10	608	81.2	1130	25
RSF-2B	10	607	82.3	960	26
RSF-2C	10	606	87.0	3510	23

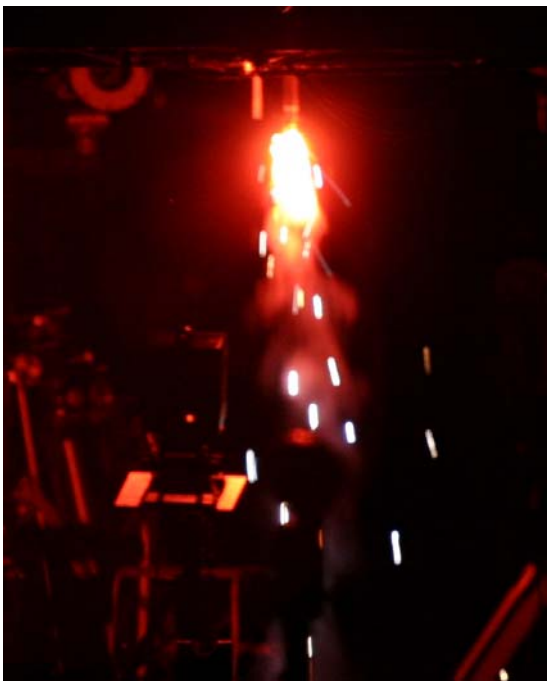
Representative digital photographs obtained from each of the three prototype scale perchlorate-free red compositions and the Mk 124 red composition are shown in Figure 14.

An examination of the detailed test data as well as the digital photographs indicates that the performance tests of the perchlorate-free red candles produced widely scattered Candle Power luminous intensity readings, ranging from less than 1000 to nearly 5000 candela. By contrast, the perchlorate-containing Mk 124 Mod 0 control standard candles produced much less scattered intensity readings generally ranging from approximately 3600 to 4200 candela. From Table 4 it

is seen that the Mk 124 Mod 0 flare specification calls for a minimum of 3500 candela. It is also apparent from the data that the intensities of the perchlorate-free compositions tended to be significantly higher on the second day of testing, June 8th. While the RSF-2A and RSF-2B candles were unable to attain the performance specification on both days of testing, 6 of 10 of the RSF-2C candles were just barely able to attain the performance specification with an average

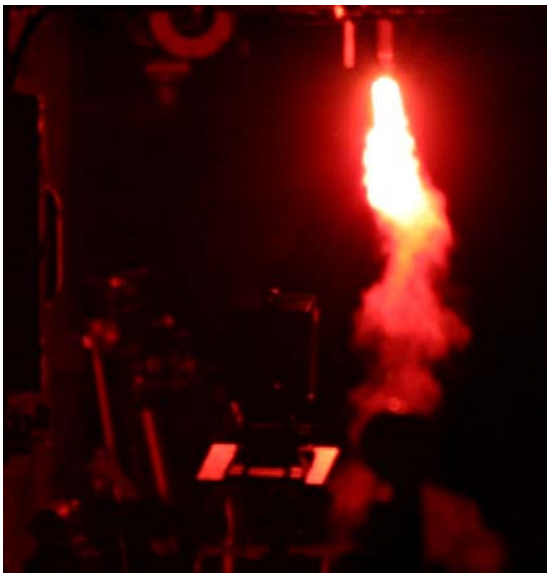


Perchlorate-Free RSF-2A Flare



Perchlorate-Free RSF-2B Flare

Perchlorate-Free RSF-2C Flare



In-Service Mk 124 Mod 0 Flare

Figure 14. Representative Digital Photographs of Prototype Scale RSF-2A, RSF-2B, RSF-2C, and Mk 124 Mod 0 Red Flares from 8 June 2006 Tests

value of 3510 candela on June 8th. The average value of their burn times was close to the upper limit of burn times in the performance specification at 23 seconds. All of the dominant wavelengths obtained were greater than 600 nm and hence met that specification. The average RSF-2C Color Purity for June 8th was 87 %, which is only one percent short of the 88 % in the specification. Since the control standard Mk 124 pellets without calcium nitrate in general produced consistently higher luminous intensities than any of the three perchlorate-free compositions with calcium nitrate, it seems reasonable to question whether the hygroscopicity of the calcium nitrate was responsible for the variable and generally lower luminous intensities. Also, the 23-25 second burn times of the perchlorate-free candles were significantly longer than the 16 second burn times of the Mk 124 pellets. This raised the question as to whether the Granulation 18 magnesium in the perchlorate-free pellets should be replaced with the smaller particle Granulation 15 magnesium that was used in the Mk 124 pellets.

Accordingly, a follow on test series was conducted in order to try to address the above two problem areas. This test series was conducted in mid-September 2006 and also included some green and yellow compositions. Specifically, RSF-2B' and RSF-2C' candles were prepared using the smaller Granulation 15 magnesium, as well as anhydrous calcium nitrate that had been pre-coated with 1 % by weight of palmitic acid by Kelvin Higa at the Naval Air Warfare Center (NAWC) at China Lake, California. For comparison purposes, a second RSF-2C composition used uncoated calcium nitrate along with Granulation 15 magnesium. These tests were performed at laboratory scale (15-gram pellets) with the understanding that they could be straightforwardly scaled to the Mk 124 prototype size if the results warranted. The results are summarized in Table 11. The results clearly show that the palmitic acid pre-coated candles definitely burned faster and at significantly higher intensity than did the composition containing the uncoated calcium nitrate. However, the results of this test series reveal that even the RSF-2C' composition with the Granulation 15 magnesium and the palmitic acid coated calcium nitrate may not be able to produce red candles that can *consistently* fulfill the performance specification of 3500 candela and pass all of the qualification tests. One problem was an indication of an incompatibility between the palmitic acid coating on the calcium nitrate and the epoxy binder constituents (Epon 813 and Versamid 140) that was drastically accelerating the curing process. This problem manifested itself by producing relatively high pressures as the newly press consolidated candles were being pushed out of the press tooling. Another problem was that even if the averaged Candle Power luminous intensity produced by the RSF-2C' composition candles was scaled by the difference in masses of the laboratory scale pellets and the Mk 124 prototype scale pellets (15 versus 21 grams), as well as the difference in pellet lengths (~1.28-inches versus ~0.87-inches) between the laboratory and prototype scale pellets, an estimated Candle Power of ~2500 candela would be obtained for prototype scale pellets which is significantly lower than the 3500 candela called out in the flare performance specification.

These persisting problems with the calcium nitrate containing compositions led us to question whether or not a flare composition with n*either* calcium nitrate *nor* potassium perchlorate ingredients could consistently satisfy all of the Mk 124 performance specifications. Fortunately, there is an Army in-service red star cluster composition that contains neither of these two ingredients. It is the M158 Ground Illumination Signal, Red Star Cluster. It contains only magnesium, strontium nitrate, polyvinyl chloride (PVC) and epoxy binder. When the dimensions

Table 11. September 2006 Performance Test Results of Perchlorate-Free Pellets with Granulation 15 Magnesium and with and without Palmitic Acid Pre-coated Calcium Nitrate

Composition	Pellet No.	X-bar	Y-bar	%Color Purity	Dominant Wavelength, nm	Candle Power (cd)[18]	Burn Time, sec
RSF-2B'	N-1	0.585	0.375	89	598	942	?
RSF-2B'	N-2	0.593	0.368	90	600	1110	26
RSF-2B'	N-3	0.588	0.370	89	599	838	26
RSF-2B'	Average	0.589	0.371	89	599	963	26
RSF-2C'	O-1	0.590	0.373	90	599	1070	24
RSF-2C'	O-2	0.598	0.367	91	600	1240	24
RSF-2C'	O-3	0.594	0.370	90	599	1200	22
RSF-2C'	Average	0.594	0.37	90	599	1170	23
RSF-2C	P-1	0.584	0.373	89	598	773	31
RSF-2C	P-2	0.591	0.367	89	600	871	31
RSF-2C	P-3	0.587	0.37	89	599	885	31
RSF-2C	Average	0.587	0.370	89	599	843	31

