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EFFECT OF STRONTIUM NITRATE ON EXTREMELY SLOW STROBE COMPOSITIONS

Amee L. Polk
Michael F. Kauzlarich

RESEARCH AND TECHNOLOGY DIRECTORATE

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14. ABSTRACT:
Pyrotechnic strobe compositions exhibit an oscillatory combustion characterized by a periodic alternation of a "dark phase" and a "flash phase". Many traditional strobe mixtures contain toxic substances, including dichromates and barium compounds. The investigation into a less-toxic strobe mixture using strontium led to the discovery of an "extremely slow strobe"; this mixture produced a pulse or "flash phase" approximately once a minute. This paper describes the evaluation of the slow strobe's pulse rate, based on the mesh size of the metal powder and the effect of the variation of strontium nitrate and potassium nitrate concentration. Small test pellets of this less-toxic strobe mixture, containing only 10 g of pyrotechnic composition, had burn times of more than 5 min, with a single, bright flash approximately once every 60 s. The composition's dark phase provided only an extremely faint glow that under normal circumstances would appear to have been extinguished, only to flash at the previously stated predictable instant. This composition presents an opportunity to study a potential reason for a common dangerous situation known as a "hang fire" and warrants further study.

15. SUBJECT TERMS

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Flash	Orion's Flashing Guns

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PREFACE

The work described in this report was authorized under Strobe program for Picatinny Arsenal, project number 1L162622A552. The work was started October 2013 and completed May 2014.

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EFFECT OF STRONTIUM NITRATE ON EXTREMELY SLOW STROBE COMPOSITIONS

1. INTRODUCTION

Pyrotechnic strobes are produced by the oscillatory combustion of a flash reaction and a dark reaction. When lighted, a pyrotechnic strobe burns as a semireacted mass and produces very little (if any) light, which is referred to as the “dark phase”. After a delay, this semireacted mass will suddenly react and produce a flash referred to as the “flash phase”. The dark and flash reactions alternate to produce the flickering or strobing effect. The first in-depth explanation of the theoretical mechanism of pyrotechnic strobes is attributed to Dr. Takeo Shimizu (*1*). Although Shimizu was not the first to describe strobes, he contributed a great deal to the understanding of strobe compositions with his explanation of the mechanics of pyrotechnic strobes. Figure 1 is an adaptation of the hypothesis Shimizu proposed.

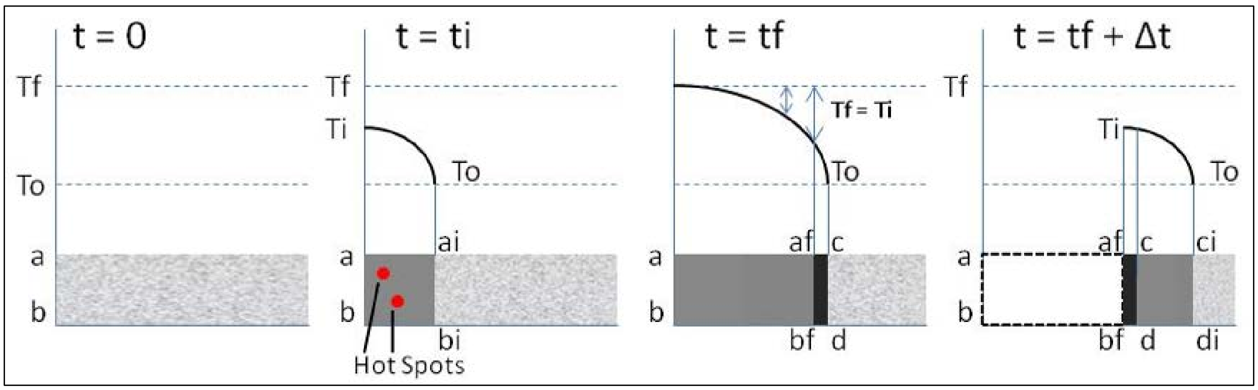

Figure 1. Pictorial representation of Shimizu’s hypothesis, which was adapted from his 1982 article (*1*). Here, temperature (T) is shown as a function of time (t), with T_0 as the initial temperature at the beginning of the dark phase and T_i as the temperature of the burning layer. Ignition occurs on the composition’s surface (ab). When the temperature (T_i) of the layer (aba_ib_i) reaches the flash reaction temperature (T_f), the layer (aba_fb_f) becomes consumed by flash. The temperature then drops, and it results in the formation of a thin layer (a_fb_fcd) on the surface (cd), which will initiate the next dark phase.

