

High-Nitrogen-Based Pyrotechnics: Development of Perchlorate-Free Green-Light Illuminants for Military and Civilian Applications

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Dedicated to the servicemen and servicewomen who serve in the United States armed forces

Abstract: The development of perchlorate-free hand-held signal illuminants for the US Army's M195 green star parachute is described. Compared with the perchlorate-containing control, the optimized perchlorate-free illuminants were less sensitive toward various ignition stimuli while offering comparable burn times and visible-light outputs. The results were also important from the perspective of civilian fireworks because the development of perchlorate-free illuminants remains an important objective of the commercial fireworks industry.

Keywords: energetic materials • fireworks • heterocycles • pyrotechnics • sustainable chemistry

Introduction

For over a decade, there has been interest in the development of environmentally friendly pyrotechnics for military and civilian applications.^[1] Although the Armament Research Development and Engineering Center (ARDEC) recently developed barium- and chlorine-free green light-emitters with acceptable burn times for pyrotechnic applications on a small scale,^[2,3] research continues in successfully scaling up these technologies on a production scale for the sake of obtaining optimal burn time and luminous intensity values. Despite the potential hazards of barium-containing compounds in pyrotechnics, no permissible limit regulation from the Environmental Protection Agency (EPA) exists at this time.

One issue that is of immediate concern to the EPA and, owing to increased regulations imposed by the EPA, has become a concern of the US Department of Defense is the

“perchlorate issue.” Potassium perchlorate and ammonium perchlorate oxidizers, once believed to be amongst ideal oxidizers owing to their inherent reactivity, stability, low cost, low hygroscopicity, and large positive oxygen balances, have now been identified as an environmental and human health hazard.^[4] Perchlorates have high water solubilities and have been shown to contaminate groundwater, thus posing a potential risk to drinking supplies. Perchlorates are believed to be teratogenic and the anion is believed to compete with iodide anion in binding with the thyroid gland, interfering with production and regulation of thyroid hormones. Although this binding effect appears to be reversible because the intake of iodide-containing food and beverages appears to lead to the replacement of the perchlorate anion with the iodide anion,^[5] the US Environmental Protection Agency has set the federal permissible perchlorate limit in groundwater to 15 parts per billion (ppb),^[6] whereas the states of California and Massachusetts have set their respective permissible levels to 6 and 2 ppb.^[7]

Because of these low permissible levels, United States military personnel have not been allowed to effectively train with perchlorate-containing munitions on training ranges within and outside the continental USA. The inability to properly train for combat endangers military readiness and decreases survivability on the battlefield.

The civilian fireworks industry is also coming under increasing scrutiny by environmental groups and the EPA to make their fireworks more “green” and to develop perchlorate-free variants. The manufacturing of fireworks is believed to lead to significant perchlorate contamination in soil and groundwater, and significant levels of perchlorates have been found in the environment following firework displays.^[8]

The use of high-nitrogen energetic salts for pyrotechnic applications as perchlorate replacements has been the sub-

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14. ABSTRACT The development of perchlorate-free hand-held signal illuminants for the US Army's M195 green star parachute is described. Compared with the perchlorate-containing control, the optimized perchlorate-free illuminants were less sensitive toward various ignition stimuli while offering comparable burn times and visible-light outputs. The results were also important from the perspective of civilian fireworks because the development of perchlorate-free illuminants remains an important objective of the commercial fireworks industry.					
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ject of intense investigation in recent years and the synthesis, characterization, and stabilities of some high-nitrogen salts has been demonstrated previously.^[1,9] Rather than deriving their combustion energy from the oxidation of a carbon backbone, high-nitrogen compounds derive their energy from their high heats of formation, attributed to the substantial amount of environmentally benign nitrogen gas released upon combustion of these materials.

