

Environmentally Benign Energetic Time Delay Compositions: Alternatives for the U.S. Army Hand-Held Signal

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ABSTRACT

Pyrotechnic delays are used to provide reproducible time intervals between energetic events. The simplicity and low cost of these “chemical timers” make them advantageous for inexpensive munitions such as hand grenades and signaling devices. For example, U.S. Army hand-held signals (HHS) use a pyrotechnic delay element to properly time the expulsion of illumination or smoke payloads once the rockets reach their apex. These items and other munitions use delay compositions containing chromates, perchlorates, and heavy metals. Over the last three years, our division has been working to develop environmentally benign replacement compositions for use in the U.S. Army hand-held signal. The large thermal mass of the HHS delay housing, combined with the long burning time requirement and short burning path, made it particularly difficult to develop suitable replacements. Many candidate compositions either burned too quickly or were quenched in this high heat loss environment. However, some of these systems, such as Si/Bi₂O₃/Sb₂O₃ and Ti/C-3Ni/Al may be suitable for other applications including grenade fuzes. Ultimately, two systems were found to meet the HHS delay time requirement (5-6 s, 7-8.5 s/cm). The first, W/Sb₂O₃/KIO₄/calcium stearate, was shown to operate across a wide range of inverse burning rates, 2-15 s/cm. The second system, B₄C/NaIO₄/PTFE, proved even more versatile (1.3-20.8 s/cm). In this article, we describe the course of research throughout the program and discuss the general challenges associated with the development of new energetic time delay compositions.

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INTRODUCTION

Pyrotechnic delays have long been used in military munitions and commercial fireworks. Delays are used to provide a reproducible time interval between two events. For example, a timed delay is needed between the ignition of a rocket engine and the expulsion of its payload at apogee. The first black powder fuzes were developed over several hundred years ago [1]. Modern pyrotechnic military delays are primarily composed of metallic or semi-metallic fuels, chromate or perchlorate oxidizers, binders, and diluents. Table 1 shows a list of military delays and their chemical components. ALL of these delays contain environmentally hazardous compounds such as chromates and perchlorates. To mitigate current and future environmental regulatory risk, the U.S. Department of Defense is developing environmentally benign energetic systems, including pyrotechnics, and is eliminating hazardous materials whenever possible.

Table 1. List of military delays with corresponding reference numbers and chemical components.

Composition	Reference Number	Components
hand-held signal delay	drawing 9251412	W, BaCrO ₄ , KClO ₄ , VAAR
tungsten delay	MIL-T-23132A	W, BaCrO ₄ , KClO ₄ , diatomaceous earth
manganese delay	MIL-M-21383A	Mn, BaCrO ₄ , PbCrO ₄
zirconium-nickel delay	MIL-C-13739A	Zr-Ni alloy, BaCrO ₄ , KClO ₄
T-10 delay	MIL-D-85306A	B (amorphous), BaCrO ₄

Three years ago we initiated a project at ARDEC with funding from the U.S. Army RDECOM Environmental Quality Technology (EQT) Program to replace the tungsten delay used in the U.S. Army's hand-held signal (HHS) rockets. These rockets are designed to produce light or colored smoke for signaling and illumination. There are nine different rockets, each producing a specific effect. For example, the M125A1 expels free-falling green clusters at peak altitude while the M126A1 deploys a long burning red candle suspended by a parachute. Approximately 180,000 rockets (all variants) are produced each year for the U.S. Army. A cross sectional diagram is shown for a generic item in Figure 1a. The HHS rocket is activated by striking the primer, which ignites a black powder pellet. In turn, this ignites the rocket motor and delay element at approximately the same time. The delay element burns for approximately 6 seconds prior to igniting a black powder expulsion charge thereby ejecting the payload from the rocket.