Pyrotechnic strobes are believed to have been a coincidental discovery brought about by the increase in use of magnalium in the late 1800s. This was likely due to the discovery of the Hall and Heroult electrolytic processes for aluminum production in 1886 (*2*). A mixing book from 1898, which belonged to the firm Brock’s Fireworks, Ltd. (London), details the first example of documented strobe compositions and refers to them as “Orion’s Flashing Guns” (*3*). These compositions used barium nitrate as the oxidizer and magnalium as the fuel. Both also contained a substantial amount of sulfur. As a basis for the slow strobe work, the different compositions, Mixes A and B, were tested. Table 1 gives these original formulas from Brock’s Fireworks, Ltd.

Table 1. Orion's Flashing Guns Formulations

Orion's Flashing Guns		
Material	% by Weight	
	Mix A	Mix B
Sulfur	51	55
Fine magnesium powder	17	18
Fine aluminum powder	6	–
Barium nitrate	26	27

–, not applicable.

Clive Jennings-White, in his chapter on strobe chemistry from *Pyrotechnic Chemistry*, hypothesized a set of reaction equations to explain the dark and light phases occurring in the Orion's Flashing Guns compositions (*4*). These hypothetical strobe reaction equations are shown below. Equation 1 is the flash reaction, and eq 2 is the dark reaction.

Flash reaction:

$$3\,Ba(NO_3)_2 + 10Al \rightarrow 3BaO + 3N_2 + 5Al_2O_3 \qquad (1)$$

Dark reaction:

$$Mg + S \rightarrow MgS \qquad (2)$$

Several classical strobe formulations include compounds that are known to be toxic and/or environmentally persistent. These toxic and persistent materials include ammonium perchlorate, barium nitrate, and potassium dichromate and are frequently seen in literature and mixing handbooks for the production of strobes. Ammonium perchlorate is an irritant, inhalation, and ingestion hazard; it also causes damage to the blood and kidneys (*5*). The perchlorate ion is known to be stable and nonreactive in aqueous systems, which leads to a high persistency in groundwater and drinking water (*6*). This is of high concern because perchlorate impairs the functioning of the thyroid gland. Barium nitrate, which is also an oxidizer, is extremely hazardous if ingested and hazardous by contact or inhalation. It is toxic to kidneys, lungs, and nervous system (*7*). Barium nitrate is known to pass the placental barrier and is excreted in maternal milk. Potassium dichromate is both acutely and chronically hazardous. It is documented to be extremely hazardous through permeation, irritation, and ingestion. It is also a confirmed class A1 carcinogen and a mutagen (*8*).

In an effort to reduce the health and environmental hazards associated with some of the most-common strobe formulas, strontium nitrate was substituted for barium nitrate. Strontium nitrate is an irritant to skin and eyes and is also hazardous by ingestion and inhalation, but it does not have the target organ toxicology of barium nitrate (*9*, *10*). During the testing of several barium nitrate strobe formulations with strontium nitrate, an extremely slow strobe was discovered. This formulation was the modification of Orion's Flashing Guns. Table 2 provides the materials used for the strontium nitrate version of Orion's Flashing Guns, which resulted in the slow strobe discovery. Equations 3 and 4 are the proposed reaction equations for this formulation.

Table 2. Modifications of Orion's Flashing Guns, Resulting in a Slow Strobe

Slow Strobe Formulations		
Material	% by Weight	
	Mix A	Mix B
Sulfur	55	55
Fine magnesium powder	–	18
Fine magnalium powder (50:50)	18	–
Strontium nitrate	27	27

–, not applicable.

