

Mitigation of Single-Point-of-Failure: Development of M127A1 White Star Illuminant Compositions Containing an Epoxy Binder System

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Abstract: A replacement for the M127A1 hand-held signal illuminant was developed to alleviate concerns associated with single-point-of-failure. In addressing single-point-of-failure, Laminac 4116/Lupersol binder system were replaced with Epon 813/Versamid 140 binder system. Powdered sodium nitrate was replaced with prilled sodium nitrate in

the disclosed formulations to minimize hygroscopicity concerns associated with this oxidizer. The performance of the prilled sodium nitrate-based formulations, their burning behaviors, and the sensitivities of the best performing illuminant toward various ignition stimuli are also described in detail.

Keywords: Pyrotechnics · Energetic materials · Illuminants · Binders · Sodium nitrate

1 Introduction

Hand-held signals (HHS) are used in signaling troop movements and aircraft. Meant to attract attention and to identify the positions of military personnel, HHS technologies find use in both training exercises and combat situations, and improvements are being sought to advance existing HHS technology. One of the most popular HHS items used by the US military for illuminating purposes is the M127A1 white star parachute, consisting of approximately 85 g of illuminant composition with a minimum burn time of 25 s and a minimum luminous intensity of 90000 cd. At this time, there is no dominant wavelength or spectral purity requirement for this illuminant. The current M127A1 HHS illuminant formulation fielded by the US Army consists of magnesium, powdered sodium nitrate, and Laminac 4116/Lupersol polyester binder system. The result of this mixture is an intense and bright burning flame, due to the formation of white-light-emitting incandescent magnesium oxide (MgO) particles, and the presence of atomic sodium (Na⁺), which is a very intense emitter of yellow light [1].

Although the in-service M127A1 HHS illuminant is successful in achieving the military specifications, Laminac 4116/Lupersol is not an ideal binder system. The binder system is a single-point-of-failure, contains a suspected carcinogenic material (styrene monomer) [2], and has a limited shelf-life [3]. Because Laminac 4116/Lupersol binder system is currently the binder present in all HHS illuminating compositions, failure to replace this single-point-of-failure binder system poses a significant risk to the future of these pyrotechnic signaling munitions remaining in the arsenal of the warfighter. Without HHS illuminants in the warfighter's arsenal, combat readiness and survivability is at risk.

In a recent paper, the use of epoxy-based binder system Epon 813/Versamid 140 was found to be a non-energetic binder than Laminac 4116/Lupersol binder system, thus prolonging the burn time of red -and green-light-emitting illuminant compositions [4]. Although longer burn times are known to reduce luminous intensity values, it was believed that altering oxidizer/fuel/binder percentages would be beneficial in raising luminous intensity values in the presence of the Epon 813/Versamid 140 binder systems. Epon 813/Versamid 140 binder systems was thought to be a suitable choice in the development of a suitable M127A1 illuminant composition because the binder system is widely commercially available, thus mitigating concerns associated with single-point-of-failure. Moreover, the Epon 813/Versamid 140 has a proven history of working well as a replacement for the Laminac 4116/Lupersol binder system. It was the binder system of choice in red- and green-light-emitting illuminating signaling formulations, which were recently proven out at the prototype level [5].

In addition to mitigating single point-of-failure concerns, it was also of interest to minimize the hygroscopic nature associated with powdered sodium nitrate-based illuminants. Despite its strong oxidizing abilities and its tendency

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to enhance light intensity, the hygroscopic nature of powdered sodium nitrate is a cause for concern with respect to long-term storage issues. Therefore, it was decided that replacing powdered sodium nitrate with prilled sodium nitrate would minimize hygroscopicity by reducing the exposed surface area of the oxidizer. To address these concerns, Armament Research, Development and Engineering Center (ARDEC) launched an investigation to develop a successful illuminant using the aforementioned approach.

2 Results and Discussion

In developing a suitable replacement for the M127A1 illuminant, formulation **A** was developed to replace the control (Table 1). Although the weight percentages of these two formulations were kept constant, formulation **A** was composed of the widely available epoxy binder system and prilled sodium nitrate to address the respective single-point-of-failure and moisture sensitivity concerns.

The performance of formulation **A** as compared to control and the minimum military requirement for the M127A1 illuminant is summarized in Table 2, and the burning behavior of these illuminants is provided in Table 3. Although the burn time and linear burn rate of the control and formulation **A** were comparable, luminous intensity and luminous efficiency values for formulation **A** were appreciably lower. This is an interesting phenomenon since mass consumption tends to have a direct relationship with observed luminosity, though the opposite trend was observed.