Within the delay element, the delay composition is surrounded by two thin pressed layers of black powder. The HHS delay housing and a typical loading scheme are shown in Figure 1b. The housing is a 14.5 gram disc of aluminum that serves as a structural component within the HHS rocket, connecting the propulsion and payload sections by a threaded hole in the middle of the disc. The delay channel is off-center and is 0.476 cm in diameter by 1.016 cm long. The current tungsten-based delay used in HHS is composed of 32% W, 56.3% BaCrO₄, 11.4% KClO₄, and 0.3% vinyl alcohol-acetate resin (VAAR). (All chemical percentages in this report are weight percentages.) This is a variant of the classic tungsten delay

(MIL-T-23132A) that uses no binder and diatomaceous earth as a diluent [2]. With this traditional MIL-spec system, inverse burning rates ranging from 0.06 to 15 s/cm can be produced depending on the relative amounts of each component as well as the tungsten particle size and granulation of the $KClO_4$.

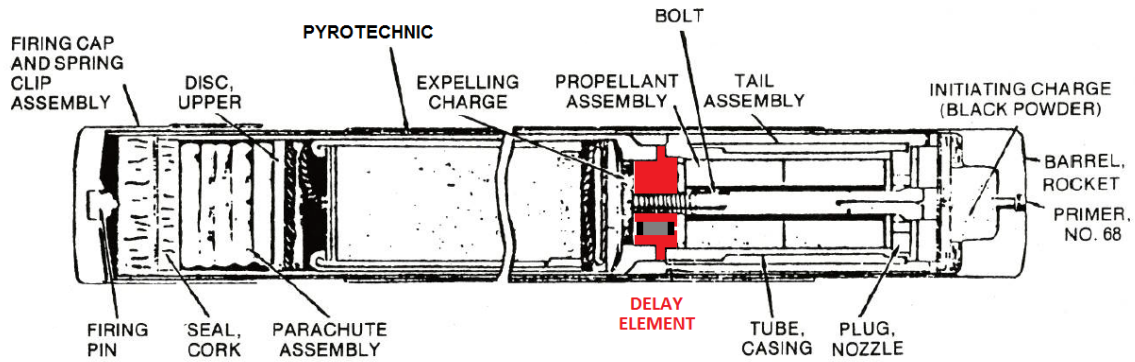


Figure 1a. Cross section of a HHS rocket.

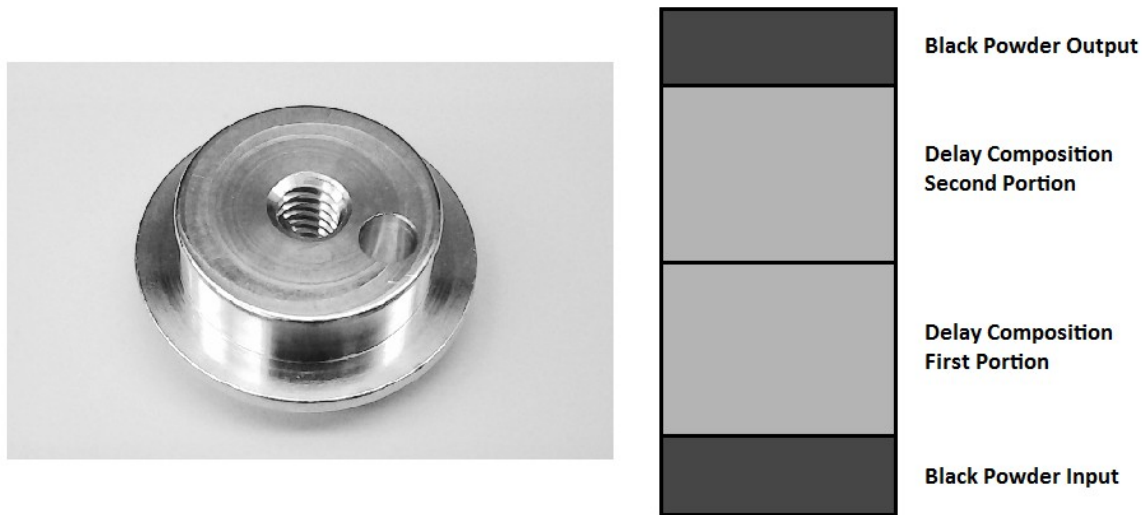


Figure 1b. The aluminum HHS delay housing (left) and a typical column loading scheme (right). Note the delay composition is pressed into the off-center opening, not the middle threaded hole.