Flash reaction:

$$3\,Sr(NO_3)_2 + 10Al \rightarrow 3SrO + 3N_2 + 5Al_2O_3 \tag{3}$$

Dark reaction:

$$Mg + S \rightarrow MgS \tag{4}$$

2. MATERIALS AND METHODS

The discovery of the slow strobe led to a desire to further investigate its properties. Modifications of the oxidizer and the particle size of the fuel were chosen to be examined. In Phase 1 of the study, the metal particle size was varied. All mixes used a 50:50 blend (magnesium and aluminum) of magnalium. Particle sizes tested are listed in Table 3.

Table 3. Magnalium (50:50) Particle Sizes

Mesh Size	Micron	Inches
–50	297	0.0116
–60	250	0.0097
–100	149	0.0058
–200	74	0.0029
–325	44	0.0017

Phase 2 involved varying the oxidizer. Potassium nitrate was substituted at different concentrations for all or part of the strontium nitrate in the mix. Potassium nitrate was chosen due to its common occurrence in pyrotechnics; it was previously shown by Shimizu (*9*) to produce intermittent burning. All mixtures used a 50:50 blend of 100 mesh magnalium. Table 4 lists the nitrate mixtures used in this portion of the test.

Table 4. Nitrate Mixture

Material	Mix Number						
	1	2	3	4	5	6	7
Strontium nitrate	–	6.75	13.5	20.25	23.6	25.3	26.2
Potassium nitrate	27	20.25	13.5	6.75	3.4	1.7	0.8
Magnalium (100 mesh)	18	18	18	18	18	18	18
Sulfur	55	55	55	55	55	55	55

–, not applicable.

Mixes were prepared by hand in 10 g sample batches. A 10% solution of nitrocellulose in acetone was used as a binder for all mixes. Batches were dried overnight in an oven at 150 °F. After drying, the mixes were pressed into pellets that weighed approximately 10 g (i.e., all material in the batch) using a 2000 lb dead load with a 3 s dwell. Approximately 0.5 g of a nitrate-based starter mixture was included on the top of each cube, with 3 in. of quick match (Precocious Pyrotechnics, Inc., Belgrade, MN) for ignition. An Olympus i-Speed high-speed video camera (Olympus Corporation, Tokyo, Japan), set at 1000 frames per second, and a Panasonic HDC-HS900 high-definition handheld video camera (Panasonic Corporation, Osaka, Japan) were used to capture the data. Figure 2 shows the equipment used for these tests.

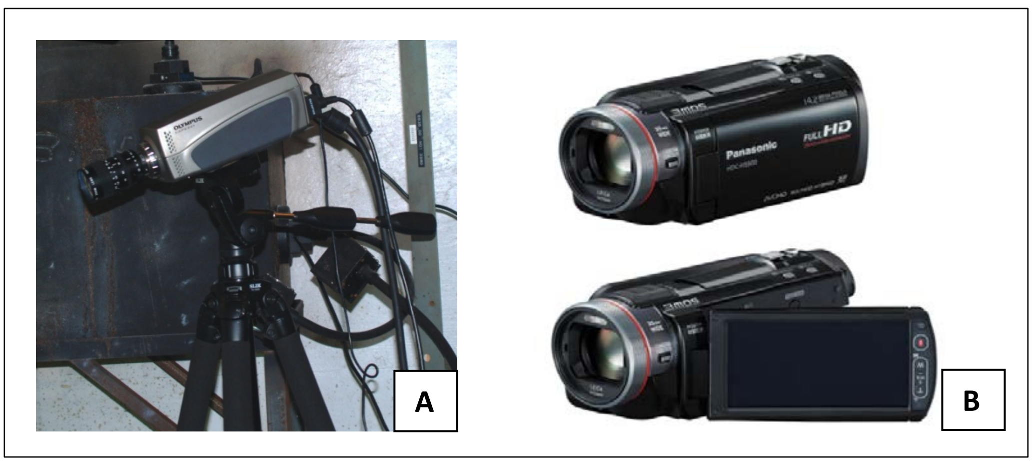

Figure 2. (A) Olympus i-Speed high-speed video camera; (B) Panasonic HDC-HS900 high-definition handheld video camera.

