DEVELOPMENT AND TESTING OF PERCHLORATE-FREE RED AND GREEN PYROTECHNIC FLARE COMPOSITIONS[1]

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ABSTRACT

Most colored flare compositions contain perchlorate oxidizers. Residual perchlorates from these devices may be absorbed into groundwater and require remediation. Therefore, we have been attempting, under funding from the Strategic Environmental Research and Development Program (SERDP), to mix and test perchlorate-free red and green signal flare formulations. Numerous safety-related questions were posed by the local safety review committee, and have been successfully answered for the red compositions. These involved compatibilities of ingredients, moisture absorption rate of the hygroscopic calcium nitrate oxidizer, binder pre-coating options to mitigate the dangerously high electrostatic ignition sensitivity of the uncoated $Al_{0.5}Mg_{0.5}$ mechanical alloy, and an accelerated aging/storage stability study. The committee has recently granted their approval for scale-up of the red compositions. Two improved green compositions also have been developed. The performance tests of these two new scale-up candidates indicated that their performance was acceptable. Thermal analysis and ignition sensitivity testing have also been performed on these two new green candidates and an accelerated aging/storage stability test is in progress.

BACKGROUND

Most colored signal flare compositions contain perchlorate oxidizers. Residual perchlorates from these devices may be absorbed into groundwater and require remediation. Ground water contamination by perchlorates from rocket propellants, pyrotechnics and other sources has been found to be a serious problem in the Western United States and elsewhere. At least two military training ranges have already been forced to close due to perchlorate contamination, and others are in danger of suffering a similar fate.[1] Accordingly, many states are taking a proactive approach to convince the EPA to set the maximum perchlorate level in drinking water as low as possible to ensure adequate protection of fetuses and the newborn.[2] Therefore, we have been attempting, under funding from the Strategic Environmental Research and Development Program (SERDP), to mix and test non-perchlorate-containing red and green signal flare formulations.

These compositions are based on various nitrates as replacements for perchlorates. Since nitrate oxidizers are less reactive than perchlorate oxidizers we reasoned that high-energy fuels would be required to make up for this energy shortfall.[3] We have teamed with an academic partner, Professor Edward Dreizin's research group at the New Jersey Institute of Technology, who has provided us samples of high-energy mechanical alloys.[4,5] $Al_{0.5}Mg_{0.5}$ mechanical alloy fuel has been included in some of the laboratory scale flare compositions.

Figure 1 shows the particle size distribution of five types of Al-Mg mechanical alloys produced at NJIT in the high-energy planetary mill type mixer, also shown in the figure. Of these, the $Al_{0.5}Mg_{0.5}$ was added to some of the green and red signal flare formulations in combination with the presently used magnesium fuel. Figure 2 shows Scanning