DEVELOPMENT APPROACH

CONDENSED PHASE REACTIONS

To develop a new delay for the HHS rocket, two different technical approaches were pursued with the eventual selection of one that showed the most promise. The first approach was based on evaluating the suitability of condensed phase reactions. These types of materials systems are ideally suited for delays because they do not produce gaseous combustion products (thereby allowing their use in vented or sealed housings).

Initial experiments focused on testing different binary exothermic systems in aluminum tubes with different diameters. Given the extreme radial heat losses expected in the HHS delay housing it was critical to understand the effect of geometry-induced heat losses on the ability of these reactions to propagate in small diameter aluminum channels. The systems investigated included mixtures of Ti/C with Ni/Al or 3Ni/Al [3]. Ti/C had the highest predicted adiabatic reaction temperature and was the most exothermic of the binary systems. By mixing Ti/C with the less exothermic binary systems 3Ni/Al and Ni/Al, mixtures with different levels of exothermicity can be produced (Figure 2a). One of the key requirements for selecting a condensed phase system of this type is that the predicted adiabatic reaction temperature should be greater than 1800 K, yet not be so high that the resulting mixture has a rapid propagation velocity [4]. Another factor that must be considered is the ability of the system to produce enough energy to overcome conductive losses to the delay housing. This is critical because if the system loses too much energy, the reaction quenches and the delay will not function as intended.

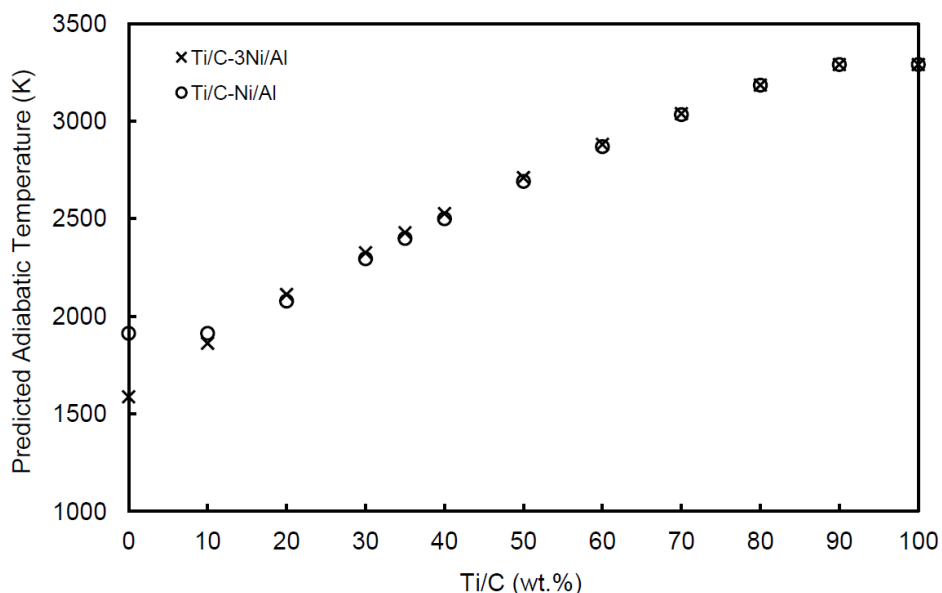


Figure 2a. Predicted adiabatic combustion temperatures (HSC 7.0) for the Ti/C-Ni/Al and Ti/C-3Ni/Al systems as a function of Ti/C content.

