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A major effort has been undertaken to review all articles for correctness. However, it is possible that errors remain. It is the responsibility of the reader to verify any information herein before applying that information in situations where death, injury, or property damage could result.

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The Semiconductor Bridge (SCB) Igniter*

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ABSTRACT

We have developed a silicon semiconductor bridge (SCB) igniter which, when driven with a low-energy current pulse, produces a plasma discharge that ignites energetic materials. Our experiments have demonstrated that SCB explosive devices function in a few tens of microseconds at one-tenth the input energy of hot-wire devices. Despite the low input energies for ignition, tests have demonstrated SCB devices to be explosively safe, passing electrostatic discharge (ESD) requirements and no-fire current levels. In fact, SCB devices can have better no-fire characteristics than hot-wire devices, because of the intimate bridge contact between the underlying thermally conductive substrate. We have tested several different prototype explosive devices. In addition, we have tested SCB actuators with breadboarded "smart" firing sets that will fire the SCB actuators only after transmission of a digital code, after a preset delay, or in a preprogrammed sequence.

Keywords: semiconductor bridge, SCB, pyrotechnic igniter, explosives

Introduction

Most explosive devices use small metal bridgewires, or hot wires, to ignite an energetic powder, such as pyrotechnic, primary or secondary explosives, that has been pressed against the bridgewire. Passage of a low current through the wire heats the wire and in turn, the energetic material in a few milliseconds. Hot wires are used in a wide variety of explosive devices including actuators, detonators, and igniters.

We have developed a different method for explosive ignition.[1] This method utilizes a heavily doped polysilicon bridge that is over 30 times smaller in volume than conventional bridgewires. Consequently, the semiconductor bridge, or SCB, can be rapidly heated when driven by a short (less than 20 μs), low energy (as little as 0.03 mJ) current pulse (30 A). In fact, within a few microseconds after the start of the current pulse, the SCB produces a plasma discharge that heats the surrounding energetic material to ignition, obtaining an explosive output in times as short as a few tens of microseconds.[2] Because the SCB is in intimate contact with a thermally conductive substrate, the no-fire capabilities of SCB devices are excellent and can exceed the no-fire current levels of hot-wires. (No fire is defined as the highest current level that can be applied for a period of time, usually 5 minutes, without the device firing; some specifications also require that the device can still function normally after application of the no-fire pulse.) In addition to no-fire safety, we have also demonstrated the electrostatic discharge (ESD) safety of SCB devices.

SCB Processing and Bonding

Figure 1 shows a portion of an SCB die processed from a wafer of polysilicon on silicon. The bridge is formed out of the heavily doped region enclosed by the dashed lines in the figure and has a thickness, *t*, determined by the depth of the polysilicon layer, a width, *W*, defined by the shape of the doped region, and a length, *L*, determined by the space between the aluminum lands. For a one-ohm bridge, 100 μm long × 380 μm wide × 2 μm thick, the polysilicon layer is doped to a concentration greater than 10^{19} phosphorous atoms/cm^3. The processing procedure consists of three steps. The first step

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*Work performed under the auspices of the US Department of Energy (DOE) by Sandia National Laboratories under contract DE-AC04-94AL85000.

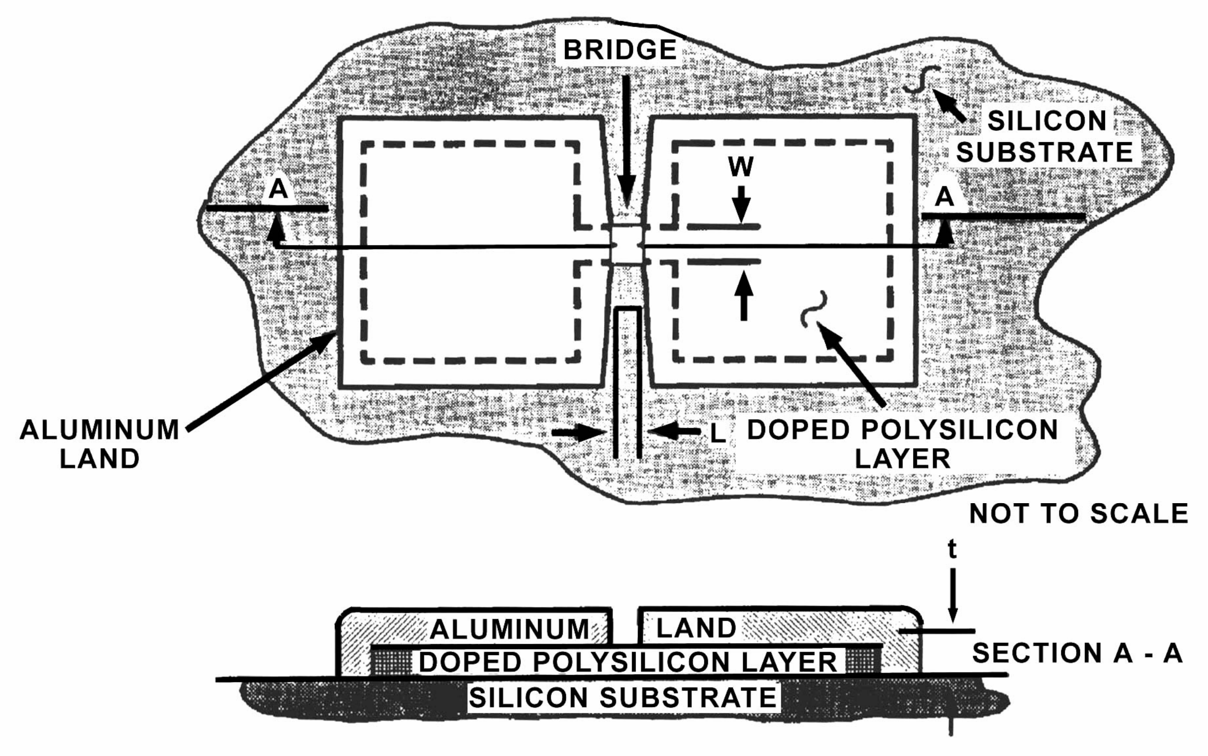

Figure 1. Simplified sketch of a semiconductor bridge (SCB). The bridge is formed out of the heavily doped polysilicon layer enclosed by the dashed lines. Typical bridge dimensions are 380 µm wide (W) by 100 µm long (L) by 2 µm thick (t). Electrical leads are attached to the 2 µm thick aluminum lands, permitting an applied current pulse to flow from land to land through the bridge. The bridge illustrated is designated as a type 3-2 design.

dopes the polysilicon layer, the second defines the n-doped region, and the third defines the lands and the finished bridge. From a single 4 inch wafer over 2000 SCB "chips" can be obtained. We can easily redesign the two masks used for steps two and three to produce SCB geometries that meet particular device requirements. For example, larger bridges have higher no-fire currents but also higher all-fire energies. We have studied many different bridge geometries, each identified by a different type designation [e.g., the rectangular design (100 µm × 380 µm × 2 µm) of the SCB illustrated in Figure 1 is identified as a type 3-2 bridge]. The aluminum lands determine the length of the bridge and also provide a very low contact resistance to the underlying doped polysilicon areas. Aluminum leads are wirebonded to the lands and the metal posts of the header on which the SCB die is mounted. This wirebonding procedure has proved to be quite rugged, capable of withstanding 60 kpsi loading pressures.

SCB Operation

When an SCB is fired in air it produces a bluish colored plasma discharge and an audible "click." Spectroscopic studies of the discharge revealed the plasma to have a blackbody temperature of approximately 550 K. The bridge burn mechanism was determined by high-speed framing photography experiments correlated with the current and voltage waveforms across the SCB. The burn process that produces the plasma discharge proceeds as follows. Application of the current produces a melting and vaporization of portions of the bridge. The process forms a weakly ionized silicon vapor above the bridge and continues until all of the bridge is consumed. Once the bridge is completely melted and vaporized the current transfers to the ionized vapor producing the plasma discharge. Typical current, voltage and impedance waveforms for this process are shown in Figure 2. The initial "bump" in the impedance waveform at 3 µs is the intrinsic/extrinsic transition; the slow rise in impedance between 4 and 11 µs is the bridge vaporization process. The sudden increase in impedance at 11 µs signals the onset of the plasma discharge which is sustained until the current pulse stops. We emphasize here the formation of the plasma discharge and the impedance waveforms, because, one, we have demonstrated that it is the plasma discharge that ignites the powder and, two, we have observed that the shape of the impedance waveform is independent of the voltage or current waveforms (i.e., independent of the firing set).

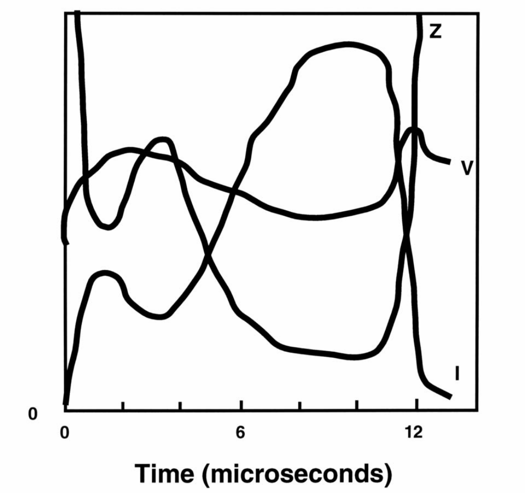

Figure 2. Current, voltage and impedance wave forms across an SCB. The onset of the plasma discharge at 11 µs produces ignition.

Hot wire heat transfer is usually modeled as a thermal conductive mechanism dependent on mechanical contact between the wire and the surrounding energetic material. In contrast, our studies indicate that the SCB transfers heat to the energetic material by a process we call a microconvective mechanism. In this hypothesis, we envision the plasma condensing on the energetic material and heating it to the ignition temperature. Based on the fast function times and low energy ignition requirements of SCB devices, we believe this process to be much more efficient than the heat transport mechanism for bridgewires. In contrast to exploding bridgewire (EBW) detonators operating at high voltages, there is not a sufficient plasma shock when SCB's are operated at low voltages to cause shock initiation.

