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Full Paper

An Examination of Binder Systems and Their Influences on Burn Rates of High-Nitrogen Containing Formulations

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Dedicated to Mr. Paul Agresti for his lifelong commitment to public service at Picatinny Arsenal in a career that spanned over four decades

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Abstract

The examination of Laminac 4116/Lupersol and Epon 813/Versamid 140 binder systems, and their influences on burn rates of pyrotechnic formulations is described. Laminac 4116/Lupersol based formulations had shorter burn times and larger heat of explosion values compared to their Epon 813/Versamid 140 counterparts. An understanding of the chemical structures and approximate oxygen balances of these binder systems served to explain their burn time differences when used in pyrotechnic formulations. Bomb calorimetry of Laminac 4116/Lupersol and Epon 813/Versamid 140 based formulations provided heat of explosion values to further explain the burn time differences of the two binder systems used.

Keywords: Binders, Energetic Materials, Hand Held Signals, High Nitrogen, Pyrotechnics

1 Introduction

Hand-held signals (HHS) are used in signaling troop movements and aircraft crew. They are meant to attract attention, day or night, and serve as a beacon for rescuers to identify the positions of military personnel. HHS technologies find use in both training exercises and combat situations, and improvements are being sought-after to advance existing HHS technology. Currently existing HHS candle formulations contain significant amounts of potassium perchlorate ($KClO_4$), which contaminates groundwater and public drinking supplies. $KClO_4$ interferes with hormonal regulation of the thyroid gland, and is teratogenic. Recently, the US Environmental Protection Agency has reduced the permissible perchlorate level to 15 parts per billion [1]. The US Department of Defense spends tens of billions of dollars annually on perchlorate remediation efforts. Therefore, efforts to eliminate perchlorate from military pyrotechnics have been a high priority over the past years.

A program was initiated at Army Research, Development and Engineering Center (ARDEC) to develop perchlorate-free formulations of the M126A1 red star parachute. To maximize the performance of these formulations, $KClO_4$ was replaced with strontium *bis*-(1-methyl-5-nitriminotetrazolate) monohydrate (**1**). In recent years, the interest of using high-nitrogen compounds for energetic properties in military munitions has gained traction. Klapötke and co-workers have recently demonstrated the remarkable stabilities of many high-nitrogen tetrazole compounds. These compounds derive their high energies from their high heats of formation instead of the oxidation of a carbon backbone [2].

Binders are commonly used in the development of pyrotechnic materials to prevent the segregation of oxidizers and fuels during the consolidation phase and throughout the lifecycle of a formulation in munitions systems. Use of a binder typically increases the homogeneity of a pyrotechnic mixture, thus increasing the chances of successful ignition and/or successful performance of a pyrotechnic. Binders fall into two main categories; energetic binders and non-energetic binders. Energetic binders, such as glycidyl azide polymer (GAP), provide substantial energy to a pyrotechnic formulation [3]. These binders typically increase the burn rate and can also enhance the sensitivity of the formulation. Non-energetic binder systems such as Laminac 4116/Lupersol and Epon 813/Versamid 140 serve as curable low-energy fuels and are not believed to provide substantial energy to a pyrotechnic

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14. ABSTRACT
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formulation. They typically serve to retard burn rates by decreasing the overall energy of a pyrotechnic formulation through the inhibition of chemical reactions between adjacent particles.

This paper discusses how chemical structures and associated oxygen balances of Laminac 4116/Lupersol and Epon 813/Versamid 140 binder systems affect burn rates and performance in pyrotechnic formulations. Bomb calorimetry of Laminac 4116/Lupersol- and Epon 813/Versamid 140-based pyrotechnic formulations offers a further explanation as to why these binders provide significant differences in burn rates.

2 Experimental Part

2.1 Materials

Mg 30/50 and Mg 50/100 were purchased from Reade. $KClO_4$, $Sr(NO_3)_2$, PVC, and $Ba(NO_3)_2$, were purchased from Hummel Croton. Dechlorane plus was purchased from OxyChem. 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. Strontium *bis*-(1-methyl-5-nitriminotetrazolate) monohydrate (**1**) was synthesized in-house (Picatinny Arsenal, NJ) by a proprietary procedure. All tested formulations were encased in 4.93 cm tall uncoated Kraft fiberboard tubes, obtained from Grucci.

