SERDP

EXECUTIVE SUMMARY

Environmentally Sustainable Gasless Delay Compositions for Fuzes

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SERDP Project WP-2518

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ACRONYMS AND ABBREVIATIONS

DE	diatomaceous earth
PTFE	polytetrafluoroethylene
SERDP	Strategic Environmental Research and Development Program
SoN	statement of need
TPP	titanium and potassium perchlorate

1.0 INTRODUCTION

In munitions, pyrotechnic delay elements are used to time sequences of energetic events. Fuzes for hand grenades must provide a reliable and safe interval between when the primer is struck (the grenade is released) and subsequent initiation of the main charge. The M201A1 fuze, fitted on U.S. Army smoke grenades, contains a pyrotechnic delay element that burns for about 1.0-2.3 seconds. The M213 and M228 fuzes are used in the M67 and M69 fragmentation and practice grenades, respectively, where delay times of 4.0-5.5 seconds are desired. Figure ES-1 shows the die-cast zinc fuze body and aluminum delay case of the M201A1, and a different die-cast zinc body used for M213/M228 fuzes. Modern hand grenade fuzes are sealed to ensure their reliability and to improve their aging characteristics.

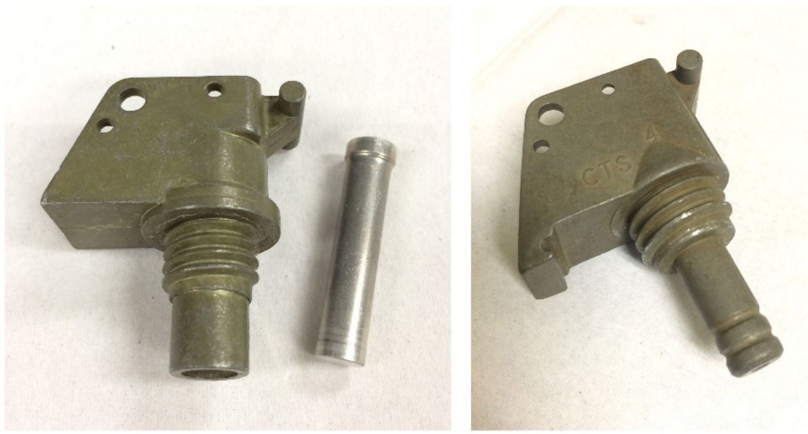

Figure ES-1. M201A1 (Left) and M213/M228 (Right) Fuze Configurations.

The detonator (for the M213) or black powder charge (for the M228) are not shown.

Delay compositions used in modern hand grenade fuzes are "gasless" or nearly so; such compositions produce very little gas upon combustion, unlike most other types of pyrotechnics. "Gaslessness" is a preferable (and necessary, in some instances) property of delays loaded in sealed housings. This is because a sealed delay housing must not rupture unintentionally or prematurely. Gasless pyrotechnic delays that have seen extensive U.S. Army use contain objectionable and problematic components—namely, potassium perchlorate ($KClO_4$) and chromates such as barium chromate ($BaCrO_4$) and lead chromate ($PbCrO_4$); see Table ES-1. For example, zirconium-nickel alloys (Zr-Ni), barium chromate, and potassium perchlorate are the primary constituents of "zirconium-nickel" delays. As of 2022, perchlorate- and chromate-containing Zr-Ni delays are still used in M201A1, M213, and M228 fuzes.

Table ES-1. Common Pyrotechnic Delays Used by the U.S. Army

Common Name	Formal Name; Spec. or Drawing	Components
zirconium-nickel delay	Composition, Delay; MIL-C-13739A	Zr-Ni alloys, $BaCrO_4$, $KClO_4$
manganese delay	Manganese Delay Composition; MIL-M-21383A	Mn, $BaCrO_4$, $PbCrO_4$
tungsten delay	Tungsten Delay Composition; MIL-T-23132A	W, $BaCrO_4$, $KClO_4$, DE [a)]

a) Here, DE is an abbreviation for diatomaceous earth.