To address the aforementioned perchlorate issues, efforts were initiated by ARDEC to remove potassium perchlorate from their green-light-emitting pyrotechnic item: the M195 green star parachute hand-held signal (HHS). HHSs are used in training and combat situations for the purposes of signaling military and allied personnel and aircraft. Although the primary focus of ARDEC lies in the area of military pyrotechnic applications, owing to increasing environmental regulations, it was believed that the development of perchlorate-free green-light-emitting pyrotechnics might also have a positive impact on the civilian fireworks community.

Results and Discussion

The US Army in-service M195 perchlorate-containing control is provided in Table 1. Magnesium served as the main fuel in the formulation, barium nitrate and potassium per-

Table 1. M195 control formulation.

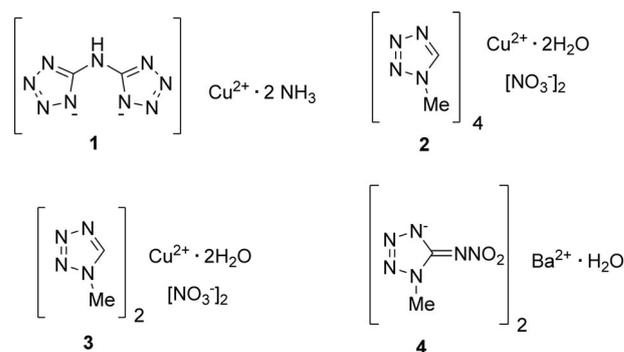
Component	Composition [wt %]
barium nitrate	48
magnesium 30/50	22
dechlorane plus	15
potassium perchlorate	10
Laminac 4116/Lupersol	5

chlorate served as the oxidizers, and dechlorane plus served as a chlorine donor. A chlorine donor in barium-containing, green-light-emitting pyrotechnics is essential to obtain a green-colored flame. The green flame arises from the formation of metastable barium(I) chloride during the combustion process and the spectral purity of the green flame is greatly enhanced by the conversion of magnesium oxide to the more volatile magnesium(I) chloride species. If sufficient levels of chlorine are not present in the barium-containing control, large amounts of incandescent barium oxide and magnesium oxide particles form and a white color is perceived by the viewer.

Laminac 4116/Lupersol served as the binder system in the M195 control formulation. Its role was to provide mechanical strength and to prevent segregation of oxidizers and fuels in a given pyrotechnic composition. Unfortunately, the Laminac binder system has a short shelf-life of about six months before decomposing and is plagued by single-point-of-failure concerns.^[10] In a controversial move, the US Department of Health and Human Services recently classified

styrene, which is the cross-linking material in the Laminac binder system, as a carcinogen.^[11] This ruling has been criticized by industries, resulting in a lawsuit filed against the government agency.^[12] To adequately address single-point-of-failure concerns, and to remain one step ahead of potential regulations associated with Laminac binder system, replacement of this binder system was imperative in ensuring that the M195 HHS would remain in the US Army's arsenal.

Because potassium perchlorate is an energetic oxidizer that typically enhances ignitability and decomposes exothermically,^[5] removing it from the formulation means that energy is removed from the pyrotechnic system. To compensate for this loss in energy, barium- and copper(II)-based high-nitrogen salts^[9,13] were proposed as perchlorate replacements. Copper(II) salts **1–3** were examined because of their ability to also contribute to green-light-emission that arises from the formation of copper(I) hydroxide. Barium-based bis-tetrazolate **4** was also selected for evaluation in the M195 HHS based on previous successful M126A1 red flare development, involving a structurally related strontium-based bis-tetrazolate derivative.^[14]



The energetic properties of high-nitrogen salts **1–4** (i.e., sensitivities, oxygen balances, decomposition temperatures, densities, and combustion energies) previously published in the literature are provided in Table 2.^[9a,13] While it is true that copper-based tetrazolates can be used as initiating primary explosives due to their high sensitivities,^[15] and that extreme caution should be used whenever handling this class of energetic compounds, copper(II) salts **1–3** exhibited

Table 2. Energetic properties of high-nitrogen salts **1–4**.