' Prime indicates 1 % Palmitic Acid Pre-Coating of Calcium Nitrate

of the two red flare candles as well as the burn times specified in the M158 and the Mk 124 performance specifications are considered, it appears that the burn rate of the M158 composition is only slightly slower than that of the Mk 124 composition. We are currently evaluating the performance of a variant of the perchlorate-free M158 composition at laboratory (15-gram pellets) scale. We are designating this M158 variant as the RSF-4 composition. In it, the Type I 30/50 mesh magnesium (MIL-P-14067) has been replaced with a 50/50 mixture of Type III Granulation 17 and Granulation 18 magnesium (MIL-M-382) in order to fine tune the burn rate as close as possible to that of the Mk 124 composition. Also the older less desirable Laminac/Lupersol DDM binder system has been replaced with the newer Epon 813/Versamid 140 epoxy binder system. Its burn rate has recently been measured to be only slightly slower than that of the Mk 124 red flare composition. Its Candle Power luminous intensity has been measured as being somewhat higher (approximately 2020 cd for the Mk 124 composition and 3120 cd for the RSF-4 composition), and its dominant wavelength and color purity are very similar to that of the Mk 124 composition, at approximately 616 nm and 91% Color Purity. Hence, when this RSF-4 composition is burned in the prototype scale 24-gram Mk 124 red flare hardware, there should be no difficulty in *consistently* attaining the Mk 124 flare performance specifications appearing in Table 4. The averaged burn rates, luminous intensities, dominant wavelengths and color purities obtained during the December 2006 performance test from both the Mk 124 standard flare composition and RSF-4 composition having both 50/50 and 40/60 mixtures of Granulation 17 and Granulation 18 magnesium are tabulated in Table 12.

Table 12. Averaged Performance Parameters of Lab Scale Flares of Mk 124 and Perchlorate-Free RSF-4 Red Compositions

Composition	Burn Rate (s/in)	Candle Power, cd^{20}	X-bar	Y-bar	Dominant Wavelength, nm	%Color Purity
Mk 124	17.5	2023	0.650	0.318	616	91
RSF-4 (50/50Variant)*	23.2	3126	0.648	0.317	616	91
RSF-4 (60/40Variant)*	22.8	3122	0.659	0.317	616	91

*Provides (Granulation 17 Magnesium/Granulation 18 Magnesium) Ratio

Green Signal Flare Compositions

Our first three perchlorate-free green signal flare compositions, GSF-1, GSF-2, and GSF-3, were also tested during the November 2003 test series. In these compositions, the removed potassium perchlorate was directly replaced with potassium nitrate. While retaining the other oxidizer, barium nitrate, boron fuel was added to the $Al_{0.5}Mg_{0.5}$ mechanical alloy fuel, or the $B_{0.5}Ti_{0.5}$ mechanical alloy was added to the conventional magnesium fuel. It is well known that boron-containing compositions typically produce a greenish flame due to the emission from boron oxides. A substitution of polytetrafluoroethylene (Teflon) for the polyvinyl chloride (PVC) color-enhancing ingredient was also made in all three of the compositions. Here it was hoped that the barium monofluoride (BaF) combustion product would produce green emission in much the same manner as the barium monochloride (BaCl) combustion product does when polyvinyl chloride is used.

In general the results of this first test series were disappointing. The submicron boron fuel tended to accelerate the burn rate of these compositions to the point that the minimum 20 second burn time in the Mk 117 and Mk 141 Green MSIS flare performance specifications could not be met. Also, the fast burn rates, and possibly the presence of the potassium nitrate ingredient, tended to make the flare plumes appear washed out (whitish green) in color. It was also determined that the BaF product species was not as intense an emitter as the BaCl species.

Accordingly, various adjustments were made on these perchlorate-free green compositions. Formualtions GSF-1A, GSF-1B, GSF-1C, GSF-4, and GSF-4A were prepared and tested in the second test series in April 2004. The Teflon and the $B_{0.5}Ti_{0.5}$ mechanical alloy were no longer ingredients. Teflon was replaced by the widely used PVC ingredient. A very low weight fraction of it was included in the GSF-1A, GSF-1B, and GSF-1C compositions, while an amount closer to that used in the Mk 117 composition was used in the GSF-4 and GSF-4A compositions. Similarly, both boron and potassium nitrate remained in the GSF-1A, GSF-1B, and GSF-1C compositions, but were removed from the GSF-4 and GSF-4A compositions, leaving barium nitrate as the sole oxidizer ingredient. Magnesium remained a fuel in all of the compositions. Either the $Al_{0.5}Mg_{0.5}$ or the $Al_{0.7}Mg_{0.3}$ mechanical alloys were included as a second fuel in all of the compositions except the GSF-4 composition. It turns out that the GSF-4 composition was the sole perchlorate-free composition that produced a burn rate very similar to that of the in-service perchlorate-containing Mk 117 composition. All of the other perchlorate-free green

compositions continued to be too fast burning. However, the dominant wavelength of GSF-4 was still somewhat more yellowish at approximately 572 nm than the Mk 117 composition at approximately 562 nm, and its color purity was slightly lower at 54% compared with 58% for the Mk 117 composition. To an observer, the GSF-4 composition produced the closest color match to the Mk 117 of all the perchlorate-free green compositions tested. However, the Mk 117 composition still produced a more vivid green.

The results of these November 2003 and April 2004 test series are summarized in Table 13. Clearly, the GSF-4 perchlorate-free candidate composition offered the most promise for eventual scale-up to the 110-gram prototype scale form factor green candle used in the Mk 117 and Mk 141 MSIS's. It is noted that the GSF-4 composition is quite similar to an in-service perchlorate-free composition used by the Army in the M125A1 Green Ground Illumination Signal.[6]

Table 13. Performance Test Results for Early Perchlorate-Free Green Flare Compositions – November 2003 and April 2004 Test Series

Formulation	Pellet No.	Burn Time (sec)	Average Candle-power, CP	X	Y	Dominant Wavelength nm	Color Purity %	Fuel make up	Fuel* Electr Sens, J	Scale -up
Mk 117 Std	A-2[f]	32	723	0.340	0.469	558	56			
	A-3[f]	32	612	0.370	.476	565	59			
GSF-1	M-2[i]	3.6	10200	-	-	-	-	B+	0.02	Opt[+]
	M-3[i]	3.6	9640	0.376	0.448	575.5	54	$Al_{0.5}Mg_{0.5}$		
GSF-1A	C-2[f]	5.5?	2376	0.423	0.424	578	59	B+	0.10	Y(2)
	C-3[f]	10	2336	0.377	0.455	568	55	Mg		
GSF-1B	D-1[f]	11.2	3103	0.385	0.403	575.5	54	B+ Mg+	0.02?	Y(3)
	D-2[f]	11.4	2839	0.409	0.412	577	54	$Al_{0.5}Mg_{0.5}$		
	D-3[f]	11.5	2723	0.415	0.417	578	55			
GSF-1C	F-1[f]	12.9	1576	0.410	0.428	575.8	57	B+ Mg+	0.02?	N
	F-2[f]	13	1483	0.427	0.419	579	59	$Al_{0.5}Mg_{0.5}$		
	F-3[f]	12.5	1564	0.425	0.423	578.5	59			
GSF-2	N-1[i]	3.4	6780	0.382	0.450	569	56	B+	0.02	N
	N-2[i]	3.4	7370	0.378	0.448	571.5	56	$Al_{0.5}Mg_{0.5}$		
	N-3[i]	3.8	6800	0.376	0.448	574.5	56			
GSF-3	O-1[i]	13	2010	0.399	0.421	575	51	Mg+	0.0002	N
	O-2[i]	13	2010	0.403	0.423	576	52	$B_{0.5}Ti_{0.5}$		
	O-3[i]	13	1780	0.409	0.420	576	52			
GSF-4	E-1[f]	31	1108	0.384	0.450	570	56	Mg	0.10	Y(1)
	E-2[f]	32	1279	0.404	0.423	576	54			
	E-3[f]	32	1053	0.394	0.450	571	58			
GSF-4A	H-1[f]	14.1	1312	0.423	0.412	577.5	61	Mg+	0.02?	N
	H-2[f]	14.6	1186	0.431	0.407	581	57	$Al_{0.7}Mg_{0.3}$		
	H-3[f]	14.5	1134	0.434	0.401	583	56			