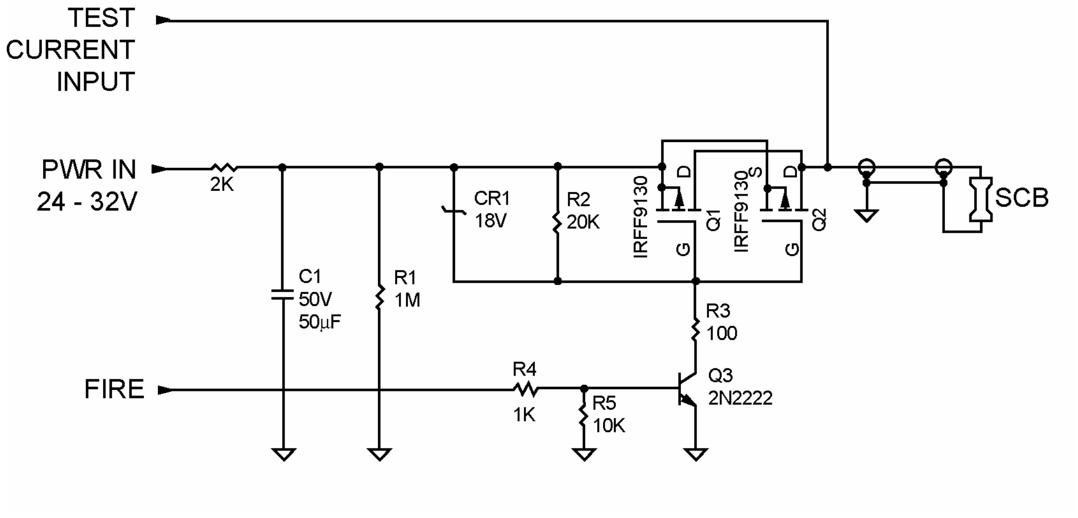

Figure 3. Schematic diagram of a SCB LVCDU firing set.

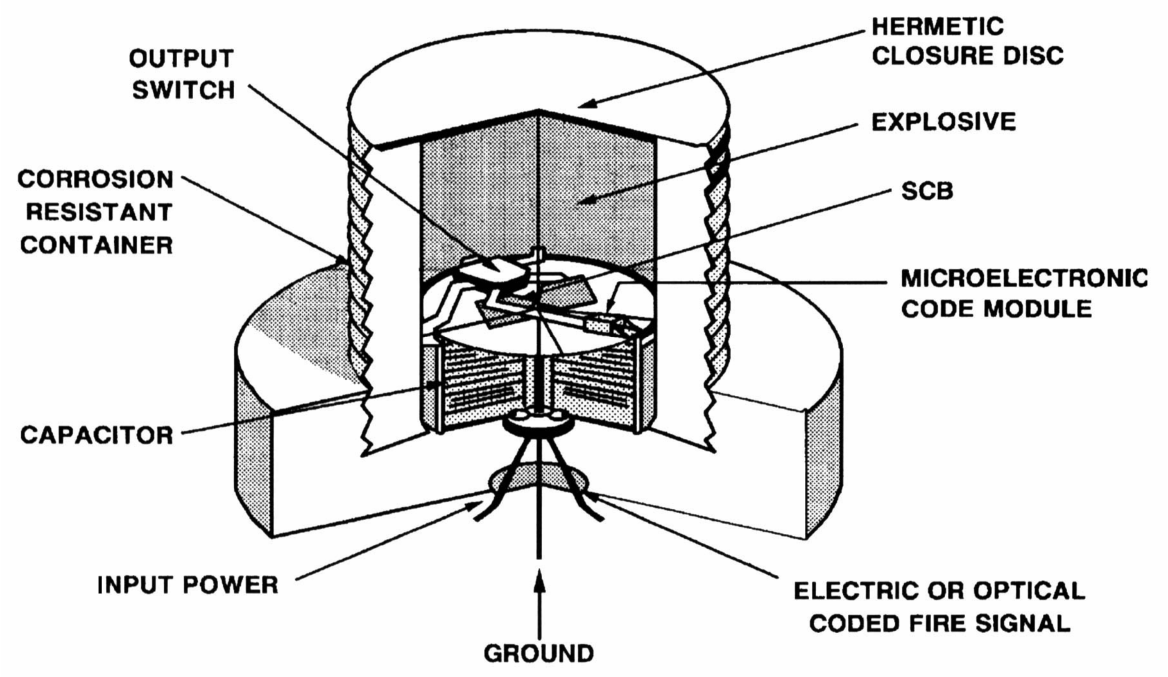

Figure 4. Smart SCB component concept; a thumb-sized, 3-lead device that contains the SCB, explosive powder, switch, capacitor and a microelectronic module used for code identification or delay timing.

Low Voltage Firing Set

We designed a low voltage (24–3 V) capacitor discharge unit (LVCDU) firing set shown schematically in Figure 3. This firing set incorporates fast FET switches, and a low voltage 50 µF capacitor. Typical current and voltage waveforms are shown in Figure 2. The test current input line serves as a continuity test which is used to assure that the SCB device is in place.[3]

Comparison of SCB and Hot-Wire Actuators

A study comparing a hot-wire pyrotechnic ($TiH_{1.68}KClO_4$) actuator with the same actuator slightly modified to accommodate an SCB was conducted.[4] The actuators were assembled using two different SCB die. Fifty units contained type 3-2 die and 50 units contained a type 15 die, same as a 3-2 but with a different land shape (see Ref. 1). All of the actuators underwent three thermal cycles consisting of 5 hours at 74 °C and 4 hours at –54 °C. Twenty unit all-fire and no-fire tests were carried out at –54 and 74 °C, respectively. Ten unit pin-to-pin ESD tests were carried out at ambient temperature for each SCB die design. The data are summarized in Table 1.

Table 1. Comparison of Hot Wire and SCB Devices.

	Hot Wire	Type 3-2	Type 15
All-Fire Energy (mJ)	32.6±1.02 (ambient)	2.72±.48 (–54 °C)	1.33±.03 (–54 °C)
No-Fire Current A	1.1 (ambient)	1.39±.03 (74 °C)	1.30 ±.12 (74 °C)
ESD Test	Passed	Passed	Passed
Function Time(µs)	3400 (ambient)	60 (ambient)	60 (ambient)

This study clearly showed the advantages of SCB devices. Namely, they function at one-tenth the input energy of conventional hot-wire units but based on the no-fire tests are safer than the hot-wire analogs. In addition, SCB devices function in a few tens of microseconds compared to the millisecond response of hot-wire units.

Smart SCB Concept

The smart SCB concept is depicted in Figure 4 and consists of a thumb-sized package that includes the SCB, explosive, fast switch, capacitor and a miniaturized CDU/logic firing set. This device has three inputs, a common, power line and coded signal line; the latter may either be a wire or a fiber optic link. In our first device, after the capacitor was charged, the unit would not function until the correct coded word was transmitted to the device's logic circuit. To improve safety, a second device required two commands; the first permitted the capacitor to charge and the second, if correct, then permitted the SCR to close. If any of the commands in either device were incorrect, the unit would not function.

Summary

We have demonstrated that an SCB can ignite a variety of explosive materials[6] at very low energies but is explosively safe, passing both ESD and no-fire requirements. Indeed, the no-fire current levels for SCB igniters are higher than for hot-wire analogs. While SCB die could be used wherever hot wires are employed this would not take full advantage of the features of SCB igniter. As we discussed, SCB igniters are readily coupled to digital circuits to produce "smart" explosive units. In addition, SCB igniters can be manufactured using cost effective, high throughput assembly techniques. We believe SCB igniters should have many uses in both commercial and military applications.[5]

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4) R. W. Bickes, Jr., S. L. Schlobohm, and D.W. Ewick, "Semiconductor Bridge Igniter Studies: I. Comparison of SCB and Hot-Wire Pyrotechnic Actuators", *Thirteenth International Pyrotechnics Seminar*, Grand Junction, CO, July11–15, 1988.

5) M. C. Grubelich and R. W. Bickes, Jr., "Gas Generator Studies Utilizing a Semiconductor Bridge Igniter", *The 18th International Pyrotechnics Seminar*, July 13–17, Breckenridge, CO, 1992, SAND92-0021C. See also, Ref. 3.

6) A partial list of SCB ignited materials includes: $TiKClO_4$, $AlKClO_4$, $BBaCrO_4$, Al-CuO, $AlFe_2O_3$, PETN, HMX, CP, BNCP.

Modern Rack and Mortar Designs for Professional Fireworks Displays

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ABSTRACT

Professional fireworks displays, as well as those performed by volunteers, have for many years relied on equipment designs and techniques that were established before the turn of the century. The use of steel mortars, the hand firing of individual aerial shells and the use of wooden racks for chain firing of finale effects have until recently been the industry standard. These techniques and designs are adequate for the use intended, as long as the shells function normally, but if a color shell "detonates" or a salute explodes in a mortar, the results can be catastrophic. Since these designs and techniques first came about, the severity of the legal repercussions from accidents at displays has increased to the point where such an event, however unlikely, now represents an unacceptable legal risk to the display company. In this article, designs are presented for finale racks and single shot mortars (for use in "dense-pack" style rack systems) that were developed at Night Musick Inc., and which significantly reduce the risk of catastrophic equipment failure in the event of a shell malfunction.

Keywords: overpressure, shell detonation, dense pack, finale rack, matrix rack, chain fusing

Introduction

Fireworks display operators, both professional and volunteer, have for many years accepted the risks associated with using equipment designed simply to perform as required under normal circumstances. Accidents involving shells that explode while still in the mortar are seldom catastrophic, since they are more likely to involve a color shell than a salute (there are usually many more color shells than salutes in a display), and these devices will generally flowerpot without causing serious damage to reasonably constructed and maintained equipment. The risk of salutes exploding in a mortar rack or color shells detonating* in a mortar rack are usually ignored, perhaps because the operator is ignorant of these possibilities (as may be the case with some "ship show" recipients), or because they are accepted as an inherent part of performing displays.