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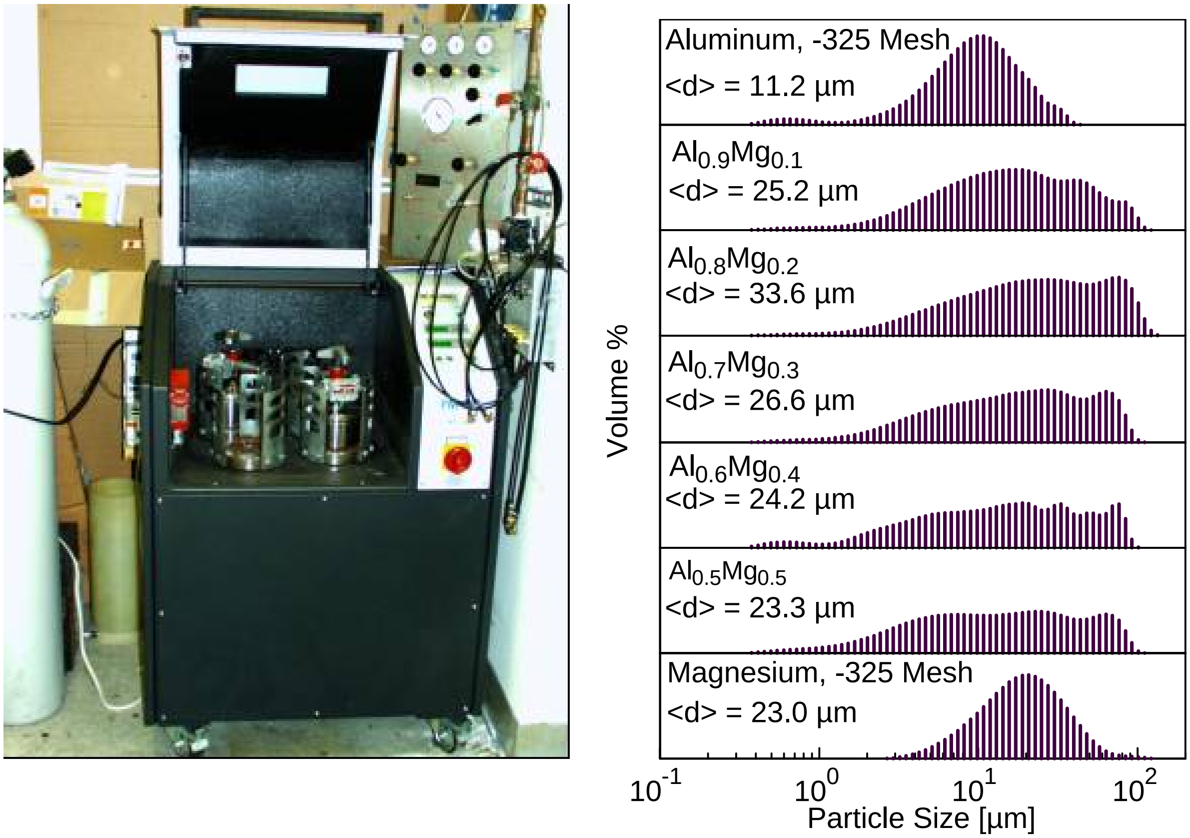


Figure 1. The New NJIT Planetary Mixer Mill and Al-Mg Mechanical Alloy Size Distribution

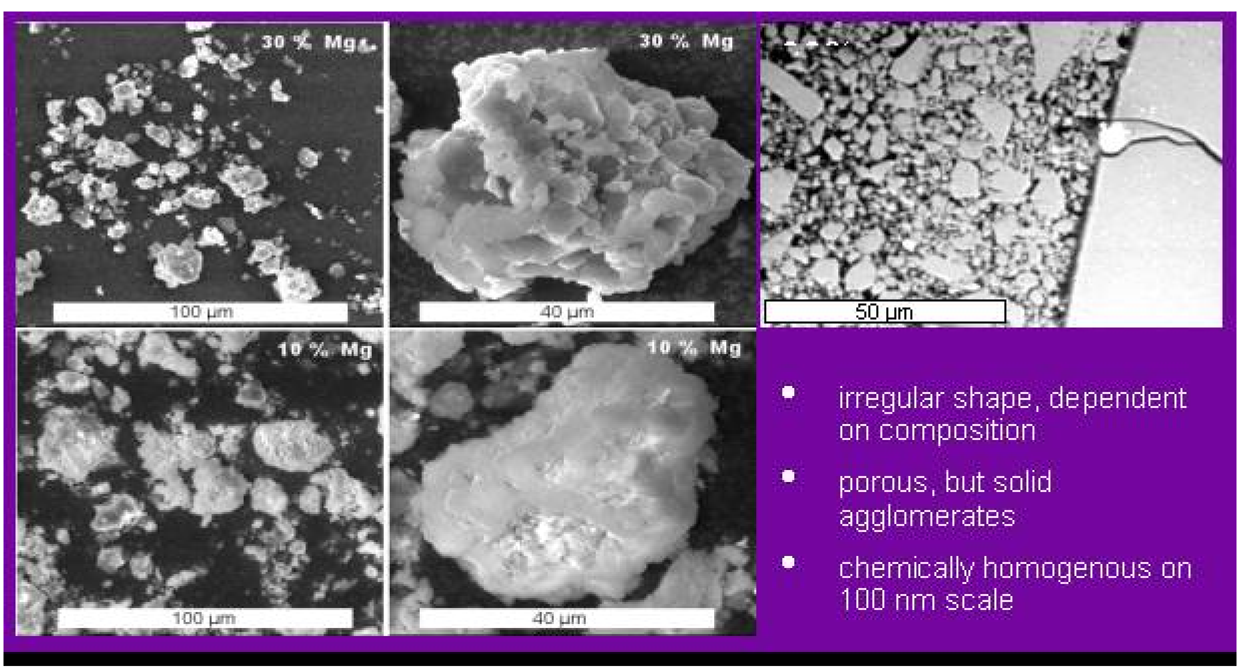


Figure 2. NJIT Scanning Electron Micrographs of Aluminum-Magnesium Mechanical Alloys