Subsequent to the April 2004 performance tests of the above green compositions, the NASA Lewis Chemical Equilibrium code[14] was used in an attempt to maximize the yield from perchlorate-free green compositions of predicted combustion products that are efficient emitters in the green region of the spectrum. From approximately a dozen and a half compositions investigated, three of the most promising candidate compositions, GSF-1E, GSF-4D, and GSF-4K were chosen for performance testing. The GSF-1E composition contained a total of four fuels, the traditional Granulation 18 magnesium, the copper fuel that is also present in the in-service Mk 117 composition, amorphous boron , and the $Al_{0.5}Mg_{0.5}$ mechanical alloy. The

GSF-4D and GSF-4K contained only magnesium fuel. All compositions contained relatively high weight percentages of the barium nitrate oxidizer, nominal amounts of the polyvinyl chloride color-enhancing ingredient, and Epon 813/Versamid 140 epoxy binder. These three compositions were subjected to performance testing during December 2004 along with the in-service perchlorate-containing Mk 117 green flare composition and the results were quite encouraging. Table 14 shows the burn times, luminous intensity, dominant wavelength, and color purity of these four compositions. Similarly, Figure 15 shows typical digital photographs of the Mk 117 in-service composition, the two most attractive perchlorate-free compositions, GSF-1E and GSF-4K, and for the sake of comparison, an early relatively "washed out green" composition, GSF-1A. From Table 14, it is seen that all three of the new compositions had similar or higher luminous intensities as well as similar or slightly longer burn times. The dominant wavelength of the GSF-1E composition most closely approached that of the in-service

Table 14. Performance Test Results of Optimized Perchlorate-Free Green Flare Compositions – December 2004 Test Series

Composition	Pellet No.	Burn Time, sec	Average Candle Power, cd	Dominant Wavelength, nm	Color Purity %	Fuel Make-up	Ign. Sens., Joule*	Scale-up?
Mk117	E-1	29.6	~507	557	52	Cu +Mg	18	Standard
	E-2	29.9	732	548	52			
	E-3	28.9	680	555	51			
GSF-1E	D-1	32	769	551	54	Mg + B	0.002	Yes
	D-2	29.2	838	553	54	+ Cu +		Yes
	D-3	30.7	837	551	54	$Al_{0.5}Mg_{0.5}$		Yes
GSF-4K	B-1	39.6	852	557	56	Mg	18	Yes
	B-2	37.8	953	553	56			Yes
	B-3	36.2	763	559	60			Yes
GSF-4D	C-1	37.7	1289	556.5	54	Mg	18	No
	C-2	31.5	1835	559	50			No
	C-3	39	1345	563	58			No

*Electrostatic Ignition Sensitivity of most sensitive fuel ingredient

Mk 117 Std. Green

GSF-1B

GSF-4K

GSF-1E

Figure 15. Photographs of Mk 117 Standard and Perchlorate-Free Compositions GSF-1B (washed out), and GSF-4K and GSF-1E (optimized)

Mk 117 composition (552 nm versus 553 nm). The other two compositions had slightly higher dominant wavelengths and hence were slightly more "yellowish green" (556 nm for the GSF-4K and 560 nm for the GSF-4D). Color purities were reasonably similar for all four compositions tested, ranging from approximately 50 – 60%, which is within the flare performance specification for the Mk 117. Because of its performance parameters and its green appearance in the digital photographs, the GSF-1E composition was selected as the primary scale-up candidate for evaluation in the prototype scale 110-gram Mk 117/Mk 141 green flare form factor. The GSF-4K composition was selected as the secondary scale-up candidate.

The only further performance testing on the perchlorate-free green scale-up candidate compositions during the final year of the project involved variations in the fuel particle size distributions. Specifically, during the September 2006 test series, laboratory scale GSF-1E and GSF-4K flare pellets were mixed and performance tested with varying percentages of the smaller particle Granulation 15 magnesium used in place of the $Al_{0.5}Mg_{0.5}$ mechanical alloy and the larger particle Granulation 18 magnesium that had been used in the earlier reported testing. Here the aim was to fine tune the burn rate of these perchlorate-free compositions so that they would closely match the burn rate of the in-service perchlorate-containing compositions in the Mk 117 Green MSIS, as well as in its Product Improvement, the Mk 141 Green MSIS, which uses the same composition. The results are summarized in Table 15. It is seen that Composition GSF-1E1 produced a very similar burn time and slightly higher luminous intensity (CP) than did the in-service perchlorate-containing Mk 141 composition. Accordingly, it will be the composition recommended for scale-up to the Mk 141 MSIS green flare 110-gram form factor. With the Granulation 15 magnesium replacing the $Al_{0.5}Mg_{0.5}$ mechanical alloy, both the flare cost and the electrostatic ignition sensitivity concerns will be reduced. This in turn should help expedite approval for scale-up, and should also result in a more favorable cost benefit comparison with the in-service Mk 141 Green MSIS.

Table 15. Summary of Averaged Green Flare Performance Test Data of September 2006

Composition	Magnesium Granulation	Candle Power, cd	% Color Purity	Dominant Wavelength, nm	Burn Time, s
GSF-1E1	33%GR15+67%GR18	763	54	547	31
GSF-1E2	50%GR15+50%GR18	794	55	547	27
GSF-1E3	67%GR15+33%GR18	1113	56	546	21
GSF-1E4	100%GR15	1587	52	550	17
GSF-4K1	33%GR15+67%GR18	870	62	555	26
GSF-4K2	50%GR15+50%GR18	1073	63	556	22
GSF-4K3	67%GR15+33%GR18	1277	63	556	20
GSF-4K4	100%GR15	1690	66	556	18
Mk 141 STD	100% GR18	526	48	544	30

Since there is expressed interest on the part of the Army's Project Manager for Close Combat Systems (PM-CCS) in our perchlorate-free compositions as replacements for the perchlorate containing compositions used in the Mk 80 red and Mk 110 green Pen Flares, we also foresee a

need for a somewhat faster burning green composition. It is felt that either the GSF-1E4 or GSF-4K4 compositions offer considerable promise for use in the green Pen Flare. The performance specifications of these two tiny 3-gram flares call for relatively intense and fast burning compositions. That is why the green flare compositions with the highest percentage of the smaller particle Granulation 15 magnesium are ideal for this application.

Yellow Signal Flare Compositions

In response to a February 2006 request from a potential customer, the Navy's Conventional Ammunition and Night Vision Program Office, PEO-IWS3C/PM-415, laboratory scale yellow signal flare compositions have also been investigated. Here the aim is to formulate a perchlorate-free yellow composition to replace the in-service perchlorate-containing composition in the Mk 118 MSIS, as well as in its Product Improvement replacement, the Mk 144 MSIS, which uses the same composition.