Display Equipment Failure Analysis

Equipment failure of the type discussed in this paper is the result of a primary failure of a fireworks shell. Equipment failure during normal operation that is the result of poor workmanship or materials is beyond the scope of this article.

It can be argued that equipment that is destroyed because of a shell malfunction has not "failed;" it has merely exceeded its design criteria. While it is true that the cause of this type of incident is the shell, it is also true that the display operator will in all probability bear the brunt of any legal repercussions if subsequent events result in injuries to the audience or the crew. In an ideal situation, there would be no need to anticipate the occasional shell malfunction and no need to limit its destructive effects. However, in reality shells do malfunction, and the responsible display company must anticipate this event and attempt to minimize the resulting damage.

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* "Detonation" as it is used here refers to a color shell in which the normal combustion rate is accelerated to approximately flash powder reaction velocities when it explodes in a mortar. It does not refer to supersonic combustion rates as in the case of high explosives.[1]

Of primary concern to the display operator are the types of accidents that can result in serious injury to the audience or the crew. Foremost among these accidents is the catastrophic loss of structural integrity of a mortar support system which repositions adjacent mortars in unsafe directions. If for any reason these mortars continue to fire, either from chain fusing or burning debris in the air, there is great potential for serious injury (or death) resulting from shells exploding in close proximity to the audience or the crew.

To avoid this situation, a mortar support system must be designed that can withstand the explosive force of the most powerful shell that the operator might use. Even if a support system is designed that meets this criterion, the additional problem of collateral damage to adjacent mortars and their unfired rounds must also be considered. If blast pressure and fragments from the primary explosion penetrate a nearby mortar, the shell it contains may also explode, adding to the net effect of the first shell failure. Further, this process could conceivably continue rendering what would otherwise be an adequate support system (one which could contain the effects of a *single* shell explosion) useless in the face of a more powerful event. Therefore, consideration should be given to mortar construction as well, especially where the support system is of the "dense-pack" design (i.e., a matrix of mortars tightly clustered together for firing).

Design Criteria

As the previous discussion indicates, the primary design criterion for a successful mortar support system must be its survivability in the face of a powerful "in-tube" shell explosion. It must not allow adjacent mortars to become repositioned, and it must not be able to fall over, or cause other racks to fall over, as a result of this type of shell failure. It is obviously impractical to test every shell that an operator may fire in a prospective system (and impossible, to date, to reliably reproduce the detonation effect seen in some star shell explosions), therefore a suitable "worst case scenario" must be used. For the purposes of this paper's designs, a cylindrical 4-inch (102-mm) salute will be used as a maximum explosion for testing dense-pack mortar systems and a cylindrical 3-inch (76-mm) salute for the finale rack system.

The secondary design criterion is practicality. There is any number of ways to achieve the primary design consideration stated above if this second requirement was neglected. These might include sinking mortars in solid high-strength concrete, making the walls several inches thick, using surplus military cannons, increasing the separation distance of the mortars by several feet, etc. All of these solutions would be effective; however, they would also be impractical to implement due to the cost and/or the inconvenience. The requirement of a practical solution is also a subjective one. It is up to individual display companies to decide if the designs presented here are practical for their situation.

These designs fulfill the above criteria for the specific situation at Night Musick. The explosion test results indicate a high degree of survivability for these types of equipment. We feel strongly that while these designs were developed for the operational environment at this company, they can, with few modifications, be utilized by others in the profession and result in an increase in display safety.

Finale Rack Design

The primary attribute of this finale rack design (and the dense-pack mortar system presented later) is that it maximizes structural integrity while minimizing surface area. The force that acts on any mortar support system for a given explosion pressure is directly proportional to the surface area exposed to the blast[2] (i.e., Force = Pressure × Area). Therefore a successful design would use as few structural members as possible, minimizing the aerodynamic, load-bearing surface area, while meeting the need for structural integrity.

A wooden finale rack is a good example of a design that does not possess these characteristics. The structural materials, wooden planks, are easily shattered by even modest applications of force. A three to five gram charge of flash powder (quite modest compared to the 70 gram charges found in 3-inch [76-mm] aerial salutes) can destroy 1 × 4 and 2 × 4 wooden boards (nominally ¾ × 3½ inch and 1½ × 3½ inch; or 19 ×

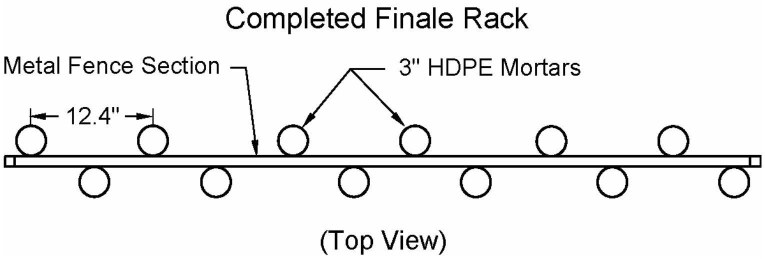

Figure 1. Top view drawing of Night Musick mortar rack design.

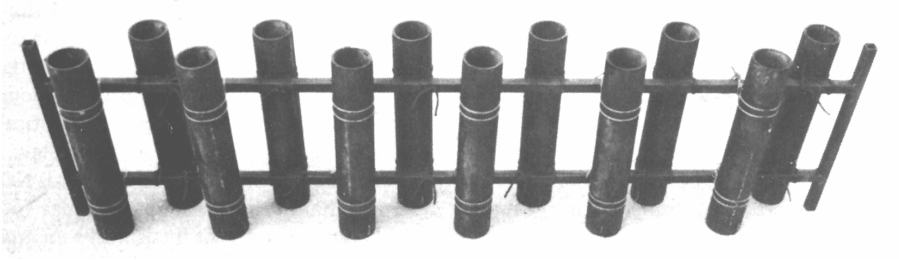

Photo 1. One section of a "fence-type" finale rack.

89 mm and 38 × 89 mm, respectively). Further, our testing has shown that a 3-inch (76 mm) aerial salute can totally destroy the average five-mortar wooden finale rack, no matter which mortar the shell is in, or where in the mortar the shell explodes. This destructive effect is achieved because this design possesses and exposes a large surface area to the explosion pressure and the structural integrity of the wood and the fasteners are not sufficient to withstand the resultant force.

Figure 1 and Photo 1 show a completed Night Musick "fence type" finale rack using common high density polyethylene (HDPE) mortars.[3] It achieves the primary design criterion in three ways. First, it uses 14 gauge, 1-inch (25-mm) square tubular steel stock to make the "fence" section, see Figure 2. This material is very strong, easily obtained and comparatively inexpensive. Most importantly, a 3-inch (76-mm) cylindrical aerial salute placed in a mortar and exploded while in contact with this material will only result in a denting of the steel on the side facing the explosion. Also, when properly welded (four welds per connection) the same test explosive does not damage the joint when the rack is in a vertical position.

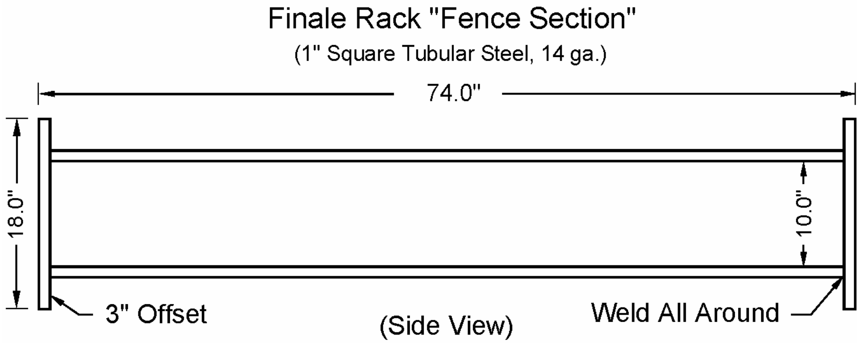

Figure 2. Side view drawing of "fence" section (back bone) of Night Musick mortar rack design.

Secondly, the attachment of the mortars to the rack is accomplished by tying them to the tubular steel fence section using 1/8-inch (3-mm) diameter, braided nylon parachute cord (see Photo 2). This method was selected for two reasons. The first is that the cord itself has a very small surface area when compared to other methods of attachment such as additional tubular steel. This significantly reduces the force that can act on the rack. The second reason is that the cord has very good shock loading ability (i.e., it can absorb large impulses without breaking, such as those experienced during parachute deployment, or, in this case, the shock experienced by nearby mortars when an adjacent mortar explodes). In fact, this material was so successful at absorbing this shock that on many occasions, shell failures (both deliberate and accidental) that totally destroyed a mortar have left the cord that attached the mortar to the rack completely intact (see Photo 3).

Finally, the rack maximizes the distance between mortars by "zigzagging" their location on the rack. As reported by Contestabile[4] the overpressure generated by an explosion decreases rapidly with the distance from the explosion. Therefore increasing the distance between mortars substantially reduces the force which can act on adjacent mortars.

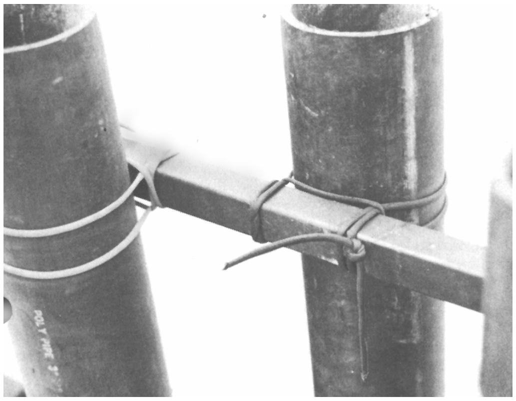
Photo 2. HDPE mortars attached to a "fence-type" finale rack using parachute cord.