Electron Microscopy (SEM) photographs of two types of Al-Mg mechanical alloys.

RED SIGNAL FLARES

As discussed in our paper at the 31st International Pyrotechnics Seminar in 2004,[6] three perchlorate-free red compositions were chosen for scale-up to the 24-gram red flare candle in the Mk 124 Mod 0 Marine Smoke and Illumination Signal (MSIS). They were the RSF-2A, RSF-2B, and RSF-2C compositions, and their ingredient weight percentages are shown in Table 1, together with the in-service Mk 66 perchlorate-containing composition tested for comparison purposes. The results of the performance tests of these four red compositions indicate that the perchlorate-free compositions performed as well as the in-service perchlorate-containing composition. Our goal is to introduce them into the Service inventories thereby eliminating the continued use of the environmentally objectionable potassium perchlorate ingredient.

Crane's Materials Processes and Equipment Review Committee (MPERC) first considered our request for scale-up of the red flare compositions in September 2004. They required that a number of additional safety-related tests be performed on these compositions and on some of their constituent ingredients before final approval for scale-up could be granted. These included compatibility testing of ingredients, a study of the moisture absorption rate of the hygroscopic calcium nitrate oxidizer, investigation of binder pre-coating options to mitigate the dangerously high electrostatic ignition sensitivity of the uncoated $Al_{0.5}Mg_{0.5}$ mechanical alloy, and an accelerated aging/storage stability study.

Compatibility Testing

A simultaneous TGA/DTA thermal analysis technique was used to verify that there were no incompatibilities between each of the three red compositions, the IM-6 ignition composition and the starter slurry composition, which are used in the in-service flare candle to aid in ignition. Both binary and ternary combinations of the red flare, the ignition, and the starter compositions were examined. 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.[7] 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. 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

Table 1. Red Signal Flare Compositions

	Mk 66	RSF-2A	RSF-2B	RSF-2C
Chemical	**Wt %**	**Wt %**	**Wt %**	**Wt %**
Mg(GR18)	29.00	22.38	27.00	13.50
Mg.5Al.5		4.62		
Mg.3Al.7				
Magnalium				13.50
KNO3				
KClO4	15.00			
Sr(NO3)2	37.00	32.40	32.40	32.40
Ca(NO3)2		21.60	21.60	21.60
PVC				
Asphaltum	14.00	14.00	14.00	14.00
Epon 813	2.50	2.50	2.50	2.50
Versamid 140	2.50	2.50	2.50	2.50

≤ 4 degrees lower temperature, then the materials are chemically compatible.

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 ^{0}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.

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 were similarly studied by DTA and TGA thermal analysis. Table 2 summarizes the results of these tests. RSF-2A is compatible with both the IM-6 and the Starter Slurry as the mixtures underwent the ignition exotherm at slightly higher rather than lower temperatures than did the RSF-2A composition by itself. These results were sufficient to convince the MPERC of the compatibility of three red compositions with both the IM-6 and the Starter Slurry Compositions.

Table 2. Ignition Temperatures of RSF-2A with IM-6 and Starter Slurry from DTA and TGA Data

Material	Ignition Temp. (^{0}C)	Temp. Shift (^{0}C)
RSF-2A	351	---
IM-6	350	---
IM-6/RSF 2A	360	+10
Ignition Starter Slurry	405	---
Starter Slurry /RSF 2A	367	+16

Moisture Absorption Testing

We also measured the moisture absorption rate of the very hygroscopic anhydrous calcium nitrate oxidizer ingredient. The results showed that approximately 1.0 – 1.5 % of the anhydrous calcium nitrate was converted to the tetrahydrate form in the first hour of exposure to ambient air at 20 ^{o}C and 70 % relative humidity. While the MPERC was willing to allow us to scale-up to the Mk 124 Mod 0 form factor using these three anhydrous calcium nitrate-containing compositions, they strongly encouraged us to find a less hygroscopic substitute for this ingredient on account of degradative aging concerns.