A hand grenade fuze, which is a relatively simple device, is effectively a functionalized delay element that is initiated by a percussion primer. At a minimum, a “delay element” consists of a metallic housing and the pressed pyrotechnics (delay and igniter compositions) within. Even though delay elements and fuzes typically contain just a few grams of pyrotechnics, some of these items are used in substantial quantities on training ranges in the United States. Most military training was suspended at Camp Edwards (near Falmouth, Massachusetts) in the late 1990s because of groundwater contamination caused by the use of various munitions, including perchlorate-containing pyrotechnics. Additionally, current Department of Defense policy calls for minimizing the use of hexavalent chromium, a constituent of chromate compounds. To reduce the risk of training interruptions and to avoid the expense of environmental remediation, the development of less hazardous, yet effective gasless pyrotechnic delay compositions is clearly imperative.

2.0 OBJECTIVES

SERDP WP-2518 was proposed and performed in response to the Statement of Need (SoN) WPSON-15-01 for fiscal year 2015, dated November 7, 2013. This SERDP SoN requested the development of sustainable gasless delay formulations free of perchlorate salts, lead, and hexavalent chromium. Importantly, the SoN stated that “Proposals should address delay elements in high use, multi-item fuze systems, including but not limited to the M201A1, M213, and M228.” And, “Proposals should discuss … [the] demonstration of delay formulations in a prototype configuration.” An environmental and toxicity assessment in accordance with ASTM E2552-08, *Standard Guide for Assessing the Environmental and Human Health Impacts of New Energetic Compounds,* was also suggested. Therefore, the overall objective of this project was to confidently identify more sustainable or “green” pyrotechnic systems for use in M201A1, M213, and M228 fuzes (hand grenade fuzes). In light of the SoN, three specific subobjectives were also conceived. The first subobjective was to reduce the chance of selecting problematic replacements by considering the potential environmental and toxicological effects of candidate materials. The second was to formulate and study alternative pyrotechnic compositions likely to meet the relevant performance requirements. The third subobjective was to test the most promising alternatives in actual fuze hardware.

3.0 TECHNICAL APPROACH

The project’s technical approach was based on the three subobjectives described in the previous section, and it involved concurrent activities at three different centers. An assessment of the potential toxicological and environmental effects of candidate materials took place at the U.S. Army’s Public Health Center, at Aberdeen Proving Ground in Maryland. The list of compounds under consideration was expanded to include a variety of anticipated combustion products that could be formed from the initial components. Because several of the compounds in question were related due to the nature of oxidation/combustion processes, it was decided to consider each of these families of substances together so as to better portray their relationship to one another. Physical properties, used to assess fate and transport in the environment, and the toxicological information needed to estimate potential human health risks, were gathered from a variety of sources. Then, the persistence, tendency for bioaccumulation, human health toxicity, and ecotoxicity of each substance or family of substances were assigned to three general categories of risk (low, moderate, or high).

Alternative pyrotechnics were formulated and studied at the South Dakota School of Mines and Technology in Rapid City, South Dakota. These studies were roughly divided into two interrelated categories. The first category comprised the more practical experiments having to do with ignition, burning rate, gas evolution, and the aging characteristics of candidate compositions. The second category encompassed those experiments specifically designed to uncloak mechanistic nuances—to provide a more coherent interpretation of gasless delay combustion. The combustion boat temperature profile measurements would fall into this category, for example (Figure ES-2). Most of the experiments involving thermal analysis, bulk calorimetry, and X-ray diffraction would fit here as well. In the aggregate, the results of such detailed, practical and academic investigations are notable because relatively little information of comparable scope can be found in the existing literature.