This configuration meets our secondary design requirements for practicality as well. In fact, in many ways these racks are easier to use than their wooden counterparts. They are considerably lighter; the average crew member can carry two 12 round racks at once. Because the mortars are "zigzagged" they interlock when stacked on top of one another for transport, thereby saving valuable truck space. This stacked configuration is remarkably stable as well. The racks have been found to be extremely durable; they can sustain much more abuse than wooden racks. The cost of each rack is comparable to most wooden rack designs; approximately 15 feet of

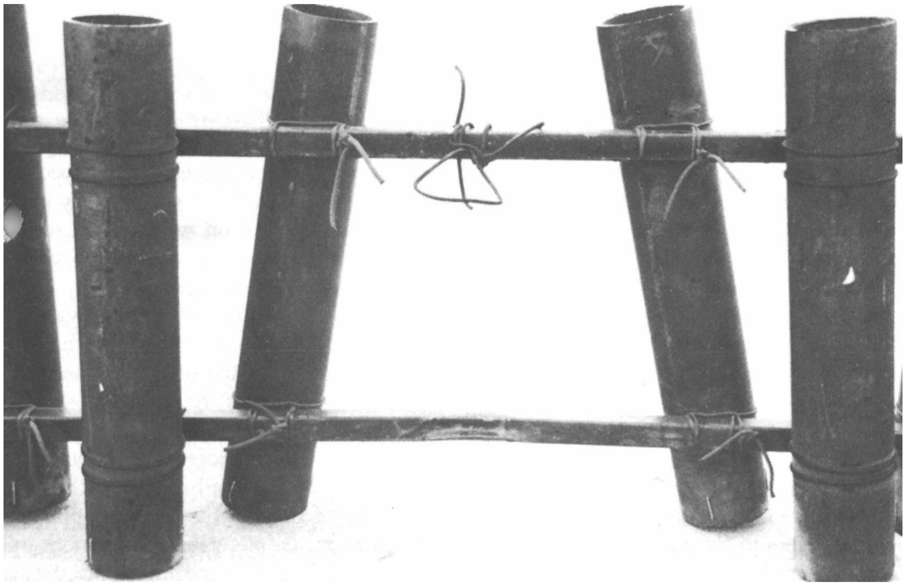
Photo 3. Typical damage to a "fence-type" finale rack produced by exploding a 3-inch (76-mm) salute in a mortar.

steel tubing ($13) and approximately 100 feet of parachute cord ($5) totals less than $20 (US). The skills required to assemble them are slightly more specialized, in that it requires welding as opposed to basic carpentry, but the assembly time is probably less. Also, they are very easy to set up on a display site, since they connect to one another (end to end with adjacent racks at 90°) using common 2-inch diameter × ½-inch wide (50 × 13 mm) automobile hose clamps (Photo 4), or they can be used singly by driving a steel bar into the ground, through the vertical member.

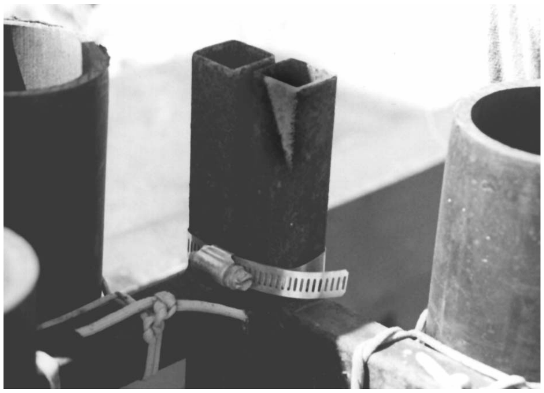

Photo 4. Two sections of "fence-type" finale racks joined using hose clamps. (Note that the second, lower, hose clamp is not shown.)

The primary operational difference between these racks and standard wooden racks is that they are not easily angled for wind direction. Also since they have no bottom, they depend on the ground to support the mortar plugs. As a result, the tension in the attachment lines should allow for adjusting each mortar's height to accommodate irregular surface features. This was not considered a serious drawback for this company, since the display equipment is mounted on trailers, and they can be angled if necessary. When a display is large enough to warrant placing the racks on the ground, the policy is to set them at the maximum distance from the audience that the site will allow, usually the NFPA's fallout distance for the largest shell in the show. If the wind conditions are so severe that a dud 3-inch (76-mm) shell fired vertically from greater than 210 feet (the NFPA required fallout radius for 3-inch [76-mm] shells) might be carried into the audience, then the conditions already exceed the permissible safety margins and the show would be canceled. This renders the question of angled finale mortar racks moot for our situation.

Finale Rack Test Results

The preliminary testing of these racks was accomplished by repeated explosions of 3-inch (76-mm) cylindrical salutes in the mortars at various locations along the racks. Attempts were made to determine whether an explosion of this magnitude could cause significant damage to the rack itself or to the adjacent mortars. Significant damage was characterized as: a) any physical alteration of the rack that could cause a subsequent aerial shell to be fired in an unsafe direction, b) any repositioning of adjacent mortars such that they would fire at an unsafe angle, c) the removal of an adjacent mortar, or d) any damage to an adjacent mortar that could cause that shell to misfire.

It soon became apparent during this testing that this system was adequate to the task at hand. Under no circumstances could we damage the rack's structural steel beyond a dent on the surface facing the explosion (Photo 3), even when the salute was placed at the top of a mortar adjacent to the intersection of two joined racks. Even under this "worst case" scenario, we did not significantly damage the steel, separate the racks, or damage the upper hose clamp holding the racks together. All subsequent tests confirmed these results, and the fundamental design requirement: *A 3-inch (76 mm) salute does not generate enough blast overpressure to produce sufficient force (over the surface area of this configuration) to cause a loss of structural integrity.* At no time did we observe more than a moderate movement of adjacent mortars and no mortar denting whatsoever. It should be noted that we performed these tests using powerful cylindrical salutes of domestic manufacture, utilizing an antimony sulfide, German dark aluminum and potassium perchlorate flash powder formula. While less than 20 rounds were fired, it was decided that further testing would be superfluous. These racks clearly performed far better than conventional wooden racks under the same conditions. Indeed, since 1987 when these racks were first put into service, over a half dozen incidents of salute explosions in finale racks (using various manufacturers' products) have been experienced. In every case, the racks survived and the remaining shells all fired in safe directions.

High Performance Mortars for "Dense-Pack" or Matrix Rack Display Systems

Another area of concern for many companies is individual mortar performance under adverse circumstances, such as an aerial shell exploding powerfully within a mortar. Extensive testing by Contestabile[5] and Myatt[6] have demonstrated the relative performance of many types of mortar materials under these conditions. However, of particular interest is the performance of mortars proximate to one which has suffered some catastrophic shell failure.

In a "dense-pack" [7] or matrix type[6] mortar support system (Photo 5), the mortars are held in close proximity to one another (1 to 3 inches or 25 to 76 mm) by some support structure that can withstand a shell malfunction of the type mentioned above without significant structural failure. Once a support system is in place that meets these requirements, consideration must be given to the level of damage that could be sustained by adjacent mortars that would be held rigidly in place by this architecture. It is conceivable that such mortars could be damaged so severely that unfired aerial shells contained therein may subsequently explode as well. At the very least, these mortars will sustain sufficient damage that shells fired from them would be expected to malfunction in some way due to severe denting or tearing of the mortar wall.

Matrix Mortar Design

Figure 3 shows a cross section of a matrix mortar design. It is essentially a 4-inch ID (10-cm) HDPE mortar placed inside a 6-inch ID (155-mm) HDPE mortar with the lengths of the mortars chosen so that the top of the 4-inch (102-mm) "inner" mortar is even with the top of the 6-inch (155-mm) "outer" mortar. The void space between the two mortars is then filled with a silicone based foam product from Dow Corning (36548 Silicone RTV Foam).

Photo 5. An example of a "dense-pack" style mortar rack containing "matrix mortars," which are "double-walled" and foamed.

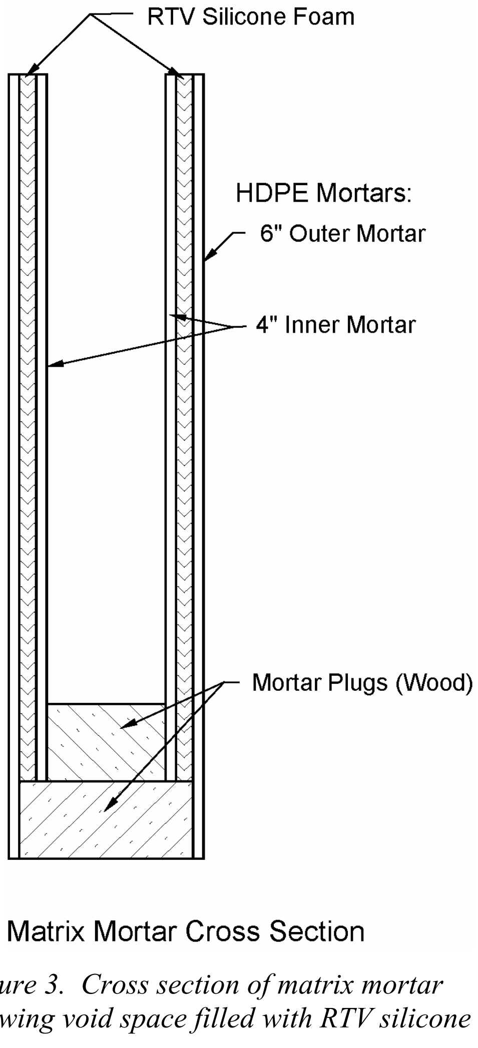

Figure 3. Cross section of matrix mortar showing void space filled with RTV silicone foam.