Any water absorbed by the calcium nitrate will potentially be available to react with the magnesium fuel to form a combination of calcium nitrite ($Ca(NO_2)_2$) and magnesium hydroxide plus ignitable hydrogen gas. It will be essential to exclude any unnecessary exposure to water vapor by both the calcium nitrate ingredient, as well as the full up compositions during and after the mixing and pressing operations.

In the future we will further address this hygroscopicity problem of the calcium nitrate. Two possible approaches include coating this material with a protective coating that has been under development at NAWC China Lake, or simply by using only strontium nitrate, and no calcium nitrate, in the red flare formulations.

It is noted that a much earlier investigation also successfully used calcium nitrate as the oxidizer for an orange/red illuminating flare formulation.[8] When we substituted calcium carbonate for calcium nitrate, the results indicated that this oxidizer slowed down the burn rate of the red flare compositions to the point that the candlepower intensity was too low to be useful.

With the chemical compatibility questions successfully answered, the MPERC approved our request for scale-up during August 2005. A Standard Operating Procedure has been prepared and all necessary approvals have been obtained. Preparation of prototype scale batches of composition and Mk 124 Mod 0 red flare candles is getting under way. Once produced, they will be performance tested in similar fashion to the lab scale candles.

Storage Stability Testing

A storage stability study of these red compositions was a pre-condition for this scale-up. It is required for all pyrotechnic compositions scaled from laboratory to prototype scale form factors. The storage stability test showed that samples of each of the three perchlorate-free red compositions that had been stored in sealed ampoules at 70 °C for a period of 87 days showed no deterioration compared with freshly prepared samples, or with samples similarly maintained under ambient conditions for the same period of time. This time scale was chosen because it is expected to result in the same degradation that would occur during a five-year period of storage under ambient conditions.

Analysis was done using a Perkin Elmer Diamond simultaneous TGA/DTA. The ignition temperatures were found to be very similar, and no significant new peaks attributable to degradation products such as magnesium hydroxide, strontium nitrite, or calcium nitrite appeared in the samples aged at the elevated temperature. As an illustrative example, Figure 3 shows the simultaneous thermograms obtained from composition RSF-2A before and after the 87-day aging period at elevated temperatures. Thermograms from RSF-2B and RSF-2C, as well as the Mk 66 in-service composition were all quite similar.