It is possible that the control exhibited a higher luminous intensity and luminous efficiency due to the finer particle

size of powdered sodium nitrate present in the mix. Pyrotechnic mixtures composed of finer particle sizes would be expected to increase the homogeneous nature of the mix, which typically results in better performance. Alternatively, since Epon 813/Versamid 140 binder system has a more negative oxygen balance compared to Laminac 4116/Lupersol binder system [4], it would be expected to be a larger consumer of available oxygen in a pyrotechnic mixture. This phenomenon can result in both a reduction of flame temperature and the amount of magnesium oxide formed, thus leading to a decrease in visible light output. Although formulation **A** had a lower performance than the control, it did exceed the luminosity and burn time values outlined in the military's minimum requirements.

With a successful formulation in hand, it was envisioned that increasing the percentage of magnesium in the formulation may lead to a further increase in luminous intensity (Table 4). Up to a point, magnesium-rich pyrotechnic mixtures are known to produce higher luminous intensities well past their stoichiometric points; a phenomenon, which results from magnesium's relatively low boiling point and subsequent air oxidation in the plume of the flame [6].

Table 1. In-service M127A1 illuminant and its epoxy "drop-in".

M127A1 Control		Formulation A	
Component	wt.-%	Component	wt.-%
Magnesium 30/50	66	Magnesium 30/50	66
Powdered sodium nitrate	29	Prilled sodium nitrate	29
Laminac 4116/Lupersol	5	Epon 813/Versamid 140	5

Table 2. Prototype performance of formulation **A**.

Formulation	BT ^a /s	LI ^b /cd	LE ^c /cd sg ⁻¹	DW ^d /nm	SP ^e /%
Military requirement	25.0	90000.0	N/A	N/A	N/A
Control	31.4	117239.0	42070.5	587.4	86.5
A	30.3	94255.4	33590.5	588.1	88.4

a) BT = Burn time. b) LI = Luminous intensity. c) LE = Luminous efficiency. d) DW = Dominant wavelength. e) SP = Spectral purity.

Table 3. Burning behavior of the control and formulation **A**.

Formulation	Height of composition/cm	Weight of composition/g	Burn rate/cm s ⁻¹	Mass consumption/g s ⁻¹
Control	7.49	84.97	0.239	2.71
A	7.21	85.66	0.238	2.83

Table 4. Composition of formulation **B**.

Formulation B	
Component	wt.-%
Magnesium 30/50	71
Prilled sodium nitrate	24
Epon 813/Versamid 140	5

Table 5. Performance of formulation **B**.

Formulation	BT ^a /s	LI ^b /cd	LE ^c /cd sg ⁻¹	DW ^d /nm	SP ^e /%
Military requirement	25.0	90000.0	N/A	N/A	N/A
Control	31.4	117239.0	42070.5	587.4	86.5
B	29.7	84479.3	29419.2	588.2	86.7

a) BT = Burn time. b) LI = Luminous intensity. c) LE = Luminous efficiency. d) DW = Dominant wavelength. e) SP = Spectral purity.

Table 6. Burning behavior of formulation **B**.

Formulation	Height of composition/cm	Weight of composition/g	Burn rate/cm s ⁻¹	Mass consumption/g s ⁻¹
B	7.38	84.93	0.248	2.86

Unfortunately, addition of more magnesium did not have the desired effect of raising luminous intensity, and a substantial amount of sparking was observed as formulation **B** burned (Table 5). The “sparking out” is a clear indication that magnesium particles were falling outside of the flame plume’s reactive zone, thus explaining the observed decrease in luminous intensity and luminous efficiency. As the burning behavior indicates, formulation **B** had a faster linear burn rate than both the control and formulation **A**, serving to explain the smaller burn time of this formulation (Table 6). Again, however, the higher mass consumption of formulation **B** did not correlate to a brighter visible light output.

Although raising the percentage of magnesium in the formulation did not result in an increase in luminosity, using a lower percentage of organic binder is also known to lead to higher luminous intensities. This presumably occurs since more oxygen in the pyrotechnic mixture is available to react with magnesium in a highly energetic process to form white-light-emitting incandescent magnesium oxide particles as opposed to reacting with the relatively low-energy and gas-generating organic binder system [7]. White-light-emitting compositions consisting of lower binder percentages are outlined in Table 7.

The performances of formulations **C** and **D** are summarized in Table 8, with the burning behaviors of these formu-

lations reported in Table 9. Formulations **C** and **D** exceeded the values outlined in the minimum military requirement when tested statically. Although reducing the binder percentage from 5% to 4% resulted in a slight increase in luminous intensity and luminous efficiency (i.e. comparing the performances of formulations **A** and **C**), a significant increase in luminosity and luminous efficiency was observed when the binder percentage was reduced further to 3%. As expected, a reduction in the amount of binder system present in a formulation correlated with increases in luminous intensity, luminous efficiency, linear burn rate and mass consumption rate.