This shock absorbing foam product is the key to the design. It is described in Dow promotional literature as a black, elastomeric foam with a density of approximately 20 pounds per cubic foot when cured. It is applied by first mixing the contents of a two component kit and pouring the mixture into the void; it should be noted that foam added after an initial application will adhere to the first foam, forming a continuous solid. The mixture cures to a "no flow" state in 1–2 minutes, and its volume expands 2 to 2.5 times. The material cures to form a highly elastic solid that is extremely fire resistant (its primary industrial use is to fill voids around electrical conduit to form a fire stop), also it remains stable in direct UV exposure. In our experience, it has undergone no noticeable degradation due to contact with lift charge combustion products. (It is available in 7-ounce, 2-pound, 16-pound, and 80-pound two-part kits from distributors around the country. Contact Bob Schroeder of Dow Corning at (517) 496-8330 for the location of a distributor in your area.)

Matrix Mortar Explosion Test Results

For the purposes of testing the dense-pack mortar design, a maximum survivable explosion standard was established as a 4-inch (102-mm) cylindrical salute. At the time, this was the largest salute Night Musick would allow in the "body" of a display (since then NFPA regulations have restricted salutes to 3-inch [76-mm]), and it was assumed that this level of explosion pressure would at least equal that of the most destructive 6-inch (155-mm) star shell to be used in this system.

Photo 6 shows the test matrix used during the destructive testing of the mortars. It is a 3 × 3 matrix constructed of welded 1-inch (25-mm), 14 gauge, square tubular steel stock. The two supporting horizontal frames (upper and lower) are held in place at the corners by four vertical 1-inch (25-mm) angle iron supports. Each mortar position in this configuration is 7-inches (180-mm) square (internal) for the 6-inch (155-mm) mortars tested. This frame can restrict the mortars to be no further than 2 inches (50 mm) apart. It should be noted that this configuration was used only for testing the mortars; our production matrix racks have 48 positions and are inherently stronger due to the extensive number of welded interconnections occurring in a matrix this large. While this configuration survived the test explosions intact, it is not recommended that such a small matrix be used for actual displays.

Photo 6. A 9-position (3×3) test mortar support system used in testing matrix mortars. (Note that at the time, the method for filling and the type of foam was being investigated.

Tests were performed by exploding a series of commercial 4-inch (102-mm) cylindrical salutes in the center mortar of the 9 position test matrix. The shell was placed about halfway up the tube. It was felt that in this position the overpressure experienced at the walls of the adjacent mortars would be maximum, since the pressure wave would not be disturbed by the presence of the steel cross members surrounding the mortar at a lower level. Tests were conducted on: (1) RTV silicone foamed double wall mortars, (2) double wall mortars foamed with expanding insulating foam, (3) double wall mortars without any material between the mortar walls, and (4) standard single wall 6-inch (155-mm) HDPE mortars.

The results of these tests were dramatic. All of the 16 single-wall HDPE mortars suffered serious denting that ranged from 30% to 80% reduction in inside diameter. Two of these mortars had small, 2 to 3 inch (50 to 76 mm) long fissures. The double-wall mortars with no filler material performed only slightly better. This configuration exhibited serious compression damage of the outer mortars and denting of the 4-inch

(102-mm) inner mortars from 20% to 40% of their original diameter. In no case was it possible to separate the inner mortar from the outer mortar after the tests.

The RTV silicone-foamed, double-walled, "matrix mortars" fared much better. In two trials, *no blast damage was immediately visible on any of the 16 mortars.* On closer examination, a slight compression of the outer mortars (<2% of the diameter) on two of the mortars was detected when they were measured for "roundness." There was no measurable change in the diameter of the inner mortar for double-wall foamed mortars. Photo 7 shows representative examples of the blast damage that occurred to each of the three mortar configurations tested.

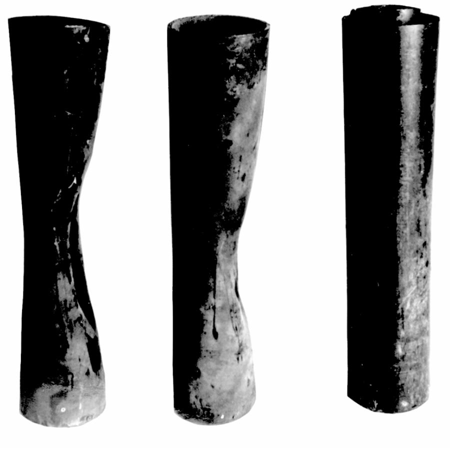

Photo 7. Typical mortar damage in tests of a matrix rack configuration. (Left, single mortar tube; middle, double tube without foam filling void; right, "matrix" mortar with foam-filled void.)

The double-wall mortars that were filled with standard insulating foam from a spray can did perform adequately. No serious denting occurred in these mortars. However, this material was found to be very difficult to work with. It was not made to fill volumes this large; it tends to form voids in the material if too much is used in a single application. It does not bond with previous applications when successive layers are applied, and it takes about 3 applications to complete the fill for the mortar size tested. It must be applied from the bottom up, through holes drilled in the side of the outer mortar. It is also *very* messy and it sticks to everything, especially clothing.

Conclusion

Both designs presented (fence-type racks and matrix mortars) meet their primary operational criterion; they survive. They can absorb the force of a powerful shell explosion within a mortar without suffering catastrophic damage that may threaten the safety of the audience or crew. They give the pyrotechnician the ability to remove an element of risk from the display that previously was beyond his control, namely, the reliability of the aerial shell, at least with respect to mortar explosions. Even manufacturers that use their own shells must assume that periodically a malfunction will occur that will result in an accident of this nature. It is the opinion of the author that to assume otherwise is wishful thinking. Six times in the last eight years, salutes (all of domestic origin) have exploded in the mortars of Night Musick's finale racks, and in every case, the shells that continued to fire, all did so in safe directions. What consequences were avoided because these racks were in place? While a mortar explosion during a display with the matrix mortars is yet to be experienced, it is anticipated that the outcome will be similar to the finale rack explosions; no injuries. Not because of luck, but because this type of accident was anticipated and prepared for.

Acknowledgments

I wish to acknowledge the invaluable contributions of the highly skilled, creative personnel that this company is very fortunate to be associated with. Without the help of these people, Night Musick would simply not exist. And a special thanks to Bob Schroeder and Dow Corning who provided the RTV material we used during testing that proved to be so successful for the application described here.

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Errata — Issue No. 1

“An Introduction to PROPEP, A Propellant Evaluation Program for Personal Computers”

Page 11 The middle initial of the author’s name is “D” not “R” as listed.

Page 15 Right column, middle of the page, some of the text was not properly superscripted, it should read:

$$r = a \cdot P_c^{n}$$

$$Kn = b \cdot P_c^{(1-n)}$$

$$P_c = c \cdot Kn^{(1/1-n)}$$

“Prediction of Flame Temperatures, Part 1: Low Temperature Reactions”

Page 40 Right column, last paragraph, first sentence is missing a “to”, it should read:
“A complication could also arise *due to* the fact ...”

Page 44 The X-axis label is incorrect. The graph should appear as follows:

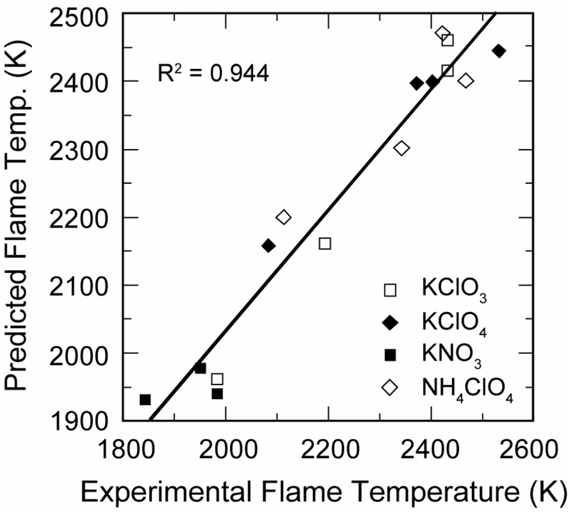

Figure 3. Predicted versus experimental flame temperatures for 15 different mixtures of oxidizer, shellac, and 10% sodium oxalate.

Introductory Chemistry for Pyrotechnists
Part 2: The Effect of Electrons

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ABSTRACT

This is the second in a series of tutorials that introduce the concepts of chemistry to practicing pyrotechnists. The behavior of electrons in atoms is given as the fundamental explanation for all pyrotechnic processes. The periodic arrangement of the elements in a table and their tendencies to unite in chemical bonds are attributed to electrons. Even the production of heat, light, sound, and color in fireworks are ascribed to electronic movements.

Keywords: chemistry, electrons, periodic table, chemical bonds, oxidation, reduction, colored flames.

Introduction

The early parts of this century brought a revolution in the way scientists thought of atoms (the subject of Part 1 of this series[1]). They found that atoms, long regarded as indivisible and featureless, were not the most fundamental ingredients of matter. They discovered, instead, that atoms themselves were composed of tiny components. Each atom consisted of a dense, central kernel, called a *nucleus*, seeming to contain a menagerie of exotic particles. That was surrounded by a swarm of different particles called *electrons*. In addition, scientists learned that none of these subatomic particles behaved as familiar, tangible pieces of matter did. Rather they acted strangely, seeming to follow their own *quantum mechanical* set of rules. Although this elaborate, new concept of the atom made things more complicated, it provided explanations for phenomena that had puzzled people for years. In particular, the idea of quantum mechanical atoms containing electrons answered a question that had been asked, off and on, for seven or eight centuries: “Why do fireworks work?”

The Quantum Picture of an Atom

Imagine that you have the ability to magnify atoms to outrageous sizes. Make one so large that is fills, a football stadium. What do you see? At first, you become aware of an annoying blurriness in your vision that you can’t clear up, even in your mind’s eye. (Quantum objects have a built-in uncertainty about them; you cannot simultaneously pin down their locations and their speeds.) Nevertheless, you see well enough to spot the nucleus, a pea-sized piece of matter writhing on the 50–yard line. And you make out the mosquito-like electrons, not so much as individuals, but as clouds pervading all the bleachers. The overwhelming impression you get from this stadium-sized atom is that it is mostly empty space; it contains very little matter for the volume it occupies. But the matter that does exist in it is dynamic.