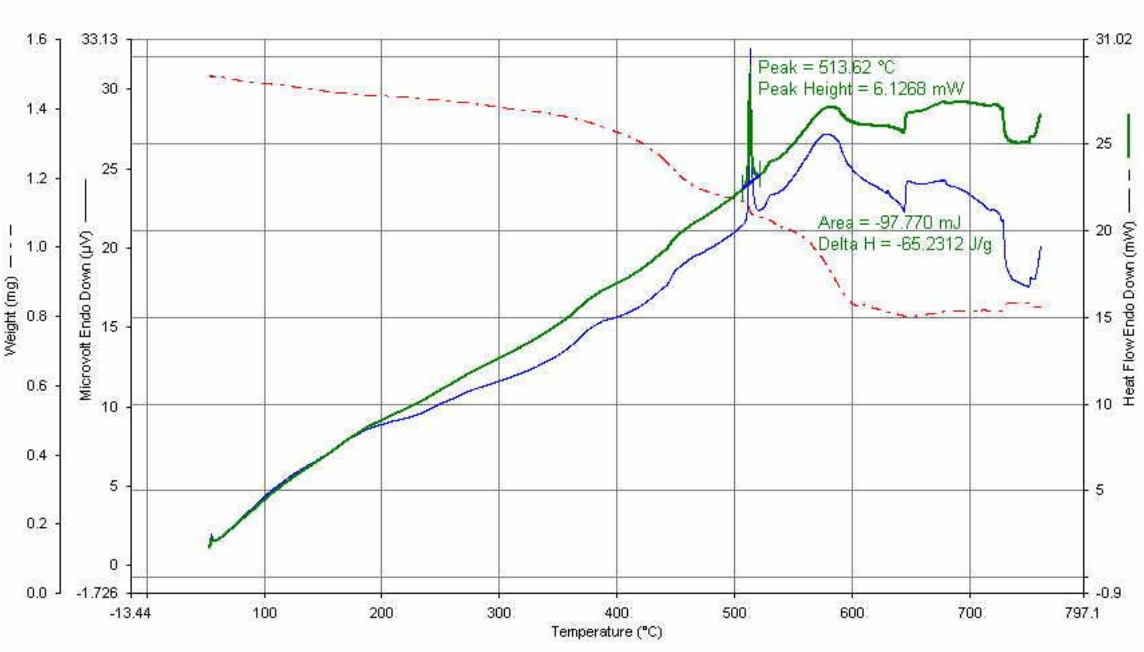
GREEN SIGNAL FLARES

In our 2004 paper, we tentatively chose three candidate perchlorate-free green compositions for scale-up to in-service device, the Mk 117 Mod 2 Green MSIS.[6] However, we noted that none of the three matched the dominant wavelength and the general green appearance of the Mk 117 perchlorate-containing composition. At this point, extensive use was made of the NASA Lewis Chemical Equilibrium computer program to optimize these perchlorate-free green flare compositions.[9] Ingredients were systematically varied in order to find compositions that produced maximized concentrations of chemical species that are known to be efficient radiators in the green region of the visible spectrum. Such species include, but are not limited to, barium monochloride radical (BaCl) and barium monohydroxide radical (BaOH). A total of fifteen green compositions were modeled and the three most promising candidates were chosen for analysis. These three compositions, GSF-1E, GSF-4D, and GSF-4K are shown in Table 3. Also included is the standard Mk 117 green composition.

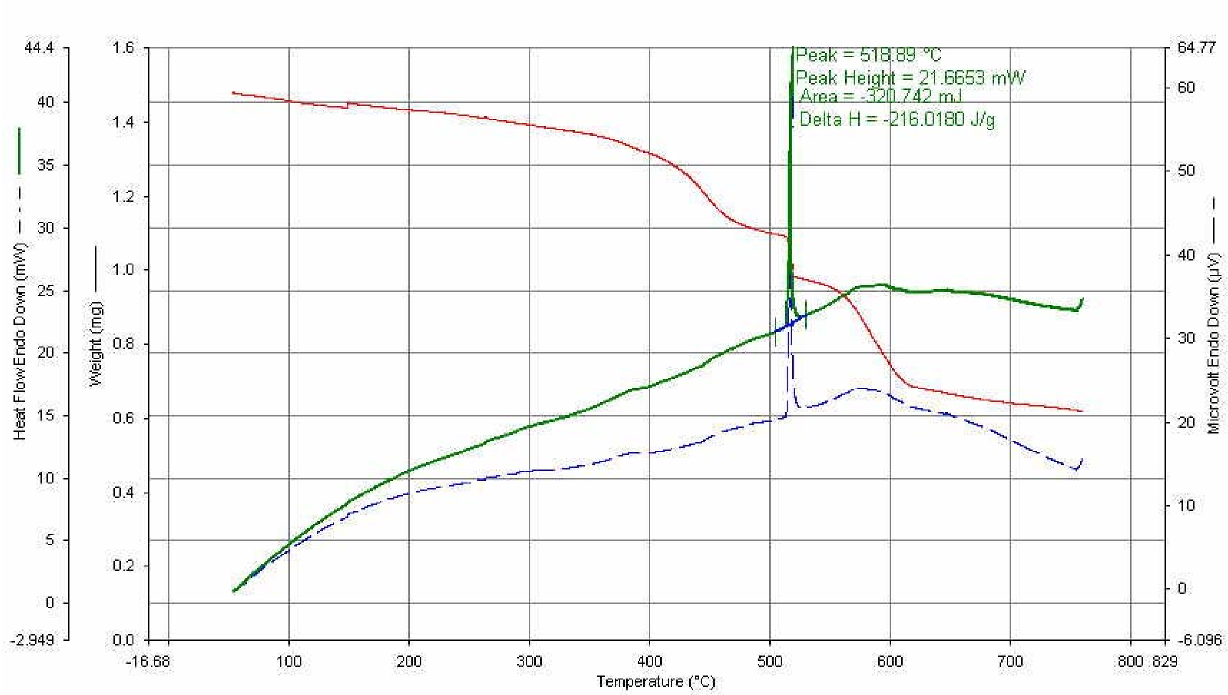
The compositions were mixed by hand in 45-gram batches. Typically the fuel ingredients were first pre-coated with the Epon 813/Versamid 140-epoxy binder system, and then the remaining oxidizer(s) and color-enhancing ingredients were added and mixed. From each batch, three 15-gram candles were pressed. The candles were then cured at 60 °C for 48 - 72 hours. They were inhibited on the sides and glued to a flare-mounting base using Miller-Stephenson No. 907 epoxy. Finally, magnesium-teflon-viton ignition slurry was applied to the top surface and an electric match was installed.