The 35-65 Ti/C-3Ni/Al system was studied in both 4.8 mm and 6 mm (inner diameter) aluminum tubes (Figure 2b). The wall thickness of the tubes was chosen so that the heat capacities of these tubes were the same. In general, as the packing efficiency (as indicated by %TMD) increased, the propagation

velocity increased from approximately 2 to 5 mm/s. Ultimately, these types of systems were not able to propagate at the *very low* rates required for hand-held signals. The HHS specification calls for a delay burning time of at least 6 seconds, which translates to a propagation rate of 1.7 mm/s or less. In retrospect, it is quite amazing that these systems were able to propagate as slowly as they did in such small metal tubes. Condensed phase systems are often very energetic, usually propagate rapidly, and are typically not used for these kinds of applications. There may be other applications requiring fast-burning gasless delays that could use this technology.

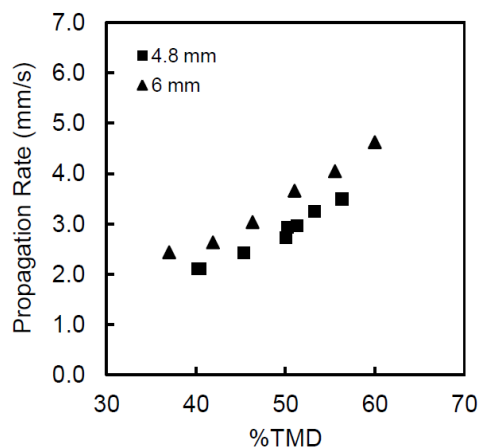


Figure 2b. Propagation rate for Ti/C-3Ni/Al (35/65 ratio) in 4.8 and 6 mm aluminum tubes as a function of %TMD (the consolidated density as a percentage of theoretical maximum).

PYROTECHNIC SYSTEMS

Early work focused on Si/KNO₃ and W/KNO₃ pressed into 2024-T3 aluminum tubes (inner diameter, outer diameter, and length of 0.48 cm, 0.95 cm, and 1.52 cm, respectively). While both of these systems were tunable and propagated in aluminum tubes, they did not function in the HHS housing. One interesting gasless system that was evaluated was a ternary system composed of Si, Bi₂O₃, and Sb₂O₃ [5]. This concept was based on combining a fast binary system (Si/Bi₂O₃) with a slow binary system (Si/Sb₂O₃) [6,7]. When Si, Bi₂O₃, and Sb₂O₃ are combined, a tunable gasless system results. Figure 3 shows the inverse column burning rate versus Sb₂O₃ percentage in aluminum and stainless steel tubes. While these results were encouraging, none of these compositions functioned when pressed into the HHS delay housing, presumably due to greater heat losses in this housing.

One of the biggest challenges in the course of our research was finding systems that would propagate fully and reliably in the 14.5-gram aluminum HHS delay housing. Given aluminum's large thermal conductivity, several times larger than lead and stainless steel, the heat generated by combustion reactions is rapidly absorbed into the body of the HHS housing. Many of the reactions that worked in aluminum and stainless steel tubes were quenched by the HHS delay housing. At this point a different approach was needed.

We originally thought that a replacement delay needed to be gasless for it to function in the HHS rocket, but this is not necessarily the case. Upon closer examination of the HHS cross section (Figure 1a),

it can be seen that the delay element is adjacent to the rocket motor chamber. Once the rocket motor is ignited, it is consumed within about 0.5 seconds, leaving an empty volume for delay gases to vent. This realization led us to explore gassy delay compositions as well. The first of these systems was developed with the traditional tungsten delay in mind, although it turned out to be gassy. In the MIL-spec tungsten delay (Table 1), KClO_4 is the “fast” oxidizer and ignition sensitizer while BaCrO_4 is the “slow” oxidizer. Keeping with the same idea, we decided to replace BaCrO_4 with Sb_2O_3 and KClO_4 with a periodate salt (KIO_4 or NaIO_4). In our laboratories, Moretti has experimented with NaIO_4 and KIO_4 as replacements for KClO_4 in flash/incendiary compositions [8] and this inspired us to try using the periodates in delay mixes.