	IS [J] ^[a]	FS [N] ^[b]	ESD [J] ^[c]	N [%] ^[d]	Ω [%] ^[e]	T _{dec} [°C] ^[f]	ρ [g cm ⁻³] ^[g]	Δ _c U [kJ kg ⁻¹] ^[h]
1	100	>360	0.70	61.95	-55	281	1.99	-9353
2	30	120	2.00	49.70	-54	168	1.71	-10840
3	30	196	2.00	39.85	-30	142	1.95	-7415
4	15	>360	0.65	38.05	-29	349	2.30	-6050

[a] IS = impact sensitivity. [b] FS = friction sensitivity. [c] ESD = Electrostatic discharge. [d] Nitrogen content. [e] Oxygen balance. [f] Decomposition temperature from DSC. [g] Determined by X-ray crystallography. [h] Combustion energy.

reasonable sensitivities to ignition stimuli and were deemed to be acceptable to handle in pyrotechnic formulations. It has been observed that the presence of crystal water or ammonia molecules is responsible for greatly reducing the sensitivities of copper(II) high-nitrogen salts.^[15b]

To determine which high-nitrogen compound yielded the best results as a perchlorate replacement, formulations A–D were prepared and evaluated on a small scale. The compositions of these formulations are summarized in Table 3.

Table 3. Small-scale high-nitrogen M195 formulations.

Formulation	Components	Composition [wt %]
A	barium nitrate	48
	magnesium 30/50	22
	dechlorane plus	15
	1	10
	Epon 813/Versamid 140	5
B	barium nitrate	48
	magnesium 30/50	22
	dechlorane plus	15
	2	10
	Epon 813/Versamid 140	5
C	barium nitrate	48
	magnesium 30/50	22
	dechlorane plus	15
	3	10
	Epon 813/Versamid 140	5
D	barium nitrate	48
	magnesium 30/50	22
	dechlorane plus	15
	4	10
	Epon 813/Versamid 140	5

The performance of formulations A–D relative to the perchlorate-containing control is provided in Table 4 and the linear burn rate and mass consumption of these formulations is provided in Table 5. All of the formulations exhibited a brilliant green flame upon ignition, as evidenced by the

Table 4. Small-scale performance of formulations A–D relative to the control.

Formulation	Burn time [s]	Luminous intensity [cd]	Dominant λ [nm]	Spectral purity [%]
control	44.6	998.3	559.4	61.2
A	36.6	1420.3	554.2	58.6
B	38.8	1516.1	552.9	56.9
C	42.0	1349.4	554.3	58.1
D	40.2	1772.6	554.0	61.0

Table 5. Burning properties of small-scale formulations.

Formulation	Height of composition [cm]	Weight of composition [g]	Burn rate [cm s ⁻¹]	Mass consumption [g s ⁻¹]
control	3.92	5.46	0.088	0.122
A	4.35	6.48	0.112	0.177
B	3.92	6.44	0.101	0.166
C	4.07	6.48	0.097	0.154
D	3.98	6.51	0.099	0.162

dominant wavelength and spectral purity values given in Table 4. Formulations A–D burned for a shorter duration, but had higher luminous intensities than the control. As expected, faster burning formulations had shorter burn rates and greater mass consumption.

In evaluating formulations A–D, it was generally observed that faster burning formulations (i.e., A and B) contained high-nitrogen compounds with a greater overall nitrogen content, a more negative oxygen balance, and a higher combustion energy compared with those formulations that burned longer (i.e., C and D). Interestingly, there was no direct correlation between burn rate, mass consumption, and observed luminous intensity. Formulation D, which was the brightest burning formulation of those tested, was not the formulation with the fastest burn rate and greatest mass consumption. The reasons why formulation D yields the highest luminous intensity and has a respectable burn time are not yet understood. Nonetheless, formulation D was determined to be the best small-scale candidate for evaluation and optimization at the prototype level due to its performance during small-scale evaluation.