Candlepower and Hunter Tri-Stimulus Colorimeter Head measurements were made on all flare compositions subjected to performance testing. These data yield the X, Y, and Z coordinates, from which the color purity and dominant wavelength values may be found from the C.I.E. Chromaticity Diagram.[10] Video and photographic data were also recorded. Such data is essential because the military specifications under which these items are procured typically require that they produce a distinct color clearly identifiable by a human observer.

Performance testing results are summarized in Table 4. Figure 4 shows typical photos taken during testing. It was observed in earlier tests that the flames of the previous scale-up candidates (GSF-1B) look washed out (whitish) when compared with the Mk 117 flame. For the optimized compositions (GSF-4K and GSF-1E) the general green appearance, as well as the dominant wavelength and color purity parameters, far surpassed those produced by the previous scale-up candidates. While all three new compositions far surpassed the earlier compositions, a decision was made to recommend only the GSF-1E and GSF-4K for scale-up. This was due to the slightly longer dominant wavelength of the GSF-4D composition, when compared with the other compositions.



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

Table 3. Green Signal Flare Compositions

Chemical	Mk 117 (Wt %)	GSF-4K (Wt %)	GSF-4D (Wt %)	GSF-1E (Wt %)
Boron				2.85
Mg (GR18)	21.00	30.00	30.00	10.00
Copper	7.00			6.70
$Mg_{0.5}Al_{0.5}$				4.72
KClO4	32.50			
$Ba(NO_3)_2$	22.50	53.00	57.00	62.73
PVC	12.00	12.00	8.00	8.00
Epon	3.50	3.50	3.50	3.50
Versamid	1.50	1.50	1.50	1.50

Table 4. Performance Data of Green Signal Flare Compositions

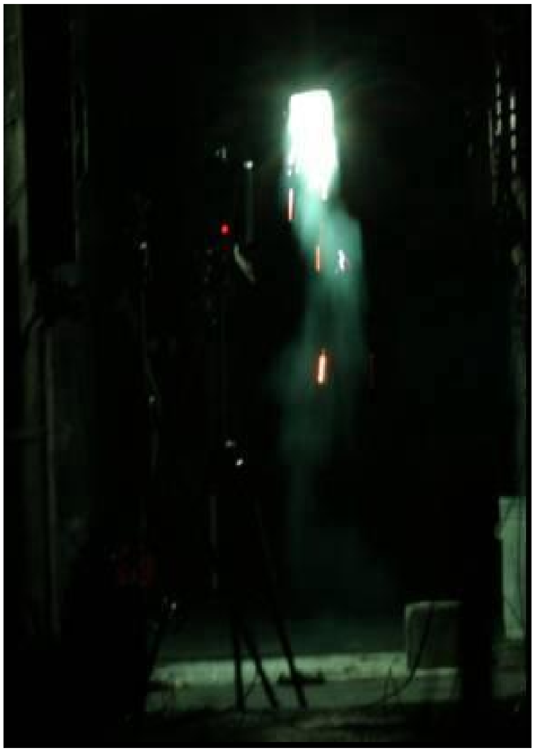
Formulation	Pellet No.	Burn Time, (sec)	Avg Candle Power (cd)	Dominant Wavelength, (nm)	Color Purity (%)	Fuel Make-up	Ign. * Sens. (J)	Scale-up?
Mk117	E-1	29.6	~507	557	52	Cu +Mg	18	Standard
	E-2	29.9	732	548	52			
	E-3	28.9	680	555	51			
GSF-1E	D-1	32	769	551	54	Mg + B	0.002	**Yes**
	D-2	29.2	838	553	54	+ Cu +		**Yes**
	D-3	30.7	837	551	54	Al0.5Mg0.5		**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	557	54	Mg	18	No
	C-2	31.5	1835	559	50			No
	C-3	39	1345	563	58			No