NASA Lewis Chemical Equilibrium modeling[14] was used for optimization of perchlorate-free yellow compositions which contain combinations of magnesium fuel, sodium nitrate and barium nitrate oxidizers, polyvinyl chloride for color enhancement, and the Epon 813/Versamid 140 binder. Here the chemistry is reasonably similar to that of the green signal flare, except that intense orange-yellow sodium D-line radiation at 589 nm is required in addition to green radiation from emitters such as BaCl and BaOH. A total of eight yellow compositions were modeled to determine their predicted product distributions and adiabatic combustion temperatures. It should be noted that with these perchlorate-free and sodium oxalate-free compositions, an additional benefit was that the predicted yields of the environmentally objectionable cyanide salt products such as NaCN and HCN, were either drastically reduced relative to the in-service Mk 144 composition or eliminated altogether. From these NASA Lewis predictions, compositions YSF-1, YSF-3, and YSF-8 were chosen for mixing and performance testing. Granulation 18 magnesium was used in the yellow candles tested during the 7 and 8 June test series. Since all of the burn times were longer than that produced by the baseline perchlorate-containing Mk 144 yellow composition, a second batch of compositions containing the smaller particle Granulation 15 magnesium was prepared and performance tested on 21 June. The burn times obtained in this test series were all significantly shorter than the Mk 144 baseline composition. Table 16 has been included to summarize the averaged results obtained from both test series. From a comparison of the results, it was obvious that either a *mixture* of the larger and smaller magnesium granulations, or possibly exclusive use of the intermediate particle size Granulation 17 magnesium would be required to closely match the Mk 144 burn time. It is also apparent that the luminous intensities of the perchlorate-free compositions tended to be slightly higher than the baseline standard composition. The dominant wavelengths and color purities of the perchlorate-free compositions also appeared to be within the performance specification given in Table 4. In fact, due to the slightly lower dominant wavelengths of the perchlorate-free compositions, the flames appeared somewhat more yellow than the baseline composition to an observer. This is illustrated in Figure 16 in which a digital photograph of a burning YSF-8 composition flare is compared with that of a Mk 144 composition flare. The other two tested compositions, YSF-1 and YSF-3, had generally similar visual appearance as the YSF-8 composition.

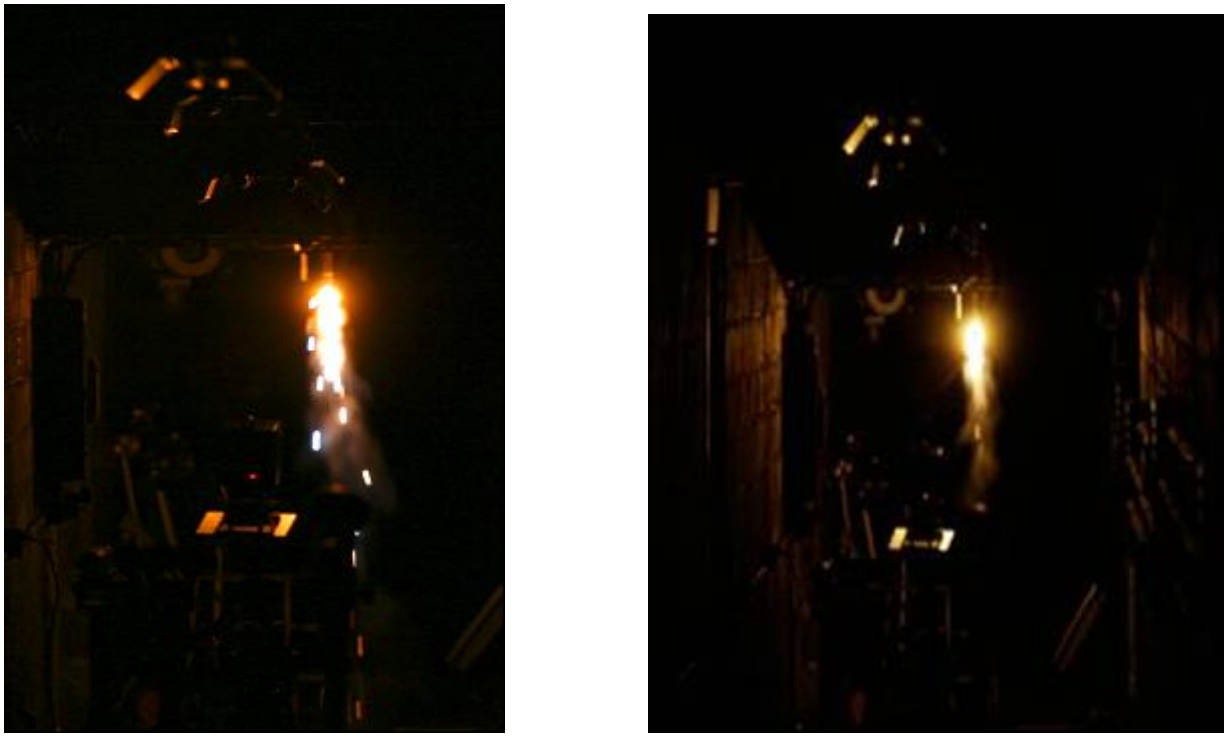
Table 16. Lab Scale Performance Test Results for Perchlorate-Free Yellow Signal Flare Compositions

Granulation 18 – Larger Magnesium Particles

Flare	#Flares Averaged	Color Purity %	Dominant Wavelength	Candle Power, cd	Burn Time, s	Scale-Up?
Mk 144	6	76.1	586 nm	1184	~45	Std
YSF-1	6	77.3	583 nm	1442	51	Yes
YSF-3	6	78.4	585 nm	1357	52	Yes
YSF-8	6	75.3	583 nm	1571	59	Yes

Granulation 15 – Smaller Magnesium Particles

Flare	#Flares Averaged	Color Purity %	Dominant Wavelength	Candle Power, cd	Burn Time, s	Scale-Up?
YSF-1	3	89	582 nm	2140	26	Yes
YSF-3	3	90	584 nm	2630	26	Yes
YSF-8	3	87	582 nm	3805	26	Yes



Mk 144 Standard Yellow **YSF-8 Perchlorate-Free Yellow**

Figure 16. Comparison of Digital Photographs of Burning Mk 144 Standard Yellow Flare Composition and YSF-8 Perchlorate-Free Yellow Flare Composition

In an effort to obtain a better match with the Mk 144 burn time, YSF-1, YSF-3 and YSF-8 compositions containing 60% of Granulation 15 magnesium and 40% of Granulation 18 magnesium were burned during the September 2006 performance test series. The averaged results for each composition are shown in Table 17. The results are seen to be quite encouraging when compared with the Mk 144 standard composition. Since the YSF-8 composition had the highest luminous intensity and the closest match in burn time with the Mk 144 composition, it was chosen as the primary candidate for prototype scale testing in the Mk 144 form factor.

Table 17. Averaged Results of September 2006 Performance Tests of Yellow Signal Flare Compositions and Mk 144 Yellow Baseline Compositions

Composition	Magnesium Granulation	% Color Purity	Dominant Wavelength, nm	Candle Power, cd	Burn Time, sec
YSF-1	60%GR15+40%GR18	86	578	1648	26
YSF-3	60%GR15+40%GR18	89	579	2152	32
YSF-8	60%GR15+40%GR18	84	578	2662	34
Mk 144 STD	100%GR18	89	581	1525	38

Ignition sensitivity measurements were also performed on the YSF-1, YSF-3, and YSF-8 compositions. As seen in Table 18, which also includes sensitivity measurements on the GSF-1E and GSF-4K green flare candidates, no dangerously high ignition sensitivities were observed. Impact sensitivities were very low, friction sensitivities were moderate, and the electrostatic sensitivities were high for the YSF-1 and YSF-3 compositions, but moderate for the YSF-8 composition. In general, the yellow compositions tended to be slightly less ignition sensitive than the green compositions.