The performance of formulation D relative to the control and the military requirement for the M195 HHS illuminant at the prototype level is summarized in Table 6 and the burning properties are given in Table 7. Formulation D

Table 6. Prototype performance of the control and formulation D.

Formulation	Burn time [s]	Luminous intensity [cd]	Dominant λ [nm]	Spectral purity [%]
military requirement	50.0	5000.0	540 ± 20	50.0
control	55.3	6973.3	562.3	64.8
D	56.2	6536.7	561.9	65.3

Table 7. Burning properties of the control and formulation D prototype formulations.

Formulation	Height of composition [cm]	Weight of composition [g]	Burn rate [cm s ⁻¹]	Mass consumption [g s ⁻¹]
control	6.08	98.99	0.110	1.79
D	6.11	98.86	0.109	1.76

yielded comparable results to the control formulation and exceeded the military requirement in the categories of burn time, luminous intensity, and spectral purity by a significant margin. Curiously, although the in-service control and formulation D both exhibited a brilliant green flame, both formulations were outside of the (540 ± 20) nm dominant wavelength requirement outlined by the military. The dominant wavelength issue was not problematic in obtaining a green flame of acceptable quality because the dominant wavelength value of the control formulation currently used in production was also observed to be outside of the military requirement. Nonetheless, the dominant wavelength issue for green light-emission is one that is worthy of further investigation. It should be noted that the military require-

ments were first obtained in the 1960s and 1970s, and more sophisticated technology now exists to determine precise and more accurate data values. It is possible that the long dominant wavelengths observed could be attributed to sodium impurities present in the Kraft fiberboard tubes. These tubes are washed with sodium hydroxide and sodium sulfite during the manufacturing process.^[16] The presence of sodium, even in small amounts, has been known to have a significant influence on the dominant wavelength due to the dominant yellow emission from atomic sodium.^[17]

Despite the good performance of formulation D, it was decided by the US Army Public Health Command that the course of the investigation needed to be changed. Although the initial investigation set out to remove potassium perchlorate oxidizer from the M195 HHS illuminant, the Public Health Command stated that dechlorane plus had been linked to its own environmental issues, showing the ability to bioaccumulate and persist in the environment for an extended period of time.^[18] Despite the successful development of formulation D, the Public Health Command recommended that dechlorane plus be replaced with poly(vinyl) chloride (PVC) to aid in achieving green-light emission. From a manufacturing perspective, replacement of dechlorane plus with PVC also made sense because dechlorane plus, like Laminac binder, is also plagued by single-point-of-failure concerns.

Taking the Public Health Command's recommendations into account, "drop-in" formulation E was prepared at the prototype level (Table 8) in an attempt to develop a success-

Table 8. PVC-based formulation E.

Component	Composition [wt %]
barium nitrate	48
magnesium 30/50	22
PVC	15
4	10
Epon 813/Versamid 140	5

ful M195 illuminant that utilized PVC as the chlorine donor.

The performance of PVC-based formulation E is provided in Table 9. Formulation E burned 17% longer with a luminosity decrease of 35% compared with formulation D,

Table 9. Prototype performance of prototype formulation E.

Formulation	Burn time [s]	Luminous intensity [cd]	Dominant λ [nm]	Spectral purity [%]
E	65.9	4260.3	565.0	71.2

thereby failing to meet the Mil-Spec in the critical category of luminosity. Owing to its low visible-light output, formulation E was not determined to be an acceptable formulation and further optimization was needed.

Despite their large differences in burn times, it is worth noting that dechlorane plus-based formulation D and PVC-based formulation E had identical burn rates (Table 10). Be-

Table 10. Burning properties of formulations D and E.