As you approach the atom for a better look, you are assaulted by the enormous forces that are coursing through it. These forces arise, in part, from the electrical charges on the electrons and on the nucleus. The electrons carry a negative charge, and the nucleus exhibits an opposite, positive charge. But the forces are more than just electrical. They seem also to impose a certain order on the electrons. You notice that the electrons are segregated according to their energies. The slowest of them occupy the clouds nearest the nucleus, while the more energetic electrons inhabit the more distant clouds.

If you observed atoms of every element on this same huge scale, you would find that the behavior of electrons is quite orderly indeed. Each atom has a similar set of segregated electron clouds, called *shells* or *energy levels*. The electrons prefer to occupy the shells with the lowest energies. Only when those are filled to capacity do electrons move into upper energy levels. The capacities of the first four shells are 2, 8, 8, and 18.

Two quantum properties of these energy levels are important in fireworks. First, only those elements that happen to have exactly enough electrons to fill up the energy levels are stable and satisfied. (There are just six of these elements, helium with 2 electrons and neon with 10, for example. They are called the noble gases, and they hardly ever participate in chemical reactions.) The rest of the hundred-odd elements have partially-filled energy levels that make them chemically reactive. They will combine with other elements in order to obtain a more favorable configuration of electrons. All pyrotechnic effects are the visible or auditory result of such electron rearrangements. Second, the energy gap between one level and another is forbidden territory. Electrons may not take on any energy in that void. It's like a step ladder. You may stand on one rung or you may stand on another, but you cannot stand between rungs. If any electron is to change energy levels, it must absorb or give off the associated amount of energy all at once. No gradual build-ups or let-downs are allowed; it's the entire amount or nothing. Colored flames are the result of electrons jumping between shells and giving off energy in the form of visible light.

The rest of this paper will examine these two quantum effects in more detail.

The Periodic Chart of the Elements

By the time electrons were discovered, chemists, as a practical matter, had already organized the elements onto a chart that was rich in information. They found that if the elements were listed in a certain order, by rows, they would line up in columns of elements with similar chemical properties. This *periodic chart* of the elements is pictured in Figure 1.

When chemists connected the concept of electrons to this well-established arrangement, it was a watershed moment for science. Not only did electrons explain the particular order, but they also accounted for the periodic or cyclic repetition of properties. It turned out that the sequencing of elements, from left to right, was by their *atomic numbers*, the numbers of electrons in their neutral atoms. And the odd way of splitting them into rows of unequal length also became clear. The lengths of the first four rows were 2, 8, 8, and 18 the exact capacities of the electron energy levels. Furthermore, the elements lining up in the same columns each lacked the same number of electrons to fill their outermost shells.

The utility of this chart—with or without an electron explanation—comes from how near the symbols of different elements are to each other. You can expect many of the elements' properties (and that of their compounds) to vary gradually as you go from one box to the next. The most useful feature, however, is the way particular elements reside above or below each other in the columns. All the elements in the same column are regarded as belonging to a *chemical family*. Although each element is a unique individual, members of the same family are alike in many of their chemical properties. For example, their compounds will have analogous formulas. Sodium is in the same chemical family as potassium. Thus, if you know that potassium nitrate is KNO_3, then you also know that sodium nitrate is $NaNO_3$, not Na_2NO_3 or $Na(NO_3)_2$. You've seen titanium (Ti, element 22) salutes giving off brilliant white sparks along with their loud reports. Many pyrotechnists know that zirconium (Zr, element number 40) also emits white sparks in salute compositions. Since zirconium is a member of titanium's family on the periodic chart, such a similarity in behavior, though not inevitable, is not surprising either. [Could there be still another element that, when added to a salute, would produce similar sparks? Perhaps you can narrow down the possibilities on Figure 1 to a singularly likely candidate.]

Unfortunately, some important pyrotechnic properties of elements and compounds do not overtly follow periodic tendencies. The green flame color produced from barium compounds, for instance, is randomly different from the red of strontium compounds and the orange of calcium compounds even though all three elements are in the same chemical family. Sodium compounds are generally hygroscopic; they absorb unacceptable amounts of moisture from the air. However, potassium compounds are generally not. The periodic table cannot easily

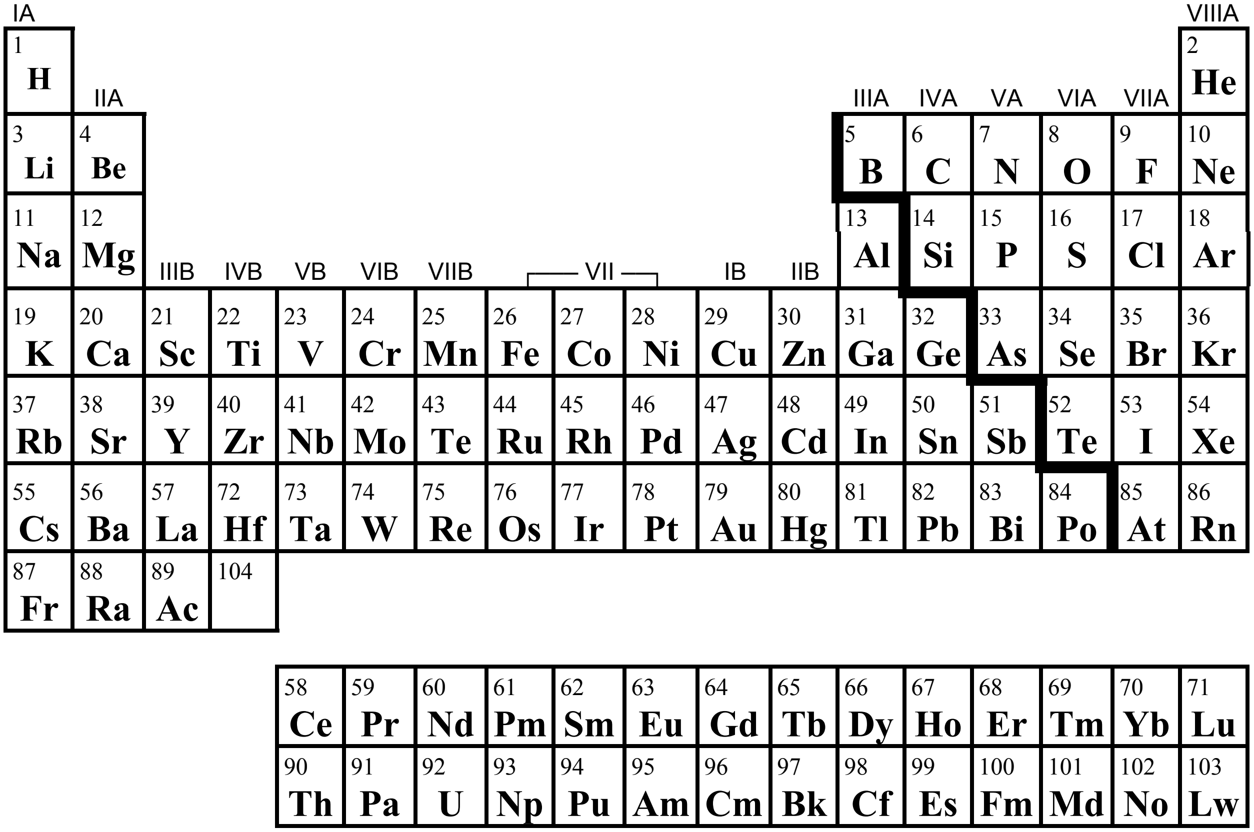

Figure 1. A simple periodic table of the elements, giving their atomic numbers and symbols. The staircase dividing line separates metals and nonmetals.

be used to predict the flame color or the hygroscopic nature of substances.

Chemical Bonding

Every element on the chart, except the six noble gases in the far right column, is composed of atoms having electron shells that are only partially filled. That means that nearly all atoms have less-than-ideal numbers of electrons in their outermost energy level. In order to remedy this situation, atoms react with one another, and they form chemical bonds. A *chemical bond* is an arrangement between two atoms for the sharing or transfer of electrons. Whenever such bonding occurs, the resulting configuration of electrons is more favorable than those of the separate, unbonded atoms: the chemically bonded atoms have less chemical potential energy.

When each of the combining atoms already has nearly ideal numbers of electrons—that is, when neither lacks more than one or two from a completely filled shell—the atoms will share electrons. They form *covalent bonds*. For example, hydrogen lacks one electron from becoming like the noble gas helium, and oxygen wants two to become like neon. If a hydrogen atom obtains a share of one of oxygen's electrons, it has improved its electron configuration. But oxygen's need is not fulfilled with its share of hydrogen's single electron; it's still short one. Thus, two hydrogen atoms must combine with one oxygen atom to satisfy all participants. The resulting H_2O molecule is a more stable combination of hydrogen and oxygen than just HO. In fact, the combination is so stable that whenever hydrogen and oxygen participate in a pyrotechnic process, the end result is the production of water.

The types of elements that form covalent bonds with one another are the *nonmetals*, those elements to the right and above the stair-case dividing line on the periodic chart.

About 80% of the elements on the chart, however, are not even close to having enough electrons to fill their outermost electron levels. Generally, it would take four or more electrons to complete their shells. These elements are the *metals*, those to the left and below the dividing line on the chart. The metals, therefore, adopt a different strategy when they combine: they transfer electrons.

Magnesium metal, for example, would need to gain six electrons to become like the noble gas argon (element 18). But if it could lose just two, it would be like neon. Magnesium's outermost shell would then be empty, leaving the remaining electrons in filled shells. Magnesium atoms, in fact, find perfect fulfillment when they encounter atoms like oxygen. Each oxygen, you remember, is in need of two electrons while each magnesium is looking to jettison two. A transfer of two electrons satisfies them both. That's why all pyrotechnic effects involving magnesium produce MgO, which often glows brightly in the flame. In the exchange of electrons, oxygen takes on two extra negative charges. It becomes a charged atom, or ion, with a –2 electrical charge. The magnesium, now free of two electrons, but with the same nucleus as before, becomes an ion with a +2 electrical charge. (Two of the positively-charged protons in its nucleus no longer have electrons to balance them.) The magnesium ion and the oxygen ion attract each other because of their opposite charges, and MgO is held together with an *ionic* bond. [Determine from the periodic chart why the ionic combination of NaCl (table salt) is so common.]