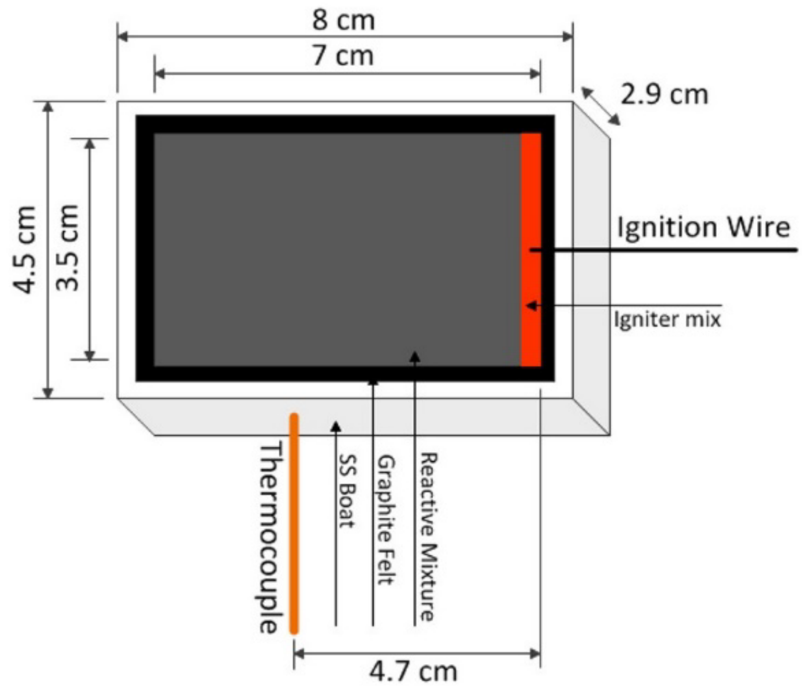

Figure ES-2. Experimental Setup for the Boat-Type Temperature Profile Measurements of the W/MnO_2 System.

The tip of the thermocouple was placed at a height of 1.6 cm above the base of the boat and inserted 1.75 cm into the mixture.

Personnel from the U.S. Army's Armaments Center, which is located at Picatinny Arsenal in New Jersey, had written the project proposal and therefore coordinated project activities to ensure they would collectively address the overall objective. Prototype delay elements and fuzes were also built and tested at Armaments Center. Alternative delay compositions were integrated with a newly developed titanium-based igniter system in M201A1 and M213/M228 fuze hardware. This required careful consideration of a number of design features specific to hand grenade fuzes. To build the prototypes, pyrotechnic compositions were loaded and pressed in as few as one or as many as four increments. Subsequently, a percussion primer and primer holder (if necessary) were fitted to each fuze and the aluminum delay case or zinc fuze body was crimped to secure them. Custom-built stainless steel blocks were used to hold the fuzes during cold and hot temperature conditioning.

These blocks served as thermal buffers due to their large size and heat capacity. To perform each functioning test, a fuze was fitted with a hinge pin and striker and was mounted in an insulated clamp attached to a rigid assembly. A steel weight was positioned above the fuze within a plastic tube and held in place by an electromagnet. The weight was dropped by turning off the power supply to the electromagnet. The action of the weight on the striker initiated the fuze by firing the percussion primer. More than 300 prototype fuzes were tested throughout the project at cold, ambient, or hot temperatures.

4.0 RESULTS AND DISCUSSION

4.1 TOXICOLOGY ASSESSMENT

Even though numerous elements and compounds were considered, only a portion were used to any extent in the experimental parts of this project. Fewer still could be considered *key* elements or compounds, essential to the alternative pyrotechnics described in later sections. Among these, manganese and tungsten and their simple oxides, as well as strontium molybdate ($SrMoO_4$) are especially relevant and are briefly discussed in the following paragraphs.