Table 18. Results of Ignition Sensitivity Tests on Yellow and Green Signal Flare Compositions

Sample	Impact Sensitivity		Friction Sensitivity			Electrostatic Sensitivity
	50% fire		Energy (ft-lb)		Response	Maximum No Fire
	Height (cm)	Energy (J)	Average	Lowest		Energy (Joules)
RDX Class5 - Standard	49.84	9.77	1162.81	916.93	No Response	0.151
Mk 141 Green Standard	91.01	17.84	103.49	29.67	100% Fired	0.250
GSF-1E	133.72	26.21	1134.26	199.42	80% Fired	0.180
GSF-4K	59.73	11.71	445.66	81.26	80% Fired	0.180
Mk 144 Yellow Standard	174.45	34.19	611.47	191.40	90% Fired	0.180
YSF-1	172.71	33.85	750.03	266.41	90% Fired	0.200
YSF-3	176.35	34.56	1152.60	109.06	70% Fired	0.800
YSF-8	178.40	34.97	730.75	188.73	70% Fired	1.250
Fuels						
$Mg_{0.5}Al_{0.5}$	159.00	31.17	N/A	997.11	N/A	0.002
$Mg_{0.5}Al_{0.5}$-17.9% Epoxy	178.40	34.97	1399.48	357.11	10% Fired	0.450
$Mg_{0.5}Al_{0.5}$-52.1%Epoxy	178.40	34.97	1520.94	1357.91	0% Fired	0.180

Dangerous High Moderate Low Very Low

Conclusions

During this final year of the project, we have extended our study of perchlorate-free spectrally balanced decoy flares to include compositions that have organic fuel ingredients only. Unlike the mixed metal and organic fueled perchlorate-free compositions tested during 2005, which are similar in spectral ratio to the in-service type of perchlorate-containing spectrally balanced flare, the proposed new compositions more closely resemble the newer developmental type of perchlorate-containing spectrally balanced flare composition. It is this newer developmental type of flare that is capable of producing the highest possible infrared spectral ratios that are necessary to provide adequate protection of high speed/high signature fighter type aircraft from the most sophisticated infrared guided missile threats. Specifically, we utilized NASA Lewis Chemical Equilibrium computer modeling[14] to simulate a number of perchlorate-free compositions that contain potassium nitrate oxidizer, miscellaneous other additives, and exclusively organic fuels including pyromellitic dianhydride (PMDA). The predicted yields of products which are efficient emitters in the sought after longer wavelength infrared band are comparable with those predicted for perchlorate-containing compositions. The only shortfall seems to be the lower predicted adiabatic combustion temperature of the perchlorate-free compositions. However, through judicious choice of ingredients we have been able to raise the temperature to near 2000 ^{o}K. This is roughly comparable to the combustion temperatures predicted for the metal/PMDA-containing perchlorate-free compositions that were performance tested during 2005. The next step will be to secure funding to actually test these newly formulated compositions at laboratory scale and compare them with the original SB-43 composition, as well as with the compositions that are used in the newer developmental type of decoy flare.

While the newer of the two types of spectrally balanced flares is a definite necessity for the self-protection of high signature/high speed fighter type aircraft, it is conceivable that the older of the two types may be adequate for the protection of low speed/low signature platforms such as helicopters. From the performance testing conducted during 2005, the perchlorate-free compositions with a mixture of metal and PMDA fuels appear to match the performance in terms of LWIR output intensity and (LWIR/SWIR) spectral ratio of this older type of spectrally balanced flare. Therefore, potential customers for these perchlorate-free metal/organic and organic fueled compositions could include the Army as well as the Navy/Marine Corps. Accordingly, we will be attempting to secure cooperative funding for these efforts with these individual service sponsors and ESTCP.

It is noted that none of these perchlorate-free spectrally balanced flare compositions contain any extraordinarily expensive ingredients. The most expensive ingredient is the ultrafine Electro-Exploded Aluminum (ALEX) that is present in the metal/organic fueled compositions. All of the other ingredients are competitive in cost with the ingredients of the perchlorate-containing in-service composition. ALEX is currently priced close to $500 per kilogram. Also, an additional step must be inserted into the manufacturing process in order to pre-coat the ALEX ingredient with viton binder in order to mitigate its dangerously high electrostatic ignition sensitivity. However, the weight percentage of ALEX in the compositions is quite low. According, it is estimated that the perchlorate-free metal/organic compositions would cost approximately 50%

more to manufacture than the in-service metal fueled composition. Obviously, the perchlorate-free compositions with no metallic ingredients will be very similar (no more than a 10 – 25 % increase) in ingredient cost when compared with the corresponding in-service perchlorate-containing composition.

We have also identified and carried out performance testing with both laboratory and prototype size form factors of the three perchlorate-free red flare compositions, RSF-2A, RSF-2B, and RSF-2C. This has included the successful completion of the 87-day storage stability (accelerated aging) tests of the three compositions at 70 ^{o}C. The ignition temperature of the aged compositions did not change significantly, and no evidence for the production of degradation products such as magnesium hydroxide, calcium nitrite or strontium nitrite appeared on the simultaneous DTA/TGA thermograms. Also compatibility studies were successfully performed on the three compositions. It was verified that there was no detectable incompatibility between each of the three new perchlorate-free compositions and either the IM-6 ignition composition or the Starter Slurry composition. With these accelerated aging and compatibility tests successfully completed, our local safety board permitted us to produce and test these three perchlorate-free compositions in the 24-gram Mk 124 Mod 0 red flare form factor. They were tested along with the in-service Mk 124 Mod 0 red flares for comparison purposes. On the first of two days of testing, all of the candles successfully functioned and produced brilliant red flare plumes with dominant wavelengths within the flare performance specification. However, the Candle Power luminous intensities were quite variable and were generally significantly below the 3500 candela level in the Mk 124 flare performance specification. Burn times were generally longer than the in-service flare. However, on the second day of testing, 6 out of 10 of the RSF-2C flares tested just barely achieved the required luminous intensity, burn time and color purity of the flare performance specification. Subsequently, we looked into ways to improve the luminous intensity performance of the perchlorate-free flares. During September 2006, RSF-2B' and RSF-2C' flares with the smaller particle Granulation 15 magnesium and with a 1% by weight palmitic acid coating on the hygroscopic calcium nitrate ingredient were tested. The luminous intensities increased somewhat, but not enough to ensure consistent production of the 3500 candela luminous intensity in the flare performance specification. There was also an apparent incompatibility between the palmitic acid coating and the epoxy binder constituent that caused a rather drastic decrease in the cure time of the epoxy. This is a definite safety issue during the press consolidation and pellet push out operations.

Since the composition used in the Army's in-service M158 Ground Illumination Signal, Red Star Cluster contains only magnesium, strontium nitrate, polyvinyl chloride and epoxy binder, and *no perchlorate or calcium nitrate* oxidizers, a close variant of this composition is also being evaluated for use as a perchlorate-free Mk 124 red flare. It is designated as the RSF-4 composition. Its burn rate was measured during November 2006 and found to be only slightly slower than that of the Mk 124. The performance characteristics were measured in a December 2006 test of laboratory scale flare pellets and found to compare very favorably with the in service Mk 124 composition. In fact, the average luminous intensity of the RSF-4 composition was approximately 55% higher than that of the Mk 124 composition (3120 cd versus 2020 cd). In light of these favorable performance test results of this RSF-4 composition, we plan to perform Mk 124 red flare prototype scale performance testing on this composition, and then proceed to

conduct the requisite formulation qualification, final type qualification, and techeval testing under ESTCP funding..