Table 1 shows the electrical charges that atoms of the first 20 elements take when they have formed stable ions those with no partially-occupied energy levels. These ionic charges are identical to the typical valence states listed in Part 1 if this series of articles. [1] In other words, each atom's electronic structure determines its combining capacity. Whenever two elements combine in these common valence states, they become as stable as they can get, electron-wise. The resulting compounds, with atoms in these states, are generally found as the products of reactions rather than as the reactants (starting materials). [The valence states of all atoms in a neutral molecule must add up to zero. Verify that all the atoms in CO_2 and K_2S, two of the by-products of black powder combustion, are in their typical valence states and thus have stable electronic structures.]

Table 1. The Electronic Charges or Typical Valence States of the First 20 Elements.

Name	Formula	Charge
Hydrogen	H^+	+1
Helium	He^0	0
Lithium	Li^+	+1
Beryllium	Be^{2+}	+2
Boron	B^{3+}	+3
Carbon	C^{4+}	+4
Nitrogen	N^{3-}	–3
Oxygen	O^{2-}	–2
Fluorine	F^-	–1
Neon	Ne^0	0
Sodium	Na^+	+1
Magnesium	Mg^{2+}	+2
Aluminum	Al^{3+}	+3
Silicon	Si^{4+}	+4
Phosphorus	P^{3-}	–3
Sulfur	S^{2-}	–2
Chlorine	Cl^-	–1
Argon	Ar^0	0
Potassium	K^+	+1
Calcium	Ca^{2+}	+2

Table 2. Oxidizers Commonly Used in Pyrotechnics.

Name	Formula	Notes
Ammonium dichromate	$(NH_4)_2Cr_2O_7$	Volcanoes
Ammonium perchlorate	NH_4ClO_4	
Barium chlorate	$Ba(ClO_3)_2$	Green Color Agent
Barium nitrate	$Ba(NO_3)_2$	Green Color Agent
Hexachloroethane	C_2Cl_6	Smoke
Iron oxide (red)	Fe_2O_3	Thermite
Lead oxide (red)	Pb_3O_4	Dragon Eggs
Potassium chlorate	$KClO_3$	
Potassium dichromate	$K_2Cr_2O_7$	Burn Catalyst/ Mg Coating
Potassium nitrate	KNO_3	
Potassium perchlorate	$KClO_4$	
Sodium nitrate	$NaNO_3$	Yellow Color Agent
Strontium nitrate	$Sr(NO_3)_2$	Red Color Agent

Oxidation and Reduction

Certain combinations of elements, however, cannot produce a maximally beneficial exchange of electrons. Two different metals like aluminum and magnesium, for example, may mix to form an alloy like magnalium, but they will not truly react with each other chemically. Other sets of elements, for the lack of better alternatives, will combine without achieving the stability of substances like H_2O or NaCl. For example, when oxygen and chlorine unite to form the perchlorate ion, ClO_4^-, they do so at chlorine's expense. Rather than being able to gain one electron and to obtain the favorable valence state of –1, the chlorine atom has to relinquish control of seven electrons to the oxygen atoms. Thus, if you allow oxygen to have its typical valence state of –2, then chlorine must take on a valence state of +7 [(+7) + 4(–2) = –1]. Although the perchlorate ion is energetically more stable than if chlorine and oxygen atoms remained uncombined under the same conditions, the chlorine atom in a perchlorate ion will seize any opportunity to improve its valence state and to give off more energy. The valence state of chlorine is highly electron-deficient.

Some elements find themselves in valence states with an excess of electrons. Lactose ($C_{12}H_{22}O_{11}$), for instance, contains carbon with a valence state of zero [12(0) + 22(+1) + 11(–2) = 0]. Carbon prefers a valence state of +4, where it has lost four electrons and has adopted the electronic structure of helium. Thus, in lactose, the valence state of carbon is electron-rich.

A substance whose atoms are in electron-deficient valence states is called an *oxidizer*. A compound or element with atoms in electron-rich valence states is called a *fuel*. Neither has an ideal number of electrons, and both have more chemical potential energy than they would like. Mixtures of oxidizers and fuels, therefore, are reactive combinations. In fact, all such mixtures can participate in *oxidation-reduction* reactions, in which electrons are transferred from one substance to another. Electron-flush fuels deliver their extra negative particles to the electron-starved oxidizers, and both transform their excess chemical potential energy to heat, light, or sound. In many such reactions, fireworks happen.

Tables 2 and 3 list the oxidizers and fuels most commonly used in pyrotechnics. [Consulting Tables 1 and 2, can you tell that the nitrogen in the nitrate oxidizers, having a valence state of +5, is electron-deficient? Likewise, can you see from Tables 1 and 3 that aluminum metal, with a valence state of 0, is an electron-rich fuel?]

Table 3. Fuels Commonly Used in Pyrotechnics.

Name	Formula	Notes
Aluminum	Al	
Antimony trisulfide	Sb_2S_3	
Charcoal	"C"	≈85% Carbon
Ferroaluminum	Fe/Al	Typical Alloy 35:65
Ferrotitanium	Fe/Ti	Typical Alloy 30:70
Graphite	C	
Hexamine	$C_6H_{12}N_4$	Hexamethylene tetramine
Iron	Fe	
Lactose	$C_{12}H_{22}O_{11}$	
Lamp black	C	
Magnesium	Mg	
Magnalium	Mg/Al	Typical Alloy 50:50
Silicon	Si	
Sodium benzoate	$NaC_7H_5O_2$	Whistles
Sodium salicylate	$NaC_7H_5O_3$	Whistles
Stearic acid	$C_{18}H_{36}O_2$	
Titanium	Ti	
Wood meal	Complex	Mostly Cellulose
Zinc	Zn	

Colored Flame

In pyrotechnic reactions, chemical potential energy is transformed into kinetic energy. This kinetic energy often appears as heat, when the atoms and molecules in a reaction are made to move faster. If the atoms and molecules are made to move fast enough, the energy appears as *incandescent radiation*, the increasingly brighter glow that is given off when objects are heated from red-hot to white-hot. All of these phenomena are explained by the atomic theory. But to understand how energy appears as colored flames, you must again look at electrons.

As you saw in the stadium-sized atom, electrons organize themselves by energy into shells. They prefer the lowest energy levels, and they leave the highest levels unoccupied. But you can change that. Call down a bolt of lightening that will increase the energy of some electrons. When the added energy is right, the electrons absorb it and move from their lower energy level to the higher one, forming an *excited* atom. This term has nothing to do with atomic emotions; it describes an atom with one or more electrons in a higher-than-usual energy level. Such excited atoms do not last long. As soon as the disturbing jolt of energy has passed, the exited electrons revert back to their original levels. But in doing so, they each can give off a photon, with an exact energy equal to the difference in the two levels (illustrated in Figure 2). If those photons have wavelengths in the range of 380 to 780 nanometers, they can be detected by your eyes, and you see colored light.

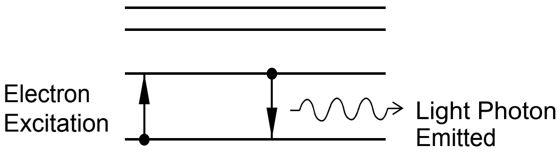

Figure 2. Diagram of atomic energy level showing electron excitation and photon emission.

For pyrotechnic formulations, you need two things to create colored flames. First, you must add an ingredient whose atoms or molecules have energy levels separated by the wavelength of color you are interested in. Table 4 lists a number of common color-producing agents. For

Table 4. Commonly Used Color Agents.

Name	Formula	Notes
Barium carbonate	$BaCO_3$	Green, Neutralizer
Barium sulfate	$BaSO_4$	Green
Calcium carbonate	$CaCO_3$	Reddish Orange
Calcium sulfate	$CaSO_4$	Reddish Orange
Copper (II) carbonate, basic	(I) $CuCO_3 \bullet Cu(OH)_2$ (II) $2CuCO_3 \bullet Cu(OH)_2$	Blue; commercially available material is usually a mixture of (I) and (II).
Copper (I) chloride	$CuCl$	Blue
Copper (II) oxide	CuO	Blue
Copper (II) oxychloride	$CuCl_2 \cdot 3Cu(OH)_2$	Blue
Cryolite	Na_3AlF_6	Yellow
Synthetic ultramarine (Sodium disilicate)	$Na_2S_2 \bullet NaAlSi_2O_4$	Yellow
Sodium oxalate	$Na_2C_2O_4$	Yellow
Sodium sulfate	Na_2SO_4	Yellow
Strontium carbonate	$SrCO_3$	Red
Strontium sulfate	$SrSO_4$	Red

instance, atomic sodium in a flame emits photons that have a yellow color.

Second, you must provide for an oxidation-reduction reaction to supply the energy necessary to produce the photons. This amount of energy is considerable for most color agents. Supplying the excitation energy to the electrons is only one step in a power-hungry process. The detailed mechanism is beyond the scope of this paper, but it involves such operations as vaporizing solids, bringing the flame to a high temperature, and creating specialized (color producing) molecules within the flame. Generally, only the chlorate and perchlorate oxidizers in Table 2 and/or the metal fuels in Table 3 are potent enough to deliver this requisite flood of energy. But once you get the flame conditions right, you can banish the darkness with rainbows of light.

The Workhorse of Pyrotechnics

For all the centuries that mankind has thrilled to the splendor of pyrotechnics, they have been experiencing the effect of electrons. Whether the electrons are moving from one atom to another or whether they are jumping energy levels within an atom, their mysterious quantum mechanical compulsions have made all fireworks possible.

Acknowledgments

The figures and tables used in this article are taken from the *Chemistry of Fireworks Lecture Notes*, published by the Journal of Pyrotechnics, Inc.