Elemental manganese, Mn(0), is of low toxicity by all routes of exposure except inhalation. Repeated inhalation exposures may cause development of metal fume fever, a flu-like condition; or manganism, a Parkinson-like condition. Manganese dioxide (MnO_2) also exhibits low systemic toxicity. Neurological symptoms may develop after oral ingestion via drinking water although evidence for these symptoms is more limited than for inhalation. The influence of manganese oxidation state on toxicity is not well understood. Results from animal studies indicate that the solubility of manganese compounds can influence the bioavailability of manganese and subsequent delivery to toxicity targets. Additionally, limited data suggest that manganese may undergo oxidation state changes within the body.

Transport and partitioning of manganese in water is dependent upon the solubility of the chemical species present and spans concentrations from 0.02 to 10,000 mg/L. Mn(II) in the form of manganese carbonate ($MnCO_3$) predominates in most waters, but all three common oxidation states (+2, +3, +4) are possible in water or soil. Little information is available on the chronic toxicity of Mn in ecosystems. Toxicity appears to be affected by water hardness, with toxicity increasing with increasing water hardness. Experiments have been conducted on blue-green and green algae species, as well as *Daphnia*, brown trout, and water plants.

Tungsten exhibits toxicity only as a fume in hard metal working or when oxidized to tungstate. Inhalation is the primary route of exposure capable of causing potential human health problems. Tungsten compounds are generally believed to not pose a significant hazard via other routes of exposure. Some occupational hazard may be present to the skin, eyes, and lungs, depending upon how the metal is worked during the production process. Use of tungsten in a delay formulation is expected to cause formation of a lower oxide of tungsten that could be oxidized to tungstate (WO_4^{2-}) upon weathering.

Manganese tungstate is of low toxicity except by inhalation, where extended exposure could possibly lead to neurological symptoms. The occupational hazard to skin and eyes is low, but standard chemical protective equipment should be employed, including respiratory protection. There is no information on developmental or reproductive, genotoxic, or cancer hazard. Ecotoxicity is likely low due to insolubility. High concentrations of manganese can inhibit the growth of plants. Effects on aquatic plants and terrestrial invertebrates are unknown.

Significant data gaps exist for strontium molybdate. Acute oral toxicity appears to be moderate, but the compound poses an irritation hazard to the respiratory system, skin, and eyes. No data could be found relating to its genotoxicity or carcinogenicity. Studies in laboratory animals suggest a possibility of reproductive issues for males, with unknown consequences. Ecotoxicity data were found for *Daphnia* only. Toxicity toward *Daphnia* is low. Due to the compound's insolubility, groundwater transport and bioaccumulation are unlikely.

In the subject design configurations (hand grenade fuzes), the alternative formulations represent low hazards to both human health and the environment. Exposure is limited to manufacture and post-use degradation. As none of the candidate components pose significant dermal contact hazards, occupational exposures are anticipated to be of low hazard. The human health and environmental effects of released materials are expected to be minimal, as their groundwater transport potential is limited, the ultimate compounds are ubiquitous in the environment, and the compounds in question are generally considered to be low in toxicity except via inhalation.

4.2 PYROTECHNIC COMBUSTION STUDIES

With the configurations and requirements of gasless pyrotechnic delays in mind, the combustion characteristics of the W/MnO_2 system were thoroughly investigated. Measured maximum combustion temperatures ranged from 1466-1670 K and varied depending on mixture stoichiometry. Combustion velocities ranged from 0.67-1.68 mm/s for 6.35 mm diameter open-air pellets, and from 1.62-4.61 mm/s when the compositions were combusted in 6.35 mm and 4.7 mm inner diameter aluminum and stainless steel housings. When the packing density was increased or decreased from 60% of the theoretical maximum, combustion velocity decreased. For all of the W/MnO_2 mixtures tested, the maximum measured gas evolution was just 9.1 mL/g-composition. Initial gas phase diffusion (a gas-solid reaction) as a result of decomposing MnO_2, followed by solid-solid reactions, drive progression of the burning front. In the W/MnO_2 system, combustion velocity is primarily limited by the availability of tungsten. An accelerated aging study was also performed on one composition for eight weeks at 70 °C and 30% relative humidity, and negligible changes in combustion characteristics were observed (Figure ES-3). Powder X-ray diffraction was used to analyze the combustion products and they appear to be benign. Therefore, the W/MnO_2 system could be a suitable alternative.