2.2 Preparation of M126A1 Formulations

Twenty-gram formulations were prepared by accurately weighing out the chemicals according to their respective weight percentages in the HHS formulations. After drying the chemicals overnight, they were introduced to a binder system (Laminac 4116/Lupersol or Epon 813/Versamid 140), and the mixture was hand-blended for 20 min. The composition ratio of Laminac 4116/Lupersol is 95/5. The composition ratio of Epon 813/Versamid 140 is 80/20. After hand-mixing, Laminac/Lupersol-based formulations were dried in the oven overnight at 60 °C, and Epon 813/Versamid 140-based formulations were dried in air for 2–3 h at ambient temperature to ensure proper curing. After curing, bomb calorimetry was performed to measure the heat of explosion of each formulation.

Formulations were weighed out in two 3 g increments, and were 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 5.91–6.04 g of energetic material was used per pellet, and 6–7 pellets were tested for each formulation.

2.3 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 mm^2 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 transimpediance amplifier. Voltage output was collected and analyzed from the amplifier using a NI-6115 National Instruments datacard and in-house developed Labview™ based data acquisition and analysis software.

The heat of explosion was measured using a Parr 1261 Bomb Calorimeter. Three 1 g samples of each formulation were tested, and the performance of these samples for each formulation was averaged together to yield an average energy output. For each test, 1 g of formulation mix was placed into a Parr stainless steel capsule. A 15 cm length of nichrome wire attached to two leads was imbedded into the formulation, and the material was placed inside of a Parr 1108 oxygen combustion vessel. The vessel was charged to 3.10 MPa with argon, placed into the calorimeter cell, and the heat of explosion was digitally recorded in joules per gram.

3 Results and Discussion

In connection with a program to develop an environmentally benign and perchlorate-free M126A1 HHS, the decision was made to modify the existing formulation so that the new "green" formulations would still meet or exceed military specification values of the currently existing formulation (Table 1). In hopes of achieving optimal burn

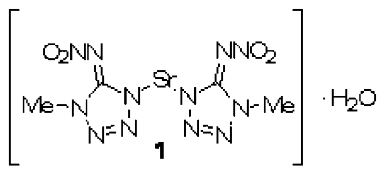


Figure 1. Strontium *bis* (1 methyl 5 nitriminotetrazolate) mono hydrate.

Table 1. Existing formulation (baseline) for the M126A1 hand held signal.

Components	wt. %
Strontium Nitrate	39.3
Magnesium 50/100	14.7
Magnesium 30/50	14.7
Polyvinyl Chloride	14.7
Potassium Perchlorate	9.8
Laminac 4116/Lupersol	6.8

Table 2. Prepared mixes containing Laminac/Lupersol binder.

Formulation **A**		Formulation **B**		Formulation **C**	
Components	wt. %	Components	wt. %	Components	wt. %
$Sr(NO_3)_2$	39.3	$Sr(NO_3)_2$	40.3	$Sr(NO_3)_2$	41.3
Mg 30/50	29.4	Mg 30/50	30.4	Mg 30/50	31.4
PVC	14.7	PVC	15.7	PVC	16.7
High Nitrogen **1**	9.8	High Nitrogen **1**	6.8	High Nitrogen **1**	3.8
Laminac/Lupersol	6.8	Laminac/Lupersol	6.8	Laminac/Lupersol	6.8

times, $KClO_4$ was replaced with strontium *bis*-(1-methyl-5-nitriminotetrazolate) monohydrate (**1**) (Figure 1).

When this "drop-in" experiment failed to meet desired burn time requirements, the existing formulation underwent further modifications. A series of Laminac 4116/Lupersol-based formulations using Mg 30/50 as the sole magnesium source to extend the burn time were developed, thus taking advantage of its larger particle size (Table 2).

Although using Mg 30/50 as the sole magnesium source resulted in a substantial increase in burn times, all Laminac 4116/Lupersol-containing formulations fell short of the perchlorate-containing baseline (Table 4, formulations **A**–**C**).

Although useful in pyrotechnics, Laminac 4116/Lupersol binder system contains carcinogenic styrene monomer and has a limited shelf life [4]. To address the human health concerns and to extend the lifecycle of the M126A1 HHS, the commonly used Epon 813/Versamid 140 binder system was chosen as its replacement (Table 3). As detailed in Table 4, the burn time of the perchlorate-containing baseline outperformed all Laminac 4116/Lupersol-based formulations (**A**–**C**), whereas all Epon 813/Versamid 140-based formulations (**D**–**F**) had significantly longer burn times compared to Laminac 4116/Lupersol-based formulations.