Although formulation **D** had the highest luminous intensity of all formulations that were tested, its relatively short burn time makes it a poor choice for systems demonstration testing. Since systems demonstration involves ballistic testing of illuminants, formulation **D** is at risk of failing the burn time requirement since ballistic burning is faster than static burning. The burn time of formulation **C** is closer to that observed in the control, and is therefore the logical choice to be evaluated further at the systems demonstration phase.

Formulation **C** was compared to the control with respect to their impact, friction, electrostatic discharge, and thermal stabilities, as outlined in Table 10 [8]. Formulation **C** had

Table 7. Composition of formulations **C** and **D**.

Formulation C		Formulation D	
Component	wt.-%	Component	wt.-%
Magnesium 30/50	66	Magnesium 30/50	66
Prilled sodium nitrate	30	Prilled sodium nitrate	31
Epon 813/Versamid 140	4	Epon 813/Versamid 140	3

Table 10. Behavior of the control and formulation **C** toward various ignition stimuli.

Formulation	Impact/J	Friction/N	ESD ^a /J	Thermal onset/°C
Control	11.3	> 360	> 0.25	590.7
C	11.8	> 360	> 0.25	425.0

a) ESD = Electrostatic discharge.

Table 8. Performance of formulations **C** and **D**.

Formulation	BT ^a /s	LI ^b /cd	LE ^c /cd.sg ⁻¹	DW ^d /nm	SP ^e /%
Military requirement	25.0	90000.0	N/A	N/A	N/A
Control	31.4	117239.0	42070.5	587.4	86.5
C	29.6	97253.7	33800.5	588.0	85.1
D	26.2	129059.9	39888.6	588.8	83.8

a) BT = Burn time. b) LI = Luminous intensity. c) LE = Luminous efficiency. d) DW = Dominant wavelength. e) SP = Spectral purity.

Table 9. Burning behavior of formulations **A**, **C**, and **D**.

Formulation	Height of composition/cm	Weight of composition/g	Burn rate/cm s ⁻¹	Mass consumption/g s ⁻¹
A	7.21	85.66	0.238	2.83
C	7.23	84.97	0.244	2.87
D	7.32	84.91	0.279	3.24

comparable sensitivities compared to the in-service M127A1, and was therefore deemed to be a safe alternative to the in-service M127A1 illuminant.

3 Experimental Section

3.1 Materials

Magnesium 30/50 was purchased from Magnesium Elektron. Powdered sodium nitrate and prilled sodium nitrate was purchased from Hummel Croton. Laminac 4116 was purchased from Ashland Chemical Company. Lupersol was purchased from Norac. Epon 813 was purchased from Hexion Specialty Chemicals. Versamid 140 was purchased from Cognis. Kraft uncoated fiberboard tubes were obtained from Security Signals, Inc. All materials were used "as received" from the respective companies.

3.2 Preparation of M127A1 Formulations

With the exception of the binder system ingredients, all chemicals were dried overnight in the oven at 60 °C prior to mixing. The following procedure describes the formulation preparation and consolidation process of full-up prototype mixes: 400 g mixes were prepared by weighing out the chemicals according to their weight percentages in the formulations. An 80% Epon 813/20% Versamid 140 mixture was introduced into a 5 quart Hobart N50 mixing bowl, and was mixed for 1–2 min with a wooden stick. Magnesium was added to the mixing bowl, and the mixture was blended for 15 min at 30 psi with the aid of a "B" blade. Mixing was stopped, the sides of the mixing bowl were scraped manually with the "B" blade, sodium nitrate was added to the bowl, and the mixture was blended for an additional 10 min. After mixing, the 400 g formulation was transferred to a large ceramic bowl and was dried in air for 2–3 h at ambient temperature before consolidation.

After drying, the formulation was weighed out in two 42.5 g increments, and was pressed into non-coated Kraft fiberboard tubes (length of 8.13 cm; inner diameter of 4.93 cm) with the aid of a tooling die (diameter of 5.08 cm) and a manual hand press at a consolidation dead load of 3,409 kg. Between 84.91–85.66 g of energetic material was used per candle, and four candles were prepared for each formulation. After consolidation, the candles were dried overnight in the oven at 60 °C. After being conditioned in the oven, the candles were ignited with an electric match in the light tunnel at ambient temperature and pressure.

3.3 Characterization

Optical emissive properties of these formulations were characterized using both a single element photopic light detector and a 2048 element optical spectrometer. The light detector used was manufactured by International Light and is composed of a SED 033 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 using a DL Instruments 1211 transimpedance amplifier. Voltage output was collected and analyzed from the amplifier using a NI-6115 National Instruments data card and in-house developed Labview™ based data acquisition and analysis software.