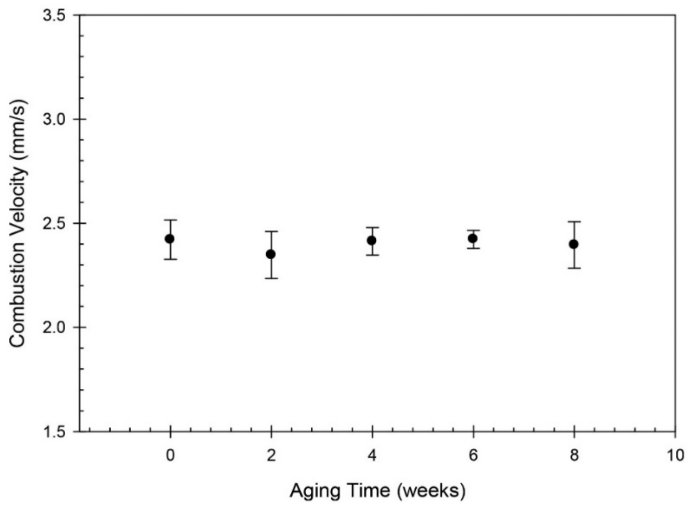

Figure ES-3. Combustion Velocity as a Function of Aging Time for the 50/50 W/MnO_2 Mixture.

In other experiments, strontium molybdate was examined as a "drop-in" replacement for barium chromate in the tungsten delay, which traditionally contains tungsten (W), barium chromate ($BaCrO_4$), potassium perchlorate ($KClO_4$), and diatomaceous earth (DE). The measured maximum combustion temperatures of $W/SrMoO_4/KClO_4/DE$ compositions ranged from 1507-1628 K and were dependent on tungsten content. Measured combustion velocities ranged from 1.36-29.87 mm/s in 4.7 mm inner diameter aluminum housings (Figure ES-4), and the maximum measured gas evolution was only 4.1 mL/g-composition. Upon further investigation of several $SrMoO_4$- and $BaCrO_4$-based compositions, large differences in apparent activation energies were found. These particular results suggested that slow-burning $SrMoO_4$-based compositions were inherently more difficult to ignite than $BaCrO_4$-based ones that combust at similar rates. The drop-in formulations containing $SrMoO_4$ in place of $BaCrO_4$ were thought to be less hazardous because they lack barium and hexavalent chromium.

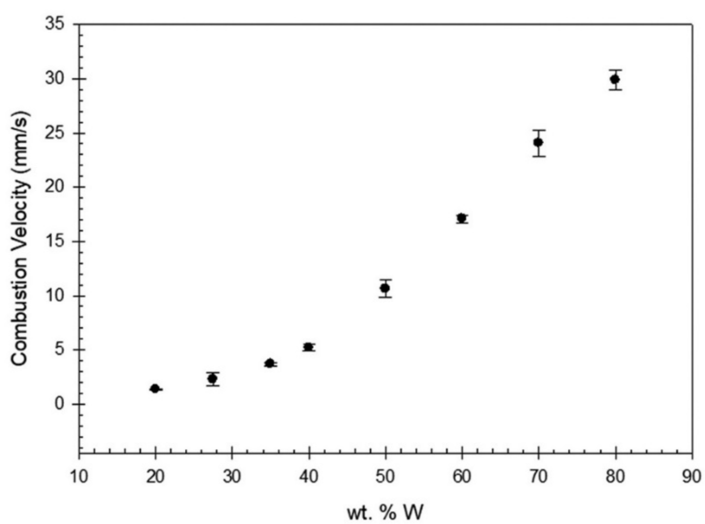

Figure ES-4. Combustion Velocities of the $W/SrMoO_4/10KClO_4/5DE$ System, with Amounts of $KClO_4$ and DE Held Constant at 10 wt-% and 5 wt-% Respectively, as Indicated by the Formulation Notation.