Although increases in burn times resulting from the Epon 813/Versamid 140 binder system were of high importance toward the development of the M126A1 HHS, it was not known why changing the binder system had a significant impact on burn times. To understand this phenomenon, the chemical structures of the two binders used in our formulations were examined.

Scheme 1 summarizes the synthesis process of cross-linked polyester resin (**7**); the product that results from curing of the Laminac 4116/Lupersol binder system. Polyester (**5**) is synthesized by a series of condensation reactions from propylene glycol (**2**), phthalic anhydride (**3**)

Table 4. Burn times of prepared formulation mixes.

Formulation	Burn Time (s)
$KClO_4$ Baseline	32.16
A	26.20
B	26.87
C	24.85
D	39.41
E	36.91
F	37.61

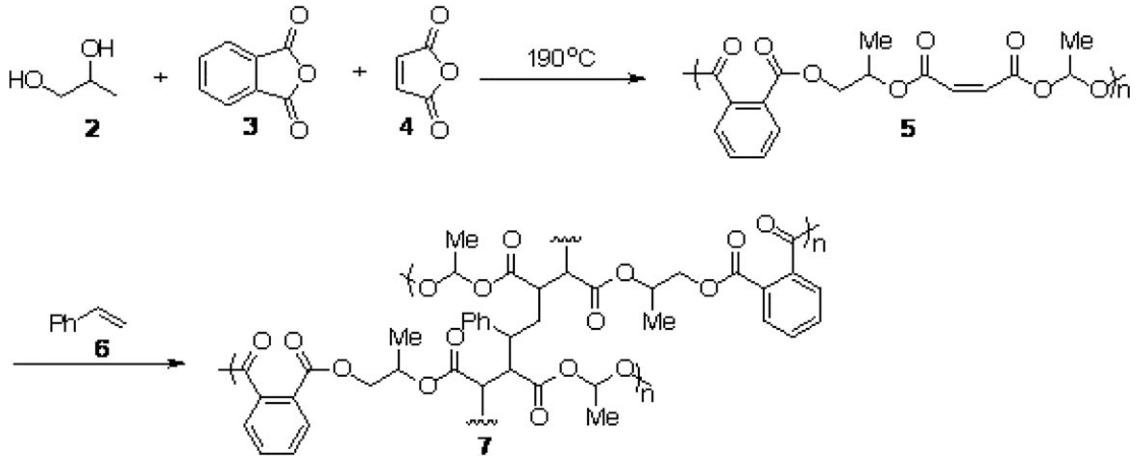
and maleic anhydride (**4**). Cross-linking of polyester (**5**) and styrene (**6**) yields polyester resin (**7**). This radical reaction is achieved by the addition of Lupersol (methyl ethyl ketone peroxide).

Scheme 2 summarizes the synthesis process of cross-linked bisphenol A epoxy resin (**12**); the product that results from curing of the Epon 813/Versamid 140 binder system. Epoxy resin (**10**) is synthesized in a bidirectional fashion from bisphenol A (**8**) and epichlorohydrin (**9**). Treating epoxy resin (**10**) with triethylenetetramine (TETA), a main component of Versamid 140, promotes cross-linking, affording epoxy resin (**12**).