The GSF-1E and GSF-4K perchlorate-free green compositions that had been formulated with the help of chemical equilibrium modeling[14] and successfully performance tested at laboratory scale during December 2004, were found to compare quite favorably in terms of Candle Power luminous intensity, dominant wavelength and color purity with the in-service perchlorate-containing composition in the green Mk 117 and Mk 141 MSIS's. However, during the final year of the project, optimization efforts have led to the selection of the GSF-1E1 composition as the primary scale-up candidate for the Mk 141 green flare candle. Rather than the GSF-1E fuel mixture consisting of Granulation 18 magnesium and a small percentage of the $Al_{0.5}Mg_{0.5}$ mechanical alloy from NJIT, the GSF-1E1 composition contains a fuel mixture of 33% by weight of Granulation 15 magnesium and 67% of Granulation 18 magnesium, and no mechanical alloy. This optimized GSF-1E1 scale-up composition had an almost identical burn rate as the Mk 141 in-service composition, and should offer considerable cost and electrostatic ignition sensitivity safety advantages over the GSF-1E composition. However, the actual scale-up to the 110-gram Mk 141 green candle form factor, flare fabrication, and performance testing will have to await future cooperative funding from ESTCP and/or a potential service customer such as the Navy's 2T Cog Conventional Ammunition and Night Vision Program Office, Code PEO-IWS3C/PM4. The successful composition would also have to undergo formulation qualification, final type qualification, and techeval testing prior to its introduction into the service inventories.

Finally, in response to a Navy customer who is interested in replacing the perchlorate in red, green and yellow signal flares, we have recently formulated and performance tested at laboratory scale, three perchlorate-free yellow flare compositions designated YSF-1, YSF-3, and YSF-8. They contain optimized mixtures of magnesium, barium nitrate, polyvinyl chloride, sodium nitrate, and epoxy binder. The in-service perchlorate-containing yellow Mk 144 MSIS composition was tested alongside for comparison purposes. It should be noted that in addition to removing the perchlorate, sodium nitrate was substituted for the sodium oxalate ingredient in the Mk 144. This has the added advantage that the predicted yields of environmentally objectionable cyanide combustion products such as NaCN and HCN are either greatly reduced or totally eliminated. The measured performance test results in terms of Candle Power luminous intensity, burn time, dominant wavelength, and color purity compared very well with the perchlorate-containing Mk 144 composition. To an observer, the perchorate-free compositions appeared slightly more yellow in color than the perchlorate-containing Mk 144 composition which was more orange in color. The YSF-8 composition was chosen as the primary scale-up candidate owing to its high luminous intensity, favorable color characteristics, and a burn rate very similar to the Mk 144 composition. As with the similar perchlorate-free green composition, we continue to seek cooperative funding from such sources as ESTCP and the PM4 office for scale-up to the prototype Mk 144 MSIS yellow flare form factor which is also a 110-gram yellow flare candle. Also, as with the green flare, performance testing, formulation qualification, final type qualification, and techeval testing would then need to be performed prior to the introduction of this item into the service inventories.

It is noted that none of the perchlorate-free red, green and yellow candidate compositions, RSF-4, the GSF-1E1 and the YSF-8, have any exotic or extraordinarily expensive ingredients. For the

most part, they have been developed by removing the perchlorate from in-service compositions and readjusting the weight percentages and particle size distributions of the remaining ingredients. The only exceptions to this are the small amount of boron fuel that is substituted for a portion of the magnesium fuel in the green composition, and the sodium nitrate that is substituted for the sodium oxalate in the yellow flare. Therefore, it is estimated that the manufacturing costs for these perchlorate-free red, green and yellow signal flares will not increase significantly (i.e. more than 10 – 25%) relative to the corresponding in-service flares.

When one considers the economic impact of the perchlorate remediation costs once the perchlorate action level has been reached in the ground water at a contaminated site, the perchlorate-free spectrally balanced flare and red, green and yellow signal flare compositions would certainly be favored on a "cradle to-grave" cost comparison basis.

Let us take the example of the Mk 124 Mod 0 Red MSIS unit that presently costs approximately $60 and might be expected to cost approximately $75 for a perchlorate-free version. Despite this slight price increase for the ingredients in the perchlorate-free compositions, money will actually be saved over the life cycle of the new red flares (cradle to grave). This is because of the typical multi-million dollar price tag associated with the cleanup, remediation and monitoring costs of a typical perchlorate-contaminated training or testing range covering extensive acreage and containing millions of gallons of contaminated ground water. There are a large number of factors that influence the clean up cost for such contaminated sites including the chemical and biological nature of the remediating agent, the permeability of the soil, the depth and the total quantity of the water table at the contaminated site, and the set up (capital) and annual operating costs of the remediation system. In general, two types of remediation are in widespread use, chemical anion exchange resin systems and systems involving biodegradation pathways. Fortunately, a recently completed ESTCP Project, No.ER-0221, 'Edible Oil Barriers for Treatment of Perchlorate Contaminated Groundwater" included a cost analysis in their final report which can serve as a typical example. The goal of their Emulsified Oil Substrate (EOS®) injection was to create a reducing zone conducive to anaerobic biodegradation of perchlorate and chlorinated solvents at their contaminated ground water site in Maryland. They constructed a pilot scale EOS barrier at the contaminated site which they estimated had a 2-year life time. Based upon their installation and operational cost, they estimated their treatment cost to be either $46 per square foot of barrier, or $0.13 per gallon of treated water. However, they felt they could reduce these costs to approximately $19 per square foot of barrier and $0.02 per gallon of treated water in a full scale EOS barrier system. However, even with the full scale system, clean up costs could easily reach the million dollar level at a site containing millions of gallons of contaminated ground water.[21] Another ESTCP funded program, "Ammonium Perchlorate Biodegradation for Industrial Wastewater Treatment" (ER-9710) similarly estimated a biodegradation-based perchlorate treatment cost "less than $0.10 per gallon" in their final report.[22] Accordingly, we can calculate that if one million dollars could be saved in the clean-up, remediation and monitoring costs incurred at one or more perchlorate contaminated test sites, that money could be used to cover the increased price of up to 66,000 of the perchlorate-free Mk 124 Mod 0 MSIS units.

It must be emphasized that the *pace* of the transition process and the availability of cooperative funding for the qualification and techeval testing that is required in order to introduce these

perchlorate-free flares into the service inventories will be strongly dependent on how quickly and at what concentration the final perchlorate action levels are promulgated by the EPA and the individual states. What is critically needed are action levels that are low enough to prompt DOD policy makers to mandate perchlorate replacement programs for the widely used pyrotechnic-based munitions used for training and warfighter support. Such actions have been suggested in general terms in a recent DOD report to Congress, but have to date been accomplished for only a very few perchlorate-containing items. The report does point out that on-going DOD-sponsored studies have already identified several additional types of pyrotechnic and rocket propellant compositions that are amenable to perchlorate replacement, and that these compositions are awaiting DOD mandates so that they may be introduced into the service inventories as product improvement programs.[23]

Therefore, the red, green and yellow Marine Smoke and Illumination Signals discussed in this report, such as the Mk 124, the Mk 141, and the Mk 144, should be regarded only as *examples* of abundant colored signal devices in the service inventories. There are many additional similar devices that will ultimately need to be converted to perchlorate-free pyrotechnic compositions. Many of them are similar pyrotechnic devices with larger flare form factors such as the Mk 1 Mod 1 Red (55 grams), the Mk 146 Green (315 grams), and the Mk 147 Yellow (315 grams) MSIS's. It is planned to seek future cooperative funding for perchlorate-replacement in these devices as well. However, their larger size will necessitate additional scale-up steps. Furthermore, these larger units tend to have substantially higher price unit prices (often in excess of $1,000) than the smaller devices.

References

1) D. A. Anders, "Risk Communication: Perchlorate and its Significance to You", Technical Session 4B, Perchlorate Monitoring and Treatment, Program Guide of the SERDP/ESTCP Partners in Environmental Technology Technical Symposium and Workshop, 2-4 December 2003, Washington DC, p. 84.