The compositions were pressed into 4.7 mm ID Al housings.

4.3 FUZE DESIGN, ASSEMBLY, AND TESTING

In a hand grenade fuze, an input charge is often used to ignite the delay composition (Figure ES-5). After a period of time, the delay composition typically ignites an output charge, causing hot gases, incandescent combustion products, and sparks to be ejected. For a fuze sealed at both ends, conventional pyrotechnic wisdom calls for an input charge that produces little or no gas and an output charge that produces enough gas to rupture the delay case at the desired time. In the United States, the gasless A-1A igniter (Zr/Fe_2O_3/DE) has been used as an input charge whereas an explosive mixture of titanium and potassium perchlorate (TPP) has been used as an output charge. A-1A and TPP have been used in various fuzes for decades, but the latter composition contains potassium perchlorate, a component that is now objectionable.

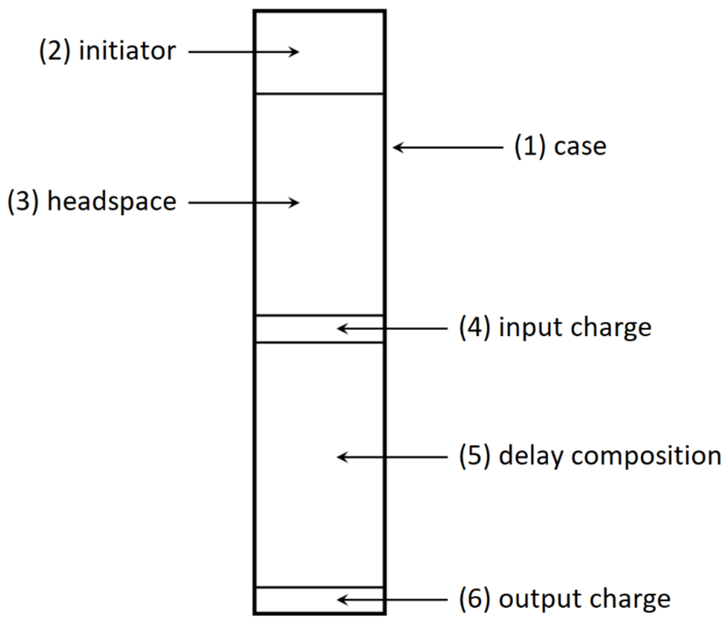

Figure ES-5. Cross-sectional Representation of an Exemplary Pyrotechnic Delay Element.

Components include a case (1), an initiator (2), headspace (3), an igniter composition (the input charge, 4), a delay composition (5), and another igniter composition (the output charge, 6).

The project team has discovered that a ternary mixture of titanium (Ti), manganese dioxide (MnO_2), and a polymeric binder such as polytetrafluoroethylene (PTFE), was effective as an input charge and as an output charge in sealed fuzes. Here, the polymer is present at about 5 wt-% and serves as a gas generator, lubricant, and dry binder. Pressed layers of this titanium-based igniter possess adequate mechanical strength and effectively retain delay increments that do not contain any binder. Importantly, as an input charge, the alternative igniter does not prematurely rupture delay cases or eject percussion primers provided the fuzes are assembled correctly. Yet, as an output charge, it produces a brilliant burst of sparks similar to that produced by TPP. Although an igniter composition containing 5 wt-% PTFE was used in the fuze experiments described in this report, it should be possible to use variants of this igniter containing alternative, fluorine-free polymers if the use of per- or poly-fluoroalkyl substances in munitions becomes unacceptable in the future.