Formulation	Height of composition [cm]	Weight of composition [g]	Burn rate [cm s ⁻¹]	Mass consumption [g s ⁻¹]
D	6.11	98.86	0.109	1.76
E	7.22	98.87	0.110	1.50

cause the respective densities of dechlorane plus and PVC are 1.80 and 1.40 g cm⁻³, formulation D occupied less space per unit volume than formulation E despite both formulations being pressed at an identical consolidation dead load of 2273 kg. Therefore, while the chlorine donor appeared to have no influence on burn rate, it did have a significant impact on the loading density and mass consumption of the consolidated composition; this explains the differences in burn time and luminous intensity between formulations D and E.

Although PVC-based formulation E had a low luminous intensity, its extended burn time provided the opportunity to sacrifice some of the burn time for an increase in observed luminosity. It has been well established that increasing the amount of magnesium used results in faster burn times and larger luminous intensities well beyond the stoichiometric point of the pyrotechnic mixture.^[19] Therefore, it was believed that this concept would be of beneficial value in pursuit of a PVC-based formulation (Table 11) that exceeded the military requirement.

Table 11. PVC-based formulation F.

Components	Composition [wt %]
barium nitrate	48
magnesium 30/50	27
PVC	15
4	5
Epon 813/Versamid 140	5

The performance of PVC-based formulation F is provided in Table 12, and its burning profile is summarized in Table 13. Gratifyingly, the increase in magnesium did lead to a substantial increase in luminous intensity and yielded a respectable burn time. Moreover, the burn time, luminous intensity, and spectral purity of formulation F exceeded the

Table 12. Prototype performance of prototype formulation F.

Formulation	Burn time [s]	Luminous intensity [cd]	Dominant λ [nm]	Spectral purity [%]
F	59.3	6608.7	564.6	69.4

Table 13. Burning properties of formulation F.

Formulation	Height of composition [cm]	Weight of composition [g]	Burn rate [cm s ⁻¹]	Mass consumption [g s ⁻¹]
F	7.21	98.68	0.122	1.66

values of the military requirement and were comparable to the perchlorate-containing control. The respective burn rate and mass consumption of formulation F were faster and higher than those of formulation E, which further explains the decreased burn time and increase in observed luminosity of formulation F.

With formulation F now in hand, the sensitivity^[20] of this illuminant was compared with dechlorane plus-containing formulation D and the perchlorate-containing control (Table 14). Formulations D and F were comparable in their

Table 14. Behavior of formulations D and F and the perchlorate-containing control toward various ignition stimuli.

Formulation	Impact [J]	Friction [N]	ESD [J]	Thermal onset [°C]
control	6.9	120	>0.25	292.6
D	11.8	>360	>0.25	279.7
F	11.8	>360	>0.25	239.3

sensitivities to impact, friction, and ESD, and both formulations had reasonable thermal stabilities. Compared with the control, formulations D and F were considerably more stable toward impact and friction with good ESD sensitivities and thermal stabilities. Owing to its performance during testing, its insensitivity toward various ignition stimuli, and its perchlorate- and dechlorane plus free nature, formulation F was considered to be a viable environmentally sustainable alternative to the perchlorate-containing M195 control.

This formulation will now be evaluated at the systems demonstration level, where the illuminant will be incorporated into an HHS, launched into the air, and its ballistic performance will be measured. While an incompatibility concern may exist with the incorporation of **4** into magnesium-containing pyrotechnic formulations, this compound did not experience outgassing when subjected to the vacuum thermal stability test (100 °C for 48 h). Analysis of **4** by X-ray diffraction^[9a] has shown that the water molecule is not simply crystal water, but is instead coordinated to barium metal and this species is stable up to 349 °C, which is the decomposition temperature of the salt. However, in accordance with energetic material qualification protocols, if formulation F passes the system demonstration, it will also undergo vacuum thermal stability testing for safety assurance.