2) C. Hogue, "Federal Policy on Perchlorate Evolves – EPA, FDA, and military continue work on assessing and cleaning up contaminant", *Chemical & Engineering News*, On-line Edition, 21 September 2005.

3) Massachusetts Department of Environmental Protection – News Release of July 28, 2006, "Massachusetts First-in-Nation Perchlorate Standards Take Effect Today – Drinking Water, Cleanup Standard of 2 ppb Are Set to Protect Public Health".

4) California Code of Regulations, Title 22, Chapter 15, July 14, 2006.

5) Memorandum of the Office of the Under Secretary of Defense, Jan. 26, 2006, "Policy on DOD Required Actions Related to Perchlorate".

6) Technical Manual NAVSEA SW050-AC-ORD-10, *Ordnance Data for Toxic Hazards Associated with Pyrotechnic Devices*, Second Revision, 10 July 2001.

7) J. S. Benjamin, Metal Powder Rept., 45, 122 (1990).

8) C. E. Wen, K. Kobayashi, A. Sugiyama, T. Nishio, and A. Matsumoto, Journal of Materials Science, 35, 2099-2104 (2000).

9) M. Schoenitz and E. L. Dreizin, "Structure and Properties of Al-Mg Alloys", *J. of Materials Research, 18(8)*, 2003, pp 1827-1836.

10) M. A. Trunov, M. Shoenitz, and E. L. Dreizin, "Ignition of Al-Mg Mechanical Alloys", *2003 Technical Meeting of Eastern States Section of the Combustion Institute*, University Park, PA, 29 October 2003, pp 313-316.

11) M. Schoenitz and E. L. Dreizin "Consolidated Energetic Nanocomposites: Mechanical And Reactive Properties", *Proceedings Of Thirty-Sixth Annual Conference of I.C.T. and Thirty-Second International Pyrotechnics Seminar*, 28 June-1 July 2005, Karlsruhe, Federal Republic of Germany, Poster 133.

12) Edward L. Dreizin, Mirko Schoenitz, Yuriy L. Shoshin, Mikhaylo A. Trunov, Swati Umbrajkar, Trent S. Ward and Xiaoying Zhu, "Highly Energetic Nanocomposite Powders Produced By Arrested Reactive Milling", *Proceedings of Thirty-Sixth Annual Conference of I.C.T. and Thirty-Second International Pyrotechnics Seminar*, 28 June-1 July 2005, Karlsruhe, Federal Republic of Germany, Poster 138.

13) T. S. Ward, W. Chen, M. Schoenitz, R. N. Dave, and E. L. Dreizin, "A Study of Mechanical Alloying Processes using Reactive Milling and Discrete Element Modeling", accepted by *Acta Materialia*, *53* (2005) , pp. 2909-2918.

14) Bonnie J. Mc Bride and Sanford Gordon, *Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications, II. Users Manual and Program Description*, NASA Reference Publication 1311, 1996.

15) *Military Standard, Safety and Performance Tests for Qualification of Explosives, MIL-STD-1751 (USAF)*, 20 August 1982.

16) *Chemical Compatibility of Ammunition Components with Explosives (Non-Nuclear Applications)*, *STANAG 4147* (Edition 2) dated 5 June 2001.

17) P. L. Posson and A. J. Baggett, Jr., "Pyrotechnic Compositions and Uses Therefore", U.S. Patent No. 6,427,599, granted August 6, 2002.

18) S. K. Poehlein, R. G. Shortridge, and D. E. Stark, "Engineering Investigation into Ignition Malfunction of In-Service Decoy Flares and Related Degradative Aging Studies", *Fifth International Symposium on the Heat Flow Calorimetry of Energetic Materials*, Indianapolis, IN, 12-15 September 2005.

19) T. Griffiths, "The Role of Strontium Nitrite in the Aging of the Magnesium-Strontium Nitrate Pyrotechnic System", *Fifth International Symposium on the Heat Flow Calorimetry of Energetic Materials*, Indianapolis, IN, 12-15 September 2005.

20) A. Stimson, Photometry and Radiometry for Engineers, John Wiley and Sons, New York, 1974, p. 346. (Defines Candlepower as luminous intensity expressed in candelas (cd), where the candela is defined as, $1cd = 1\ lm\ sr^{-1}$.)

21) R. C. Bordern, C. E. Zawtocki, M. T. Lieberman, "Edible Oil Barriers for Treatment of Perchlorate Contaminated Groundwater", Final Report for ESTCP Project No. ER-0221, 16 February 2006.

22) "Final Report: Operational Implementation of Ammonium Perchlorate Biodegradation", Air Force Research Laboratory, Airbase & Environmental Technology Division, Final Report for ESTCP Project No. ER-9710, 19 June 1998.

23)"Report to the Congress: Perchlorate in the Southwestern United States," Office of the Secreatary of Defense, Undersecretary of Defense (Acquisition, Technology & Logistics), July 2005.

Appendix B

List of Technical Publications

1) Journal Articles

1. M. A. Trunov, M. Schoenitz, E. L. Dreizin, "Effect of Polymorphic Phase Transformations in Alumina Layer on Ignition of Aluminum Particles", *Combustion Theory and Modeling,* 10 (4), pp. 603-624 (2006)

2. A. Ermoline, M. Schoenitz, E. L. Dreizin, "High Temperature Phase Equilibria in the System Zr-O-N", *J. Materials Research,* 21 (2), pp. 220-228 (2006)

3) T. S. Ward, W.Chen, M. Shoenitz, R. N. Dave, and E. L. Dreizin, "A Study of Mechanical Alloying Processes Using Reactive Milling and Discrete Element Modeling", *Acta Materialia,* 53, pp. 2909-2918 (2005)

4) M. Schoenitz, X. Zhu, and E. L. Dreizin, "Carbide Formation in Al-Ti Mechanical Alloys", *Scripta Materialia,* 53 (9), pp. 1095-1099 (2005)

5) S. M. Umbrajkar, M. Schoenitz, S. R; Jones, and E. L. Dreizin, "Effect of Temperature on Synthesis and Properties of Aluminum-Magnesium Mechanical Alloys", *Journal of Alloys and Compounds,* 40, (1-2), pp. 70-77 (2005)

6) M. Schoenitz and E. L. Dreizin, "Oxidation Processes and Phase Changes in Metastable Al-Mg Alloys", *Journal of Propulsion and Power,* 20 (6), pp. 1064-1068 (November 2004)

7) M. Schoenitz, X. Zhu, and E. L. Dreizin, "Mechanical Alloys in the Al-rich Part of the Al-Ti Binary System", *Journal of Metastable and Nanocrystalline Materials,* 20-21, pp. 455-461 (July 2004)

8) B. Z. Eapen, V. K. Hoffmann, M. Shoenitz, and E. L. Dreizin, "Combustion of Aerosolized Spherical Aluminum Powders and Flakes in Air", *Combustion Science and Technology*, 176 (7), pp. 1055-1069 (2004)

9) M. Schoenitz and E. L. Dreizin, "Structure and Properties of Al-Mg Alloys", *Journal of Materials Research,* 18 (8), pp. 1827-1836 (2003)

10) E. L. Dreizin, "Effect of Phase Changes on Metal Particle Combustion Processes", *Combustion Explosion and Shock Waves,* 39 (6), pp. 92-96 (2003)

11) M. Shoenitz, E. L. Dreizin, and E. Shtessel, "Constant Volume Explosions of Aerosols of Metallic Mechanical Alloys and Powder Blends", *Journal of Propulsion and Power,* 19 (3), pp. 405-412 (2003)

12) Y. Shoshin and E. L. Dreizin, "Particle Combustion Rates in Pre-mixed Flames of Polydisperse Metal-Air Aerosols", *Combustion and Flame,* 133, pp. 275-287 (2003)

2) Technical Reports/Presentations

1) R. G. Shortridge (Presenter), C. K. Wilharm, C. M. Yamamoto, E. L. Dreizin, "Perchlorate-Free Colored Flares", Navy Energetics Enterprise (NEE)/Raytheon IR&D Review, China Lake, CA, 12 December 2006.