Video assessment was conducted using the Olympus i-Speed Viewer software suite and Windows Movie Maker (Microsoft Corporation, Redmond, WA). These software programs provide the ability to view a video frame by frame. The time between pulses was determined from the termination of one flash to the initiation of the following flash. The total burn time was defined as the time from ignition of the strobe until complete burnout of the pellet. A single flash was defined as ignition of the pellet into the flash phase through the initiation of the dark phase.

The proposed light- and dark-phase reactions for the slow strobe were modeled using the ICT Thermodynamic Code software, version 1.00 (Fraunhofer Institut für Chemische Technologie; Pfinztal, Germany).

3. RESULTS AND DISCUSSION

Phase 1 of the study resulted in the successful reproduction of the first serendipitously discovered slow strobe. Table 5 details the total burn time, number of pulses, and average time between pulses for each of the mesh sizes.

Table 5. Pulse Data for Phase 1 Strobes

Property	Test Number					
	1	2	3	4	5	6
MgAl mesh size	–50	–60	–60	–100	–200	–325
Total burn time (min)	4:41	4:51	4:41	5:01	4:32	3:44
Total pulses	8	8	5	10	7	7
Average time between pulses (min)	0:28	0:32	0:45	0:27	0:36	0:29

All of the mixtures followed the same flash and smolder pattern, as shown in Figure 3.