Impact sensitivity tests were carried out according to STANAG 4489 [8a] using a BAM drop hammer. Friction sensitivity tests were carried out according to STANAG 4487 [8b] using the BAM friction tester. Electrostatic discharge sensitivity tests were carried out with an electric spark tester (Albany Ballistic Laboratories). Thermal stability was determined with a Perkin-Elmer DTA/TGA instrument. Particle size analysis was determined with a Malvern Morphologi G3 Analyzer.

4 Conclusions

Several M127A1 HHS illuminant formulations were developed to replace the Army's in-service M127A1 illuminant. The approaches taken were beneficial because all formulations utilized a widely available epoxy binder system not plagued by concerns such as single-point-of failure and limited shelf-life. An added benefit of all formulations was their consisting of prilled sodium nitrate oxidizer as opposed to the powdered form. Since the use of the prilled material reduces the exposed surface area of the oxidizer, it is logical to conclude that the moisture sensitivities of these formulations would be minimized.

In evaluating the prilled sodium nitrate-based formulations containing the epoxy binder system, raising magnesium percentages led to excessive sparking and reduced visible light output. The best way to enhance the light intensity and efficiency for this pyrotechnic system without using a finer oxidizer was to reduce the amount of epoxy binder system used. Of the prilled sodium nitrate-based formulations, formulation C afforded the best performance. Formulation C exceeded the values outlined in the military requirements, and it had comparable sensitivities to various ignition stimuli. The performance of formulation C will be evaluated ballistically as part of the systems demonstration phase.

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References

- [1] J. A. Conkling, C. J. Mocella, *Chemistry of Pyrotechnics: Basic Principles and Theory*, 2nd ed., CRC Press-Taylor & Francis Group, Boca Raton, FL, USA, **2010**, pp. 180–183.
- [2] B. E. Erickson, Formaldehyde, Styrene Cancer Warning, *Chem. Eng. News* **2011**, *89*, 11.
- [3] G. R. Lakshminarayanan, G. Chen, R. Ames, W. T. Lee, J. L. Wejsa, K. Meiser, *Mitigation of Critical Single Point Failure (SPF) Material-Laminac 4116 Binder Replacement Program for Parachute and Cluster Stars Illuminant Compositions for Hand Held Signals*, Report ADA481835, Defense Technical Information Center, Fort Belvoir, VA, USA, **2006**.
- [4] J. J. Sabatini, C. T. Freeman, J. C. Poret, A. V. Nagori, G. Chen, An Examination of Binder Systems and Their Influences on Burn Rates of High-Nitrogen Containing Formulations, *Propellants Explos. Pyrotech.* **2011**, *36*, 145–150.
- [5] a) J. J. Sabatini, A. V. Nagori, G. Chen, P. Chu, R. Damavarapu, T. M. Klapötke, High-Nitrogen-Based Pyrotechnics: Longer- and Brighter-Burning, Perchlorate-Free, Red-Light Illuminants for Military and Civilian Applications, *Chem. Eur. J.* **2012**, *18*, 628–631; b) J. J. Sabatini, A. V. Nagori, J. C. Poret, E. A. Latalladi, G. Chen, R. Damavarapu, T. M. Klapötke, Applications of High-Nitrogen Energetics in Pyrotechnics: Development of Perchlorate-Free Red Star M126A1 Hand-Held Signal Formulations with Superior Luminous Intensities and Burn Times, *Propellants Explos. Pyrotech.* **2011**, *36*, 373–378; c) J. J. Sabatini, J. M. Raab, R. K. Hann, R. Damavarapu, T. M. Klapötke, High-Nitrogen-Based Pyrotechnics: Development of Perchlorate-Free Green-Light Illuminants for Military and Civilian Applications, *Chem. Asian J.* **2012**, *7*, 1657–1663.
- [6] D. Dillehay, *Pyrotechnic Reference Series, No. 4, Pyrotechnic Chemistry* (Eds.: K. Kosanke, B. J. Kosanke, I. von Maltitz, B. Sturman, T. Shimizu, M. A. Wilson, N. Kubota, C. Jennings-White, D. Chapman), Journal of Pyrotechnics Inc., Whitewater, CO, USA, **2004**, Chapter 10, pp. 1–4.
- [7] J. A. Conkling, C. J. Mocella, *Chemistry of Pyrotechnics: Basic Principles and Theory*, 2nd ed., CRC Press-Taylor & Francis Group, Boca Raton, FL, USA, **2010**, pp. 89–93.
- [8] a) *NATO Standardization Agreement (STANAG) on Explosives, Friction Sensitivity Tests*, No. 4487, 1st ed., August 22, **2002**; b) *NATO Standardization Agreement (STANAG) on Explosives, Impact Sensitivity Tests*, No. 4489, 1st ed., September 17, **1999**.

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