*2) R. G. Shortridge, C. K. Wilharm, and E. L. Dreizin, "Performance of Perchlorate-Free Spectrally Balanced Decoy Flare Compositions", 16th Annual ATEDS (Advanced Technology Electronic Defense Systems) Review, San Diego, CA, 4-6 April 2006

3) Conference Symposium Proceedings

1) R. G. Shortridge, C. K. Wilharm, C. Y. Yamamoto, and E. L. Dreizin, "Development and Testing of Perchlorate-Free Red and Green Pyrotechnic Flare Compositions", *Proceedings of 33rd International Pyrotechnics Seminar,* pp. 281-290, Fort Collins, CO, July 16-21, 2006

2) X.Zhu, M. Schoenitz, V. K. Hoffmann, and E. L. Dreizin, "Reactive Al-Li Powders Prepared by Mechanical Alloying", *Materials Research Society Proceedings,* Boston, MA, Dec. 2005

3) S. M. Umbrajkar, M. Schoenitz and E. L. Dreizin, "Structural Refinement in Al-MoO3 Nanocomposites Prepared by Arrested Mechanical Milling", *Materials Research Society Proceedings,* Boston, MA, Dec. 2005

4) Sara K. Poehlein, Robert G. Shortridge, and Douglas E. Stark, " Engineering Investigation Into Ignition Malfunctions of In-Service Decoy Flares and Related Degradative Aging Studies", *Proceedings of 5th International Symposium on the Heat Flow Calorimetry of Energetic Materials* (CD), Indianapolis, IN, September 13-15,2005

5) Edward L. Dreizin, Mirko Schoenitz, Uriy L. Shoshin, Mikhaylo A. Trunov, Swati Umbrajkar, Trent S. Ward, and Xiaoying Zhu, "Highly Energetic Nanocomposite Powders Produced by Arrested Reactive Milling", *Proceedings of 36th International Annual Conference of ICT and 32nd International Pyrotechnics Seminar,* pp. 138-1 to 138-12, Karlsruhe, Germany, June 28, 2005.

6) Mirko Schoenitz and Edward L. Dreizin, " Consolidated Energetic Nanocomposites: Mechanical and Reactive Properties", *Proceedings of 36th International Annual Conference of ICT and 32nd International Pyrotechnics Seminar,* pp. 133-1 to 133-11, Karlsruhe, Germany, June 28, 2005.

*7) Robert. G. Shortridge, Caroline K. Wilharm, and Edward L. Dreizin, "Elimination of Perchlorate Oxidizers from Spectrally Balanced Decoy Flare Compositions", *Proceedings of 2005 Military Sensing Symposium (MSS) on Infrared Countermeasures* (CD), Eglin AFB, FL, April 26-28 (2005)

8) S. Umbrajkar, X. Zhu,, M. Schoenitz, and E. L. Dreizin, " Effect of Compositional and Structural Refinement on the Ignition and Combustion of Reactive Nanocomposite Powders", *Proceedings of 4th Joint Meeting of the U. S. Section of the Combustion Institute* (Omnipress, CD-ROM.), Philadelphia, PA, March 2005

9) X. Zhu, M. Schoenitz, and E. L. Dreizin, "Reactions in Nanocomposite Al-CuO Thermite Powders Synthesized by Arrested Mechanical Milling", *Proceedings of 4th Joint Meeting of the U. S. Section of the Combustion Institute* (Omnipress, CD-ROM.), Philadelphia, PA, March 2005

10) T.S. Ward, M. Schoenitz, and E.L. Dreizin, " Heat Transfer Model for Ignition of Metal Powder on a Heated Filament", *Proceedings of 4th Joint Meeting of the U. S. Section of the Combustion Institute* (Omnipress, CD-ROM.), Philadelphia, PA, March 2005

11) W-L. Chen, M. Schoenitz, T. S. Ward, R. N. Dave, and E. L. Dreizin, "Numerical Simulation of Mechanical Alloying in a SPEX 8000 Shaker Mill", *Proceedings of Eleventh International Conference on Composites/Nano Engineering,* Hilton Head Is., SC, August 8-12, 2004

12) M. Schoenitz, T. S. Ward, and E. L. Dreizin, "Fully Dense Nanocomposite Energetic Powders Prepared by Arrested Mechanical Milling", *Proceedings of 30th International Symposium on Combustion,* Chicago, IL, July 13, 2004

13) M. Shoenitz, T. Ward, and E. L. Dreizin, "Preparation of Energetic Metastable Nano-Composite Materials by Arrested Reactive Milling", *Materials Research Society Proceedings,* 800, pp. AA2.6.1-AA2.6.6, December 5, 2003

14) M. A. Trunov, M. Shoenitz, and E. L. Dreizin, "Ignition of Al-Mg Mechanical Alloys", 2003 *Proceedings of Technical Meeting of the Eastern States Section of the Combustion Institute,* pp. 313-316, University Park, PA, October 29, 2003

15) Y. L. Shoshin, A. G. Ermoline, and E. L. Dreizin, "Effect of Aluminum Particle Size and Surface Morphology on the Laminar Aerosol Flame Speed", *Proceedings of Fall Technical Meeting of the Eastern State Section of the Combustion Institute,* University Park, PA, October 29, 2003

16) Edward L. Dreizin, "Metal-based Metastable Solid Solutions for New HEDMs", *Second Advanced Energetics Technical Exchange,* Aberdeen Proving Ground, MD, Sept. 22, 2003

4) Published Technical Abstracts (e.g. SERDP Symposium Abstracts)

1) R. G. Shortridge, C. K. Wilharm, C. M. Yamamoto, "Elimination of Perchlorate Oxidizers from Pyrotechnic Flare Compositions", Poster No. 91, p. E-56, Program Guide Memory Stick of the SERDP/ESTCP Partners in Environmental Technology Technical Symposium and Workshop, November 28 – 30, 2006, Washington DC

2) R. G. Shortridge, C. K. Wilharm, C. M. Yamamoto, E. L. Dreizin, "Elimination of Perchlorate Oxidizers from Pyrotechnic Flare Compositions", Poster No. 114, p. F-137, Program Guide of the SERDP/ESTCP Partners in Environmental Technology Technical Symposium and Workshop, November 29 – December 1, 2005, Washington DC

3) R. G. Shortridge, C. K. Wilharm, F. E. Montgomery, E. L. Dreizin, "Elimination of Perchlorate Oxidizers from Pyrotechnic Flare Compositions", Poster No. 190, p 183, Program Guide of the SERDP/ESTCP Partners in Environmental Technology Technical Symposium and Workshop, November 30 – December 2, 2004, Washington DC

4) R. G. Shortridge, C. K. Wilharm, F. E. Montgomery, E. L. Dreizin, "Elimination of Chlorine Containing Oxidizers from Pyrotechnic Flare Compositions", Poster No. 261, p. 254, Program Guide of the SERDP/ESTCP Partners in Environmental Technology Technical Symposium and Workshop, 2-4 December 2003, Washington DC

5) Published Text Books or Book Chapters

None

Appendix C

Other Technical Material

4) Awards:

2006 SERDP Project of the Year Award for Weapons and Platforms (WP), Project WP-1280, "Elimination of Perchlorate Oxidizers from Pyrotechnic Flare Compositions" at Plenary Session of the SERDP/ESTCP Partners in Environmental Technology, Technical Symposium and Workshop, November 28, 2006, Washington DC
Principal Investigator: Dr. Robert G. Shortridge
Co-Performers: Dr. Caroline K. Wilharm, Ms Christina Yamamoto, and Dr. Edward L. Dreizin