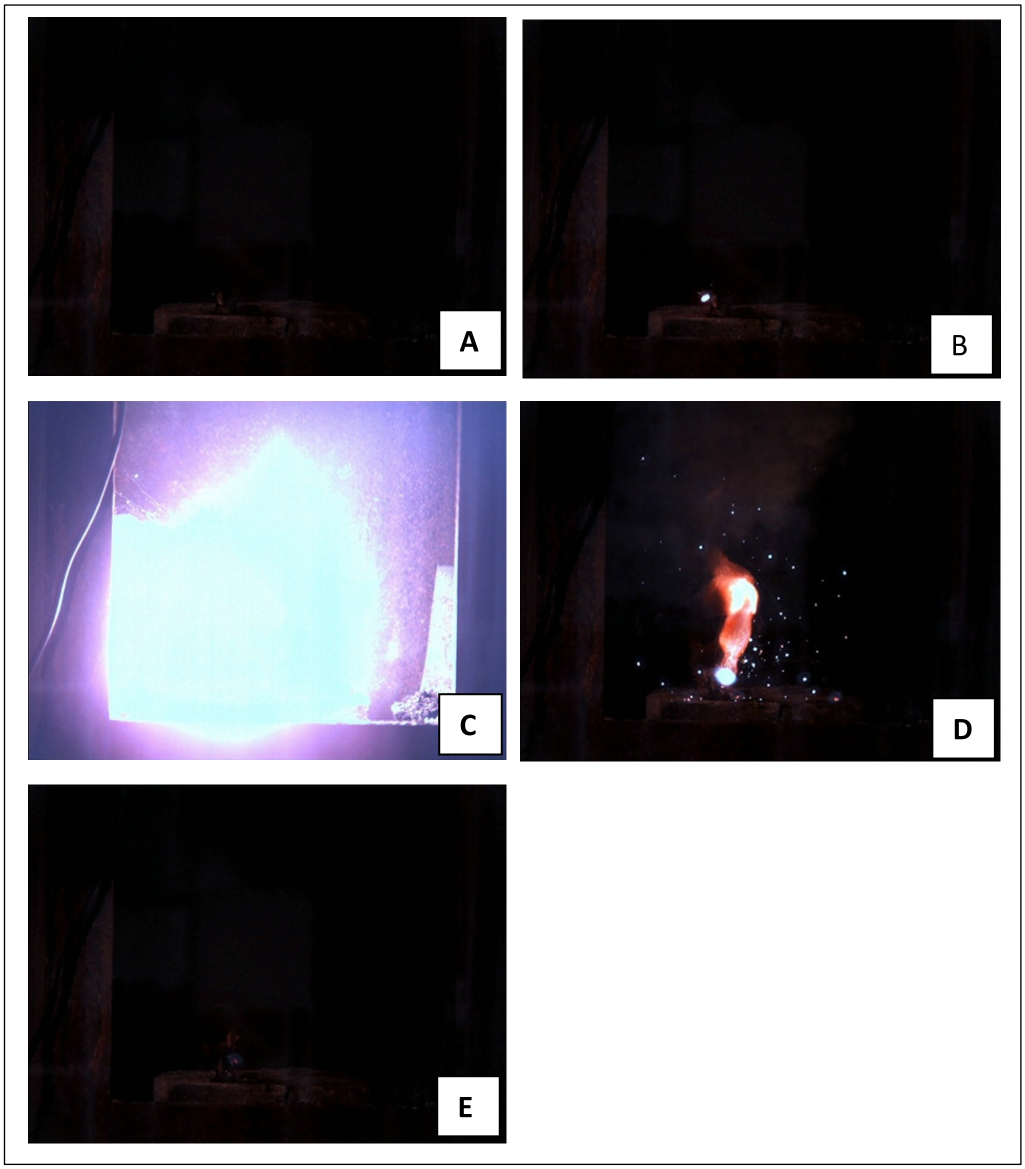

Figure 3. Slow strobe burn pattern.

Figures 4 and 5 provide a graphical representation of the burn time versus mesh size and number of pulses versus mesh size, respectively.

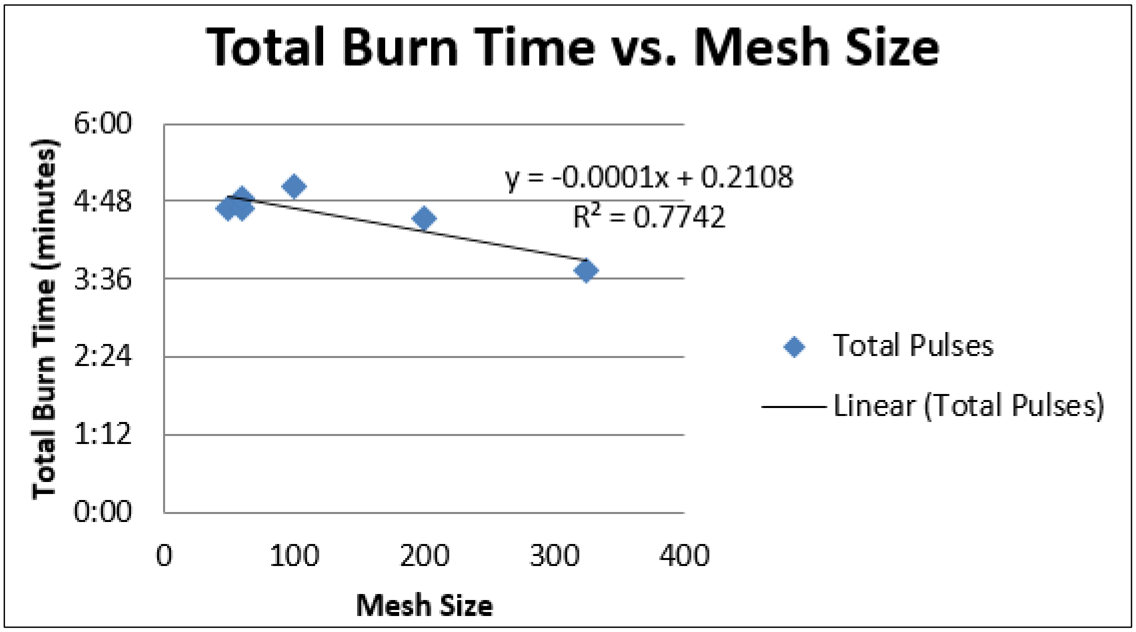

Figure 4. Burn time vs magnalium mesh size.