*Electrostatic Ignition Sensitivity of the most sensitive fuel ingredient.

Mk 117 Std. Green

GSF-1B

GSF-4K



GSF-1E

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

The MPERC safety board has not yet given final permission for scale-up of these two new green candidate compositions. However, it is anticipated that their concerns will be reasonably similar to those raised during the scale-up of the red compositions. We have conducted similar thermal analysis and compatibility studies of the green compositions while we were studying the red compositions. An accelerated aging (storage stability) study at 70 °C for a minimum of 85 days of the GSF-1E and GSF-4K compositions is currently under way. For comparison purposes, the in-service perchlorate-containing composition in the Mk 117 MSIS is also being included in the accelerated aging study.

IGNITION SENSITIVITY TESTING

In order to investigate their safety in handling characteristics, the flare formulations were also subjected to ignition sensitivity measurements to impact, rotary friction and electrostatic stimuli, according to MIL SPEC 1751.[11] Obviously, no composition with dangerously high ignition sensitivity may be permitted for scale-up and introduced into the inventory for fear of unintended initiation.

Table 8 includes the measured values of ignition sensitivity to impact, rotary friction and electrostatic stimuli.[11] Included are the in-service red and green compositions, as well as the three red and two green scale-up candidate compositions. The RDX included in the table is the internal standard included in all sensitivity measurements for comparison purposes. Also included are the measured sensitivities of many of the pyrotechnic fuels by themselves including, magnesium (Gran 18), commercial magnalium alloy, and the $Al_{0.5}Mg_{0.5}$ mechanical alloy from NJIT. Since the latter was found to be dangerously sensitive (at 0.002 Joule) to electrostatic stimuli in its "as-received" uncoated state, it was shown that by pre-coating it with either epoxy or viton binder the sensitivity can be lowered to the more acceptable "high" region. None of the red or green candidate compositions have dangerously high sensitivity to impact, rotary friction or electrostatic stimuli. The dangerously high frictional sensitivity of the in-service Mk 117 composition is regarded as an anomalous measurement as this in-service composition has been safely handled in the field for decades.

Table 5. Ignition Sensitivity Measurements of In-Service and Perchlorate-Free Red and Green Flare Compositions and Selected 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
Mk 117 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 66 Red Standard	178.40	34.97	1655.00	916.93	10% Fired	0.250
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
Mg0.5Al0.5-Viton	178.40	34.97	2364.97	59.17	20% Fired	0.450
Mg0.5Al0.5-17.9% Epoxy	178.40	34.97	1399.48	357.11	10% Fired	0.450
Mg0.5Al0.5-Epoxy-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

Dangerous High Moderate Low Very Low

FUTURE PLANS

Scale-up of the perchlorate-free RSF-2A, RSF-2B, and RSF-2C red compositions will continue. Based upon the performance and safety related test results of the three compositions at prototype scale, the three compositions will be down-selected to a single most promising composition for incorporation into the fielded red signal flare devices.

As soon as the MPERC Board approves the laboratory to prototype scale-up of the perchlorate-free GSF-1E and GSF-4K green compositions, they will be subjected to the same battery of performance and safety related tests as the red compositions. They will be down-selected to a single most promising composition for incorporation into fielded green signal flare devices.

It is also planned to produce and test perchlorate-free yellow signal flare compositions. NASA Lewis modeling has already resulted in the choice of three promising compositions that will be fabricated and performance tested initially at laboratory scale. If these are successful, they will be selected for scale-up.

Additional safety related tests required for the qualification of the new compositions, as well as final device qualification, will be conducted so that the devices can be introduced into the Service inventories as Product Improvement Programs (PIPs).

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