The Mn/MnO_2 thermitic system can tolerate the addition of powdered soda-lime glass—a diluent that extends delay burning times. In M201A1 fuze hardware, a binary Mn/MnO_2 delay or a ternary composition with added glass appeared to be viable options, provided variations in delay column height and loading procedure were deemed acceptable. Delay times within the desired 1.0-2.3 second window can be achieved at cold, ambient, and hot temperatures with single-increment or double-increment M201A1 designs (Figures ES-6 and ES-7). For example, single-increment fuzes containing a delay composition with +7.5 wt-% glass burned for 1.83 s (−32 °C), 1.50 s (22 °C), and 1.31 s (49 °C). Double-increment fuzes containing a delay with no added glass burned for 1.95 s (−32 °C), 1.67 s (22 °C), and 1.57 s (49 °C). Further adjustments could be made by changing the amount of delay composition loaded in each increment (1.0 gram of delay composition was used per increment in these prototypes).

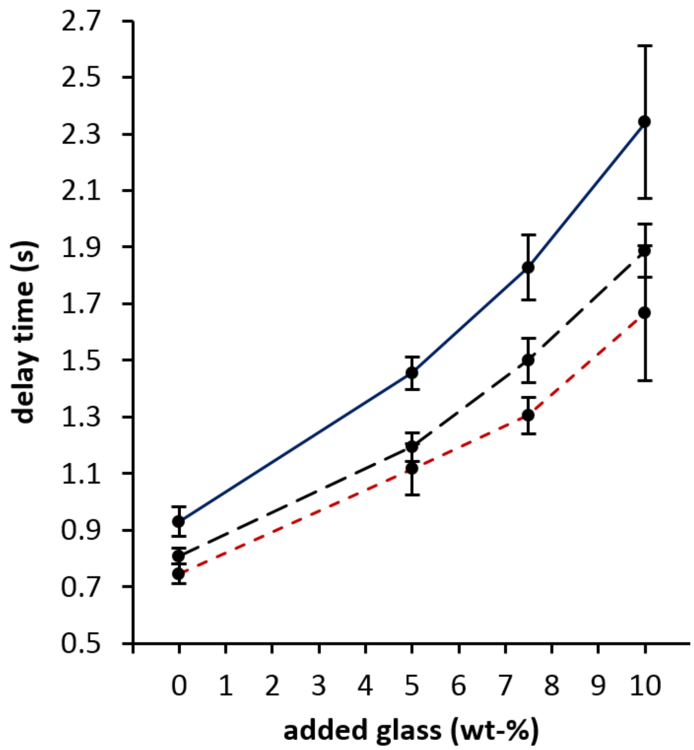

Figure ES-6. Delay Times for Single-increment M201A1 Prototypes Containing Mn/MnO_2 Delay Compositions.

The error bars show two standard deviations. Conditioning temperatures of −32 °C (solid blue line), +22 °C (long-dashed black line), and +49 °C (short-dashed red line) are shown.