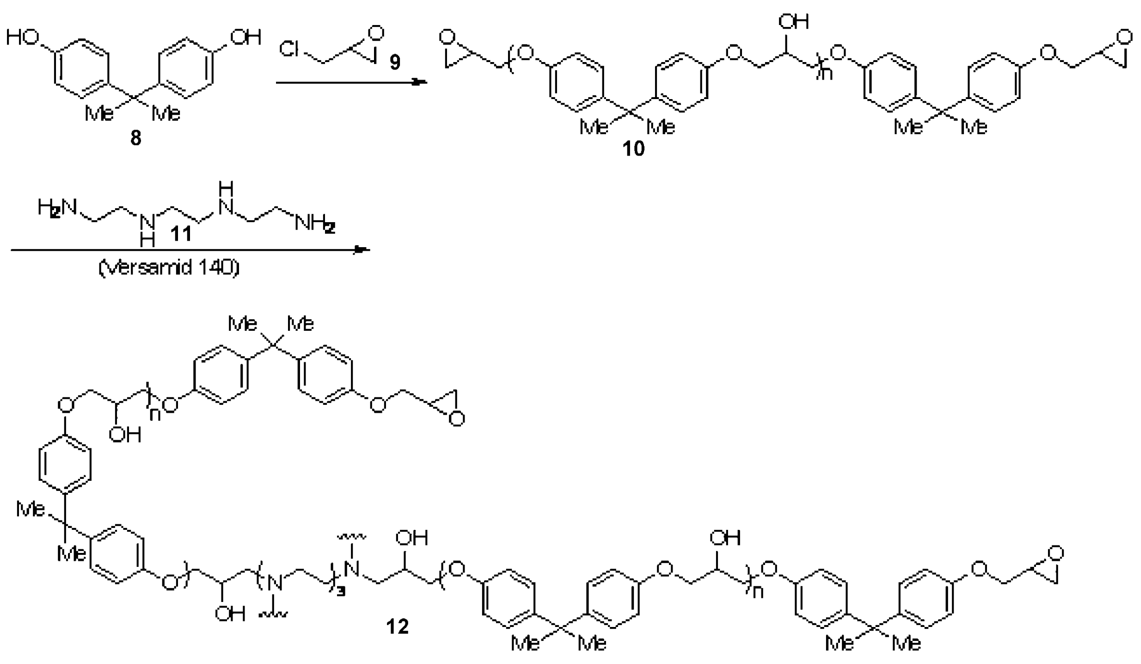
Upon examination of their respective chemical structures, it was noticed that large differences between the Laminac 4116/Lupersol (**7**) and the Epon 813/Versamid 140 (**12**) binder systems were evident. It was believed that the structural differences played a significant role in the differing burn rates. To gain a further understanding of binder system differences, oxygen balance calculations were performed. For simplicity purposes, it was assumed that the polymer length of the binders were $n=1$. Therefore, the molecular formula of the Laminac 4116/Lupersol binder system (**7**) was $C_{42}H_{39}O_{16}$ and the molecular formula for the Epon 813/Versamid 140 binder system (**12**) was $C_{83}H_{98}N_4O_{14}$. The oxygen balance (OB%) of these two binder systems was calculated according to Eq. 1, where X is the number of carbon atoms, Y the number of

Table 3. Prepared mixes containing Epon 813/Versamid 140 binder.

Formulation **D**		Formulation **E**		Formulation **F**	
Components	wt. %	Components	wt. %	Components	wt. %
$Sr(NO_3)_2$	39.3	$Sr(NO_3)_2$	40.3	$Sr(NO_3)_2$	41.3
Mg 30/50	29.4	Mg 30/50	30.4	Mg 30/50	31.4
PVC	14.7	PVC	15.7	PVC	16.7
High Nitrogen **1**	9.8	High Nitrogen **1**	6.8	High Nitrogen **1**	3.8
Epon 813/Versamid 140	6.8	Epon 813/Versamid 140	6.8	Epon 813/Versamid 140	6.8



Scheme 1. Synthesis of cross linked Laminac polyester resin.



Scheme 2. Synthesis of cross linked bisphenol A epoxy resin.

hydrogen atoms, M the number of atoms of metallic oxide formed in the reaction upon combustion, and Z is the number of oxygen atoms.

$$\mathrm{OB\%} = \left(\frac{-1600}{MW\,\mathrm{Compound}}\right) \times \left(2X + \left(\frac{Y}{2}\right) + M - Z\right) \quad (1)$$

The oxygen balance of Laminac 4116/Lupersol binder system was calculated to be -175% and the oxygen balance of Epon 813/Versamid 140 binder system was calculated to be at most -234%. The oxygen balance of the Epon 813/Versamid 140 binder system is likely more negative than calculated because Epon 813 epoxy resin is diluted with cresyl glycidyl ether, and Versamid 140 curing agent contains C18 unsaturated fatty acid dimers and their resulting products with polyethylenepolyamines [5]. These carbon-rich compounds have very negative oxygen balances, but the percentages to which these compounds exist in the binder formulation is not known. Therefore, the existence of these additives in the Epon 813/Versamid 140 binder system was not included in the calculations. Nevertheless, the underlying differences between the Laminac 4116/Lupersol and the Epon 813/Versamid 140 binder systems remain the same; Laminac 4116/Lupersol binder system has a higher oxygen balance than Epon 813/Versamid 140 binder system.

Because the oxygen balance of the Laminac 4116/Lupersol binder system was higher (i.e. closer to zero) than the Epon 813/Versamid 140 binder system, it was theorized that less oxygen was required for complete combustion of the binder material (i.e. CO_2 and H_2O formation). With less oxygen being consumed by the Laminac 4116/

Table 5. Heat of explosion of formulations **A**–**F**.