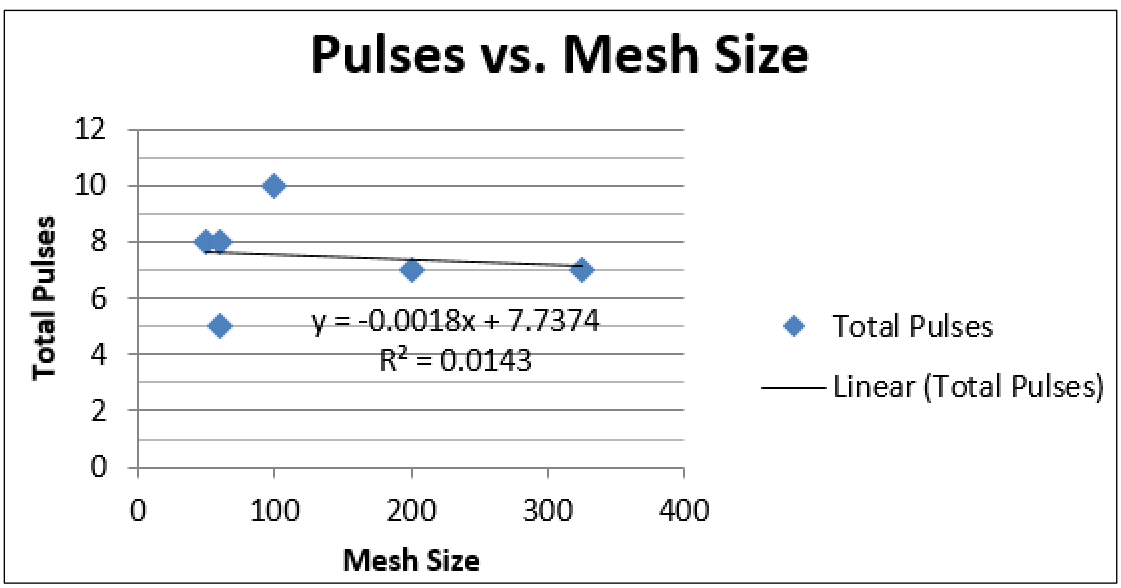

Figure 5. Number of pulses vs magnalium mesh size.

The overall time to burnout of all formulations was 4.58 ± 0.42 min. Phase 1 had an average of 7.5 ± 1.6 pulses per formulation, with an overall average of 0.57 ± 0.12 s between pulses.

During Phase 2 of the study, the addition of potassium nitrate resulted in the loss of the strobe characteristic for samples 1 through 4, which instead acted as flares; in other words, no pulses were seen in any of the first four mixes. However, mixes 5–7 did produce a strobe effect to varying degrees; using a higher parts by weight of potassium nitrate in the mixture resulted in less time between pulses. The actual percentage of potassium nitrate needed for the mixture to lose its ability to exhibit strobe pulses was not determined. Table 6 details the total burn time, number of pulses, and average time between pulses for each of the potassium nitrate/strontium nitrate hybrid strobes. Figure 6 shows the relationship between the increasing percentage of potassium nitrate and the number of pulses per minute for the studied mixtures.