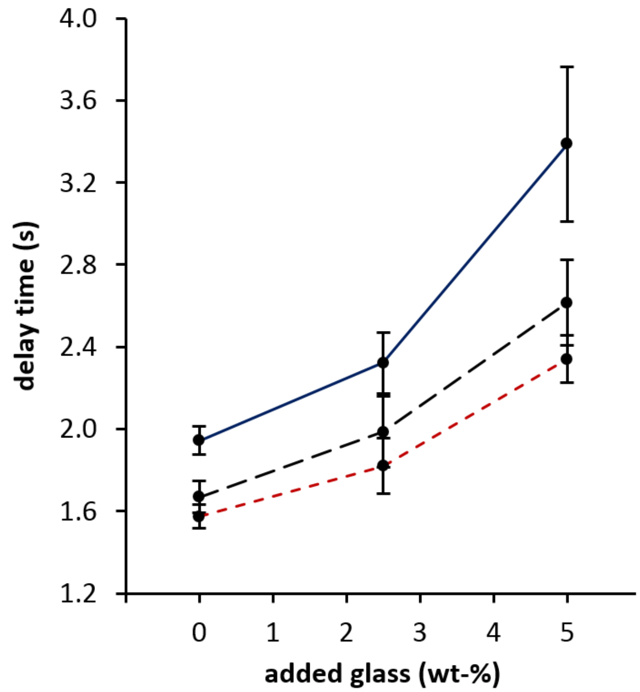

Figure ES-7. Delay Times for Double-Increment M201A1 Prototypes Containing Mn/MnO_2 Delay Compositions.

The error bars show two standard deviations. Conditioning temperatures of −32 °C (solid blue line), +22 °C (long-dashed black line), and +49 °C (short-dashed red line) are shown.

Binary W/MnO_2 delay compositions, without any added diluents or binders, seemed to work well in M213/M228 fuze hardware. The delay element common to the M213 and M228 fuzes should burn for 4.0-5.5 seconds after being conditioned at an ambient temperature (16-26 °C), and Table ES-2 shows that this criterion was met by prototypes containing a W/MnO_2 delay. Additionally, the average delay time at 63 °C (4.82 s) was still comfortably above the lower end of the desired range. At a cold temperature of −51 °C, the average delay time exceeded 5.5 seconds, but it should be possible to reduce it by using less delay composition. However, this would also decrease hot-temperature delay times, and would bring them closer to 4.0 seconds. As far as the safety of grenadiers is concerned, avoiding a short delay time is arguably more important.

Table ES-2. Summary Experimental M213/M228 Delay Element Results [a)]

Temperature (°C)	Average Time (s)	Standard Deviation (s)	Lowest (s)	Highest (s)
−51	6.139	0.136	5.965	6.374
+18-22	5.179	0.173	4.829	5.448
+63	4.822	0.149	4.501	5.027

a) Each fuze contained 1.89 grams of W/MnO_2 delay (50/50) loaded in four increments. The delay columns were consolidated to 64% of the theoretical maximum density, and were approximately 18.5 mm long. At each temperature, 10-12 fuzes were tested.

5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

The results summarized above lend strong support to the original working hypothesis—that objectionable materials are not necessary components of effective gasless delay compositions. Although the anticipated conditions of use (that is, no significant inhalation exposure) mean that additional toxicological studies are not needed at this time, such studies may become necessary, especially if inhalation exposure is found to be an issue. Regarding the prototypes containing tungsten, leachate studies of tungsten oxidation products would be needed to determine the concentrations and kinetics of formation of possible ecotoxicants.

While much was known about the Mn/MnO_2 system before this project began, relatively little was known about the W/MnO_2 system. Accordingly, a thorough interpretation of the pyrotechnic properties of W/MnO_2 compositions was developed. A better understanding of $W/MM'O_4/KClO_4$/DE delay compositions was also achieved (where $MM'O_4$ is $SrMoO_4$ or $BaCrO_4$). Through these studies, it became apparent that multistep decomposition phenomena and delay reliability may be connected. In other words, the occurrence of a multistep decomposition process involving one or more oxidizers during combustion may promote more reliable combustion wave propagation. However, more work would need to be done to determine the strength and scope of this apparent connection.

Delay compositions containing Mn or W, MnO_2, and powdered soda-lime glass (in some instances) were shown to be effective in M201A1 and M213/M228 fuze hardware. This project, SERDP WP-2518, has transitioned into a demonstration—ESTCP WP20-5045, called *"Green" M213/M228 Fuze.* ESTCP WP20-5045 will culminate in the demonstration of fully assembled M213 fuzes that contain "green" energetic subcomponents entirely free of lead, chromium, barium, and perchlorate. The results will be applicable to both M213 and M228 fuzes, which share a common delay element.