Laminac 4116/Lupersol Based Formulations	Epon 813/Versamid 140 Based Formulations
Formulation **A**	Formulation **D**
4494.54 $J\,g^{-1}$	4136.88 $J\,g^{-1}$
Formulation **B**	Formulation **E**
4385.77 $J\,g^{-1}$	3735.95 $J\,g^{-1}$
Formulation **C**	Formulation **F**
4598.27 $J\,g^{-1}$	4145.99 $J\,g^{-1}$

Table 6. Perchlorate containing M195 baseline formulations.

Formulation **G**		Formulation **H**	
Components	wt. %	Components	wt. %
Barium Nitrate	48	Barium Nitrate	48
Magnesium 30/50	22	Magnesium 30/50	22
Dechlorane	15	Dechlorane	15
Potassium Perchlorate	10	Potassium Perchlorate	10
Laminac 4116/Lupersol	5	Epon 813 Versamid 140	5

Lupersol binder system, more oxygen was available to react with high-energy magnesium and high-nitrogen fuels, resulting in shorter burn times. On the other hand, the lower oxygen balance of the Epon 813/Versamid 140 binder system (i.e. more negative value) resulted in more oxygen being required for complete combustion of the binder material. With more oxygen being consumed by the Epon 813/Versamid 140 binder system, less oxygen was available to react with the high-energy fuels in the formulations, resulting in longer burn times.

Although chemical and mathematical explanations for the large differences in burn times between Laminac 4116/Lupersol- and Epon 813/Versamid 140-based formulations were provided, heat of explosion data by means of bomb calorimetry was obtained for formulations **A**–**F** to further prove-out the analysis. Since Laminac 4116/Lupersol-based formulations had higher oxygen balances and shorter burn times (Table 4, formulations **A**–**C**), they were expected to possess higher heat of explosion values compared to their Epon 813/Versamid 140-based formulation counterparts (Table 4, formulations **D**–**F**).

As summarized in Table 5, bomb calorimetry data showed that regardless of the formulation, Laminac 4116/Lupersol-based mixes yielded larger heat of explosion values compared to the Epon 813/Versamid 140-based mixes. To truly appreciate the data, note the differences in heat of explosion between mixes that contain identical formulations with the sole exception of the binder system used. For example, with the exception of the binder system, the makeup of formulations **A** and **D** are identical. The fact that Laminac 4116/Lupersol-based formulations afforded significantly higher heat of explosion values relative to Epon 813/Versamid 140-based formulations provided further justification of the chemical and mathematical explanations used to explain the effect these binder systems had on influencing burn rates.

Although the choice of binder system effected burn times in formulation development for the M126A1 HHS,

Table 7. Burn time and heat of explosion of prepared M195 baseline formulations.

Formulation	Burn Time (s)	Energy Output ($J\,g^{-1}$)
G	44.58	4088.50
H	51.28	3782.68

it was of interest to see if these studies were solely limited to the M126A1 HHS system, or if these studies could be applied toward the development of other HHS systems. To further leverage these studies, formulations relating to the M195 green star parachute HHS were investigated (Table 6). Formulation **G** is the US Army in-service M195 signal formulation, but its Epon 813/Versamid 140-based derivative (formulation **H**) was developed to conclude the binder study.

As summarized in Table 7, the Laminac 4116/Lupersol-based formulation had a shorter burn time and a larger heat of explosion value compared to its Epon 813/Versamid 140 counterpart, making this trend applicable to more than one HHS system.

4 Conclusion

In summary, Laminac 4116/Lupersol-based formulations consistently afforded larger heat of explosion values and shorter burn times compared to their Epon 813/Versamid 140-based formulation counterparts. This phenomenon arose due to significant differences in chemical structures between the two binder systems that led to substantial differences in oxygen balance. Laminac 4116/Lupersol binder system consumed less oxygen, meaning that more oxygen was available in the formulations to react with other high-energy fuels such as magnesium and high-nitrogen compounds. The Epon 813/Versamid 140 binder system consumed more oxygen, meaning less oxygen was available in the formulations to react with other high-energy fuels. Although both are thought of as being non-energetic binders, bomb calorimetry data indicated that Laminac 4116/Lupersol is a more energetic binder system than Epon 813/Versamid 140. Studies showed that depending on the binder system used, pyrotechnic formulations could be tuned to accommodate shorter or longer burn times. It has been demonstrated that the aforementioned trends apply not only to the M126A1 red HHS parachute, but also apply to the M195 green HHS parachute.

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