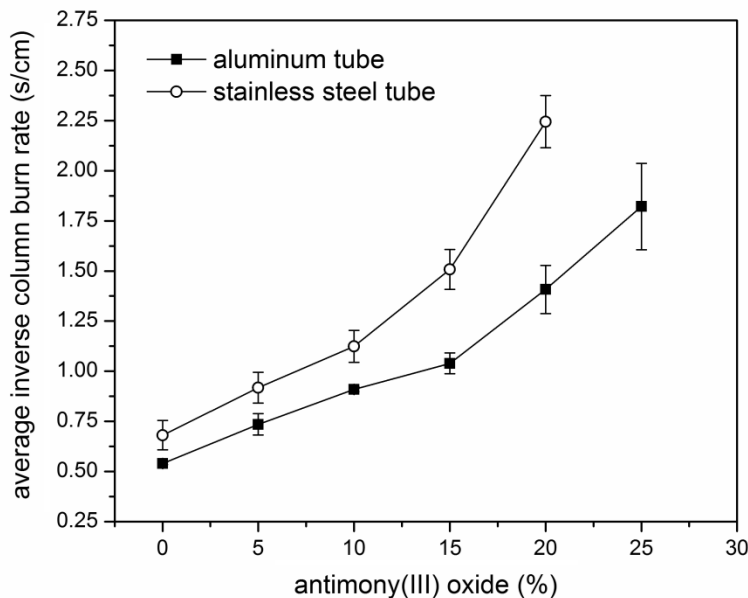


Figure 3. Average inverse column burning rate versus antimony(III) oxide percentage for delays pressed in aluminum and stainless steel tubes.

One of the first observations about the $\text{W/Sb}_2\text{O}_3/\text{KIO}_4$ system was that it was difficult to press due to the abrasive nature of its components. Various lubricants were added in small percentages to prevent binding of the tooling. Of the lubricants tested, calcium stearate was found to have the greatest effect on burning rate. Figure 4 shows the inverse burning rate for mixtures containing different $\text{W/Sb}_2\text{O}_3/\text{KIO}_4$ ratios as a function of calcium stearate level. In this system, inverse burning rates ranging from 2-15 s/cm can be easily produced in the HHS delay housing. The required inverse burning rate of the HHS delay is 7-8.5 s/cm, which is well within the experimentally determined range for these compositions [9].

To validate the use of this gassy delay in HHS rockets, several delays were pressed and shipped to the manufacturer for dynamic testing. The ARDEC-fabricated delays were inserted into fourteen M159 white star cluster rockets and these were tested at ambient temperature. All of the rockets functioned correctly ejecting the payload, although the delay times were not optimal. Even so, this test validated the potential use of gassy delays in HHS rockets.

Although the $\text{W/Sb}_2\text{O}_3/\text{KIO}_4$ compositions appeared promising, it was observed that they were quite sensitive to moisture. Over time, small cracks were observed in the delay columns along with a brownish discoloration around the periphery of the delay cavities. Aqueous solutions of periodate and iodate salts have been used to etch tungsten metal surfaces [10,11]. Control experiments showed that

thoroughly dried W/KIO₄ mixtures remained unchanged over time, while those prepared in ambient conditions or intentionally wetted degraded rapidly. This degradation was accompanied by a brown discoloration (I₂). Iodine is also produced when W/KIO₄ mixtures are burned. Calcium stearate slowed the aging process but did not completely stop it when compositions were prepared and stored at the ordinary humidity used for pyrotechnic processing (40-60% RH). Presumably this is due to calcium stearate partly coating the other mixture components. Based on these findings, we decided to explore other gas-producing compositions that did not contain tungsten/periodate combinations.