Conclusion

Environmentally conscious green-light-emitting formulations have been developed and proven for the M195 green-light-emitting HHS parachute at the prototype level. Although high-nitrogen compounds **1–4** served as initial potassium perchlorate replacements, barium bis-tetrazolate salt **4** was determined to be the best of the high-nitrogen compounds evaluated based on its performance in small-scale M195 formulations. Bis-tetrazolate salt **4** did not undergo outgassing when subjected to vacuum thermal stability and

X-ray diffraction has previously proven that the water molecule is not simply crystal water, but is instead coordinated to barium metal. Bis-tetrazolate salt **4** is stable up to its decomposition temperature of 349 °C. Although formulation D had acceptable performance, was thermally stable, and had a high level of stability toward impact, friction, and ESD, a new formulation needed to be developed owing to the presence of dechlorane plus over fears associated with potential bioaccumulation. Formulation F was therefore developed and proven at the prototype level. Compared with the control, formulation F was perchlorate- and dechlorane plus-free, and it utilized an epoxy binder system instead of a Laminac binder system, thus mitigating concerns associated with single-point-of-failure concerns. The performance of formulation F far exceeded the military requirement in burn time, luminous intensity, and spectral purity. Formulation F also had similar burn times and luminous intensities, lower sensitivities toward various ignition stimuli, and reasonable thermal stabilities when compared with the perchlorate-containing control. While the dominant wavelength observed for formulation F was outside the (540 ± 20) nm dominant wavelength requirement outlined in the Mil-Spec, the US Army in-service control formulation was also observed to be slightly outside of this dominant wavelength range. It was therefore determined that the dominant wavelength issue was not problematic in obtaining a green flame of acceptable quality. Formulation F will now be evaluated at the systems demonstration level. As was the case with bis-tetrazolate **4**, formulation F will undergo vacuum thermal stability testing as part of the energetic materials qualification process if systems demonstration testing is successful.

Experimental Section

Mg 30/50 (volume-based mean particle size = 523.44 μm), KClO₄ (volume-based mean particle size = 76.96 μm), Ba(NO₃)₂ (volume-based mean particle size = 139.70 μm), and PVC (volume-based mean particle size = 123.40 μm) were purchased from Hummel Croton. Dechlorane Plus (volume-based mean particle size = 83.67 μm) was purchased from OxyChem. Compounds **1**, **2**, **3**, and **4** (volume-based mean particle size = 381.24 μm) were synthesized by using previously established procedures.^[10a,14] Laminac 4116 was purchased from Ashland Chemical. Lupersol was purchased from Norac. Epon 813 was purchased from Hexion Specialty Chemicals. Versamid 140 was purchased from Cognis. All tested formulations were encased in uncoated Kraft fiberboard tubes, obtained from Security Signals.

All chemicals used in formulation preparation were dried in the oven overnight at 60 °C and were weighed out according to their weight percentages in the formulations. For small-scale formulations, 20 g formulations were prepared by weighing out the chemical according to their weight percentages in the formulations. All fuels (magnesium, chlorine donor, and **1–4**) were introduced to a binder system (95 % Laminac 4116/5 % Lupersol in the case of the control, and 80 % Epon 813/20 % Versamid 140 in the case of formulations A–F), and the mixtures were hand blended for 5 min in a ceramic dish by using a wooden tongue depressor. All oxidizers (barium nitrate and, in the case of the control, potassium perchlorate) were added to the dish. After hand mixing for 20 min, the control formulation was dried in the oven overnight at 60 °C, and formulations A–F were dried in air for 2–3 h at ambient temperature before consolidation.

Small-scale formulations were weighed out in two 3 g increments and pressed into uncoated Kraft fiberboard tubes (length of 4.93 cm, inner diameter of 0.838 cm). A tooling die (inner diameter of 1.27 cm, height of 5.08 cm) and a manual hand press at a consolidation dead load of 287 kg was used to facilitate consolidation. Between 5.46 and 6.51 g of energetic material was used per pellet and 6–7 pellets were tested for each formulation. The pellets were dried overnight in the oven at 60 °C and then coated with a thin layer of thermite-based igniter slurry in acetone. After the pellets were dried in the oven at 60 °C for 2 h to evaporate the acetone, they were ignited with an electric match in the light tunnel at ambient temperature and pressure.