Table 6. Pulse Data for Phase 2 Strobes

Parameter	Test Number		
	5	6	7
Potassium nitrate (%)	12.5	6.3	3.1
Total burn time (min)	4:22	4:04	5:16
Total pulses	18	12	12
Average time between pulses (min)	0:14	0:19	0:25

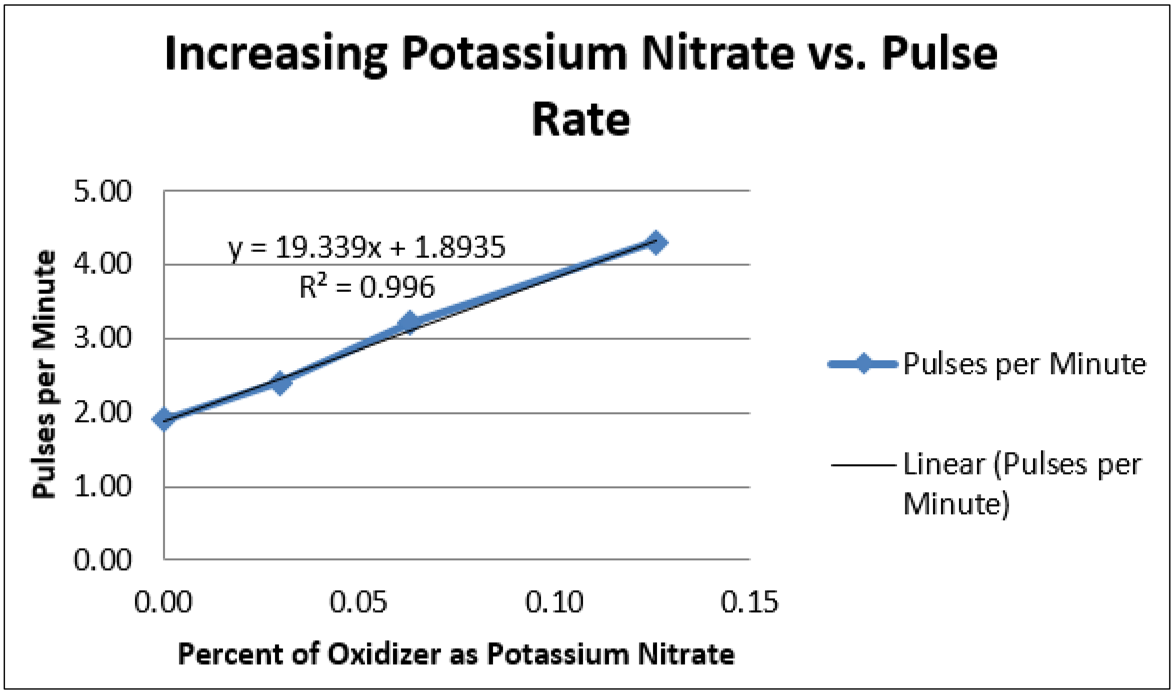

Figure 6. Increasing potassium vs pulse rate.

4. CONCLUSIONS

A strong linear correlation is shown between pulse rate and amount of potassium nitrate. As shown in Figure 4, a moderate correlation was seen between the burn time and mesh size. The correlation between mesh size and the number of pulses was poor, which indicated that amount of potassium nitrate was the primary factor in pulse frequency.

The figures presented for Phase 1 of the experiment showed little correlation between the mesh size and variation of the pulse rate. Based on this data, it was concluded that the strontium nitrate “flash” reaction is responsible for controlling the pulse rate. This conclusion was further bolstered by Phase 2 of the experiment, where a very strong correlation was seen between the number of pulses per minute and the percentage of potassium nitrate comprising the oxidizer.

This mechanism of reaction is most likely explained by a higher flash temperature that needs to be overcome by the strontium nitrate reaction as compared with the traditional barium nitrate strobe. The length of time required for the flash temperature to be reached was orders of magnitude larger than is typically observed with strobes.

An extremely slow strobe was developed using strontium nitrate. This substitution for barium nitrate created a less-toxic composition and reduced the pulse rate to approximately 1 pulse/min. The development of a strontium/potassium nitrate strobe was also demonstrated. This new formulation provided a much-needed environmental benefit as compared with the standard formulations. Low concentrations of potassium nitrate provided the most-consistent and frequent strobe flashes. A critical concentration range of potassium nitrate was determined, below which flashes do not occur and above which the sample burns continuously. Tuning these formulations in the future will provide a true time-dependent strobe for uses in signaling and timed explosives or pyrotechnics.

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