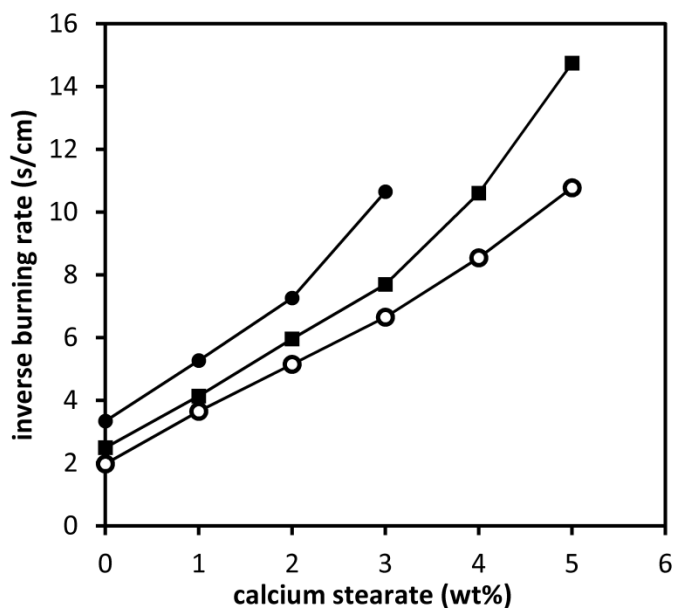


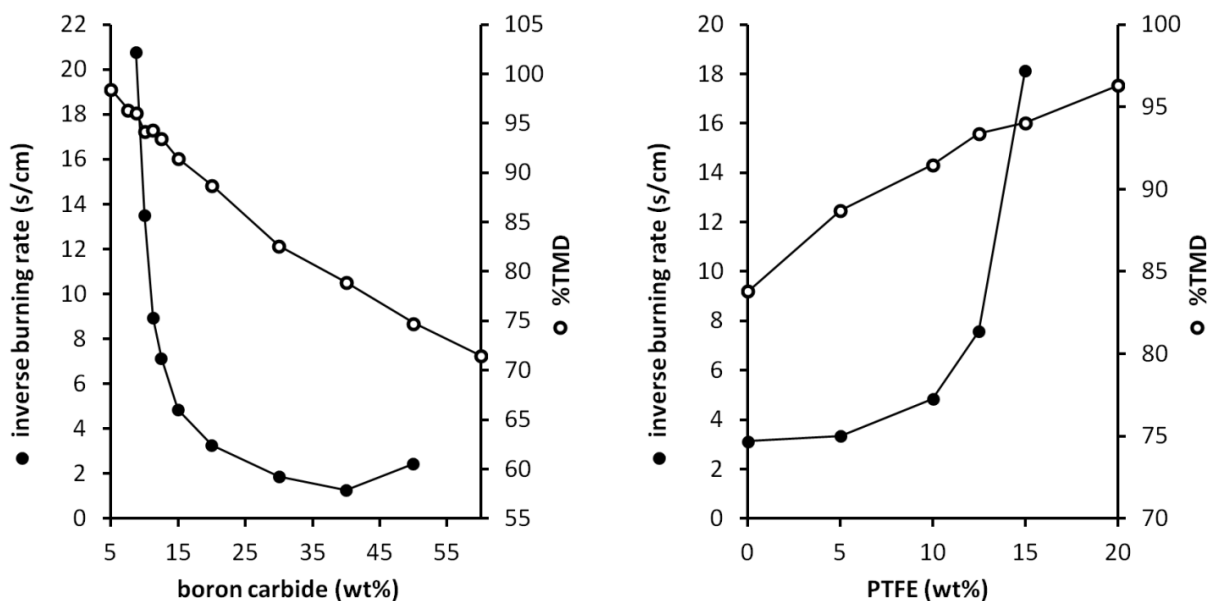
Figure 4. Effect of added calcium stearate on inverse burning rate. W/Sb₂O₃/KIO₄ ratios of 40/20/40 (bottom curve, open circles); 40/25/35 (middle curve, squares); 40/30/30 (top curve, closed circles).

Over the past several years, ARDEC has been working with boron carbide (B₄C) as a boron replacement in pyrotechnics. Boron carbide, used in light-weight armor, nuclear moderator rods, and abrasives, is re-emerging as a promising fuel for modern pyrotechnics. Boron carbide was first evaluated as a pyrotechnic fuel over 50 years ago but was never successfully incorporated into formulations that were used in commercial or military pyrotechnics. Recently, one of us (Poret) helped to develop boron carbide-based green light-emitting compositions [12]. Subsequently, we developed highly efficient white smoke compositions based on B₄C [13].