For formulation preparation at the prototype level, a binder system (95 % Laminac 4116/5 % Lupersol for the control, and 80 % Epon 813/20 % Versamid 140 for formulations D–F) was introduced into a Hobart air mixing bowl and was vigorously mixed by hand with a wooden tongue depressor for 2 min. All fuels (magnesium, 4, and chlorine donor) were simultaneously added to the bowl and the mixture was blended with the aid of a B-blade at 207 kPa for 10 min. The air was turned off and all oxidizers (barium nitrate and, in the case of the control, potassium perchlorate) were added to the bowl and the pyrotechnic mixture was blended for 10 min at 207 kPa. The air was turned off, the inside of the mixing bowl was scraped with the B-blade to remove the pyrotechnic material sticking to the sides, and the mixture was blended again for 10 min at 207 kPa. The pyrotechnic mixture was poured from the air mixer bowl to a large ceramic bowl. Laminac 4116/Lupersol-based formulations were dried in the oven overnight to ensure full curing, and Epon 813/Versamid 140-based formulations were dried in air for 2–3 h at ambient temperature to ensure partial curing before consolidation.

Each formulation was weighed out in two 49.5 g increments and pressed into uncoated Kraft fiberboard tubes (length of 8.13 cm; inner diameter of 4.93 cm) with the aid of a tooling die (inner diameter of 5.08 cm) and a manual hand press at a consolidation dead load of 2273 kg. Between 98.68 and 98.99 g of energetic material was used per pellet, three pellets were prepared for each formulation, and the pellets were dried overnight in the oven at 60 °C. After being conditioned in the oven, a thin layer of thermite-based igniter slurry in acetone was applied to the top of each pellet. After the pellets were dried in the oven at 60 °C for 2 h to evaporate the acetone, they were ignited with an electric match in the light tunnel at ambient temperature and pressure.

Optical emissive properties of these formulations were characterized by using both a single element photopic light detector and a 2048 element optical spectrometer. The light detector used was manufactured by International Light and was composed of a SED033 silicon detector (33 mm² area silicon detector with quartz window) coupled to a photopic filter (Y filter) and a field of view limited hood (H hood). The current output of the detector was converted to voltage by using a DL Instruments 1211 transimpedance amplifier. Voltage output was collected and analyzed from the amplifier by using an NI-6115 National Instruments data card and in-house developed Labview-based data acquisition and analysis software.

The optical emissive spectrum of each sample was measured by using a 2048 element Ocean Optics HR2000 spectrometer coupled to a 400 micron core optical fiber. The dominant wavelength and spectral purity was measured based on the 1931 CIE method by using illuminant C as the white reference point. The spectrometer was calibrated by using both an Hg–Ar light source (Ocean Optics HG-1 wavelength standard) and a calibrated W light source (Ocean Optics LS-1-Cal). The average dominant wavelength and spectral purity based on the full burn of the sample was calculated. Impact sensitivity tests were carried out according to STANAG 4489^[20a] by using a BAM drop hammer. Friction sensitivity tests were carried out according to STANAG 4487^[20b] by using the BAM friction tester. Electrostatic discharge sensitivity tests were carried out by using an electric spark tester (Albany Ballistic Laboratories). Thermal stability was determined by using a Perkin–Elmer DTA/TGA instrument. Particle size analysis was determined by using a Malvern Morphologi G3 Analyzer.

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FULL PAPERS

Energetic Materials

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**High-Nitrogen-Based Pyrotechnics:
Development of Perchlorate-Free
Green-Light Illuminants for Military
and Civilian Applications**



It pays to be “green”: Perchlorate-free pyrotechnic formulations with green-light-emitting qualities (see picture) for both military use and civilian fireworks have been developed. The formulations, which are stable to impact, friction, electrostatic discharge, and thermal conditions, afforded excellent burn times and luminous intensity values.