Given our experience with B₄C and periodate oxidizers, we focused on developing delay compositions containing these materials. Initial experiments involved binary B₄C/NaIO₄ powder mixtures and these produced purple smoke (I₂) upon ignition. This is similar to the combustion reactivity we observed previously with W/KIO₄ mixtures. When we tried to press B₄C/NaIO₄ mixtures into tubes and HHS housings it was extremely difficult due to the abrasive nature of B₄C. Polytetrafluoroethylene (PTFE), a well-known lubricant and pyrotechnic oxidizer, was added to increase energy output and to prevent the tooling from binding during pressing.

The ternary B₄C/NaIO₄/PTFE system turned out to be the most stable and versatile of the systems developed in the course of our research [14]. Inverse burning rates ranging from 1.3 to 20.8 s/cm are

easily and reliably produced in the HHS delay housing. This equates to burning times as long as 15 seconds. This system can be tuned by varying the mixture stoichiometry (Figures 5a-b) and loading pressure. Other variables such as the B₄C particle size have a large influence on burning rate. This system also performs well at extreme temperatures. HHS delays containing a 17.5/72.5/10 ratio of B₄C/NaIO₄/PTFE were conditioned overnight at -65 °F, ambient temperature, and +160 °F (10 at each temperature). Their static burning times were 7.01 ± 0.16 s, 6.12 ± 0.04 s, and 5.82 ± 0.05 s, respectively. As expected, the delays conditioned at -65 °F had the longest burning times and the delays conditioned at +160 °F had the shortest burning times. Although in general, these burning times were very consistent and exhibited minimal variability.



Figures 5a-b. Inverse burning rate versus B₄C percentage (**5a**, left) for HHS delays containing $x/(90-x)/10$ mixtures of B₄C/NaIO₄/PTFE. Inverse burning rate versus PTFE percentage (**5b**, right) for HHS delays containing $15/(85-x)/x$ mixtures of B₄C/NaIO₄/PTFE. Packing efficiency (as %TMD) is also shown.

SUMMARY AND CONCLUSIONS

The development of a new delay system that works in the HHS aluminum delay housing has been a very challenging effort. The project focused on evaluating two different technical approaches: condensed phase reactions and traditional fuel/oxidizer pyrotechnic systems. A new and promising condensed phase system, Ti/C-3Ni/Al, was developed that functioned in small diameter aluminum tubes. Ultimately these reactions were too fast to be used as HHS delays. Three different pyrotechnic systems were developed. A new gasless delay based on Si/Bi₂O₃/Sb₂O₃ worked in both aluminum and stainless steel tubes. This system was interesting but did not function in the HHS housing, which led to the development of two different gassy delay systems: W/KIO₄/Sb₂O₃ and B₄C/NaIO₄/PTFE. The W/KIO₄/Sb₂O₃ delays functioned statically in the HHS delay housing and also functioned dynamically in HHS rockets during live-fire testing. Further work on this system was discontinued due poor aging characteristics in the

presence of trace moisture. The second gassy system, B₄C/NaIO₄/PTFE, was tested statically at ambient and extreme temperatures, and dynamic testing has recently begun. This system does not exhibit any moisture-related aging issues like W/KIO₄/Sb₂O₃ and thus should be better suited for use in the HHS rockets. In conclusion, the B₄C/NaIO₄/PTFE system is recommended for further development. The ability to tune the system makes it easy to produce delays with different burning times. Its versatility and the wide commercial availability of each component make it ideal for large-scale manufacturing.

FUTURE WORK

Over the next few months, additional tests will be performed to determine which B₄C/NaIO₄/PTFE formulation will yield the optimal dynamic burning time. Once the new formulation is selected, more HHS rockets will be built and tested to evaluate dynamic performance at both -65 °F and +160 °F. Additional work will be performed to ascertain the suitability of the composition and delays for mass production. If successful, it is expected that this technology will be implemented and used in future hand-held signals.

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