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1) W.D. Smith, “Introductory Chemistry for Pyrotechnists, Part 1: Atoms, Molecules, and Their Interactions”, *Journal of Pyrotechnics*, Issue 1, 1995.

Hazardous Chemical Combinations: A Discussion

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ABSTRACT

All pyrotechnic compositions present some hazard due to their ability to produce energy. However, some compositions may pose an added hazard because of the combination of incompatible materials. The use of such compositions may result in more frequent accidental ignitions during processing or spontaneous ignitions during storage. Other compositions pose an added hazard because of their ability to produce especially large amounts of energy with rapid reaction rates. The use of such compositions is likely to result in especially powerful explosions in the event of an accidental ignition.

This article attempts an organized examination of some combinations of commonly used pyrotechnic chemicals, which are believed to have significantly increased hazard potentials.

Keywords: accidental ignition, spontaneous ignition, hazardous combinations, chemicals, compatibility, incompatibility.

Introduction

By their very nature, all pyrotechnic compositions could be considered hazardous because of their potential for producing energy (occasionally at inopportune times). However, some combinations of materials present a special hazard, either because of an added potential for unintentional ignition or because of the potential for producing a powerful explosion upon ignition. Note that there are other hazards, such as health hazards, which may be associated with certain chemical combinations; however, that is beyond the scope of the present article.

A pyrotechnic chemical reaction characteristically produces heat energy. This so called "Heat of Reaction" may be useful directly as thermal energy, or more usually as light, sound, or kinetic energy to achieve the desired effect. However, a pyrochemical reaction must not begin to proceed as soon as the pyrotechnic composition is mixed, for then the composition could not be safely prepared. Such spontaneity is prevented by another characteristic of pyrotechnic compositions, a so called "Activation Energy" barrier. The internal energy associated with a pyrochemical reaction is depicted in Figure 1.

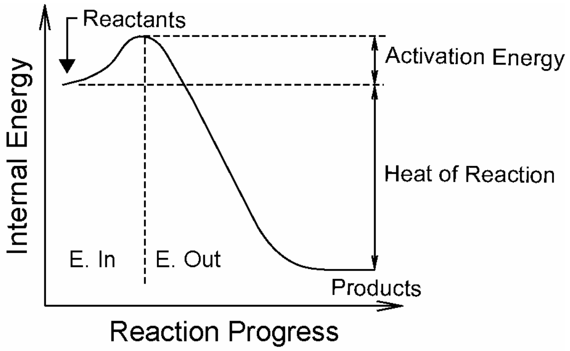

Figure 1. An illustration of the internal energy relationships in a pyrochemical reaction.

Note that initially the internal energy increases. This corresponds to the ignition process, when the composition is being heated, such as by an externally applied flame. This requirement, first to input activation energy to the composition, is what prevents spontaneous ignition. If the activation energy barrier is high, much energy is

Table 1. Some Hazardous Chemical Combinations Encountered in Pyrotechnics.

	Chlorates	Perchlorates	Aluminum	Magnesium	Zinc
ClO_3^-	0	—	X	X	X
ClO_4^-	—	0	?	?	—
Al	X	?	0	—	—
Mg	X	?	—	0	—
Zn	X	—	—	—	0
Acids	X	—	—	X	X
NH_4^+	X	—	—	X	X
Water	—	—	?	X	?
Cu^{2+}	?	—	?	X	X
S	X	X	—	X	X
S^{2-}	X	X	—	—	—

X = Generally a significantly hazardous combination.
? = Can be significantly hazardous depending on circumstances.
— = Little if any added hazard.
0 = Place filler.

required for ignition and accidental ignitions will be unlikely. If the activation energy barrier is low, less energy is required for ignition. When this is the case, accidental ignition will be more likely because a relatively small amount of mechanical, thermal or electrostatic energy can cause ignition of the composition. After ignition has been accomplished, internal energy falls as energy is released from the composition. (See reference 1 for a somewhat more complete discussion of activation energy and heat of reaction.)

Over the years pyrotechnists have tested many substances that seemed promising for use in fireworks. It turned out that some of these, such as potassium permanganate and phosphorus, have such low activation energies in pyrotechnic compositions that they invariably create a significant hazard. Because their unsafe nature in compositions is ubiquitous, it is easy to eliminate such substances from use. A much more difficult problem is the particular combinations of materials which lead to a low activation energy, even though the same materials in other combinations do not pose that hazard. Many of these hazardous chemical combinations are mentioned in the pyrotechnic literature (e.g., Reference 2), but usually without complete explanatory comments. This paper attempts to present somewhat more complete information and explanations. However, this task is often complicated by the lack of solid experimental data reported in the literature. As a result, in some cases the authors will only be able to offer conjecture and anecdotal evidence. While this is not ideal, until more studies are conducted and reported, it is the best that can be done, and it is preferable to not providing any information for these combinations.

Some combinations in pyrotechnic mixtures that can be particularly hazardous are listed in Table 1. However, it is important to note that the list is not all inclusive. Further, on occasion, because of mitigating factors, some listed combinations may not present a high degree of hazard. To better understand why particular combinations of materials can present an increased hazard, each column in Table 1 will be discussed in turn.

Chlorates

Chlorates have the lowest activation energy towards decomposition of any class of oxidizers commonly used in fireworks. Consequently, mixtures containing chlorates tend to be sensitive to all types of accidental ignition. This is evidenced by the especially low ignition temperatures of binary mixtures of potassium chlorate and low melting point or low decomposition temperature

Table 2. A Comparison of Ignition Temperatures for Some Common Oxidizers in Stoichiometric Combination with Various Fuels.[3a]

Oxidizer	Ignition Temperature (°C)				
	Sulfur	Lactose	Charcoal	Magnesium	Aluminum
Potassium chlorate	220	195	335	540	785
Potassium perchlorate	560	315	460	460	765
Potassium nitrate	440	390	415	565	890

[Note that °F = 32 + (9/5) °C.]

fuels (e.g., see sulfur and lactose in Table 2). One should pay close attention to the materials a chlorate is being mixed with, to be sure that the hazard is not thereby exacerbated. However, by no means is it intended to imply that all chlorate compositions are dangerously unsafe.

With Aluminum:

Aluminum has a highly cohesive and non-porous oxide coating which must be disrupted in order for a reaction with oxidizers to take place. This feature tends to raise the activation energy for ignition, compared with many other pyrotechnic fuels, see again Table 2. However, when assessing degree of hazard, it is necessary to consider both the probability and the consequences of a potential accident.[4] In this case the binary mixture of potassium chlorate with aluminum is the classic flash powder, and it has a relatively small critical mass for an unconfined explosion. Therefore, the consequences of such a mixture undergoing accidental ignition are likely to be significantly more severe than for an equivalent amount of a standard chlorate colored star composition. The mixture is more dangerous because of the consequence, rather than because of a decreased activation energy leading to greater probability of an accident. Indeed, the probability of accidental ignition is probably less for aluminum than with common chlorate star compositions (except perhaps when the metal powder is so fine that the mixture becomes electrostatically sensitive).

The common solution to a hazard of this type, where the consequence is particularly severe, is to attempt to reduce the probability of an accidental ignition by raising the activation energy barrier. Usually this is accomplished by using potassium perchlorate in place of potassium chlorate. One can go further in this direction and raise the activation energy more by using barium nitrate as the oxidizer. [However, one should beware of thinking that a higher activation energy automatically means "safer." It also means more difficult ignition and a greater potential for ignition failure (i.e., duds are more likely). Obviously, duds are a safety hazard just as is accidental ignition. In addition, the use of nitrate with aluminum can lead to other problems in the presence of water, as discussed below.]

Conventional wisdom for flash powders would suggest using the above approach (i.e., substituting potassium perchlorate or barium nitrate for potassium chlorate). It is certainly possible that such a substitution will indeed make the resulting flash powder more resistant to accidental ignition. Unfortunately, published sensitivity data does not fully support that. Look again at Table 2; note that the ignition temperature for potassium nitrate (presumably similar for barium nitrate) and aluminum is the highest of the three oxidizers. Also, it is the mixture with potassium perchlorate, and not that with potassium chlorate, that has the lowest ignition temperature.

Since these ignition temperature data are inconsistent with conventional wisdom, it is worth considering whether ignition temperature is the best indicator of the sensitivity of mixtures, or even that the published data may be in error. Table 3 presents impact sensitivity data for the same three oxidizers. In this case, the sensitivity of potassium chlorate and aluminum is indeed the greatest; however, it is roughly equivalent to that for mixtures with either potassium perchlorate or potassium nitrate. Based on the data in Tables 2 and 3, it is not clear that improved safety results from substituting potassium per-

Table 3. A Comparison of Impact Sensitivity for Some Common Oxidizers in Stoichiometric Combination with Various Fuels.[3b]

Oxidizer	Impact Sensitivity (kg·m/cm^2)				
	Sulfur	Lactose	Charcoal	Magnesium	Aluminum
Potassium chlorate	1.1	1.8	3.2	4.5	4.5
Potassium perchlorate	1.2	2.9	4.2	4.4	5.0
Potassium nitrate	3.6	5.0	5.0	4.6	5.0

chlorate for potassium chlorate in two component mixes with aluminum.

If it is true, that substituting potassium perchlorate for potassium chlorate does not significantly decrease the sensitivity of binary mixes with aluminum, then one is left to ponder why conventional wisdom suggests that it does. Could it be a result of experience with flash powders that are not simple binary mixtures, but rather with mixtures including sulfur or antimony sulfide? Tables 2 and 3 do not include data for antimony sulfide but do have data for mixtures with sulfur. The impact sensitivity data suggests that a sulfur-containing chlorate flash powder would be a little (but not much) more impact sensitive than that with potassium perchlorate. However, the ignition temperature data suggests that the chlorate flash powder would be considerably more sensitive.

The foregoing discussion is far from definitive in answering the question of relative flash powder sensitivity. However, it is obvious, for safety, that sulfur (and almost certainly antimony sulfide) should not be present in flash powder using either potassium chlorate or perchlorate. In addition, in the absence of more sensitivity data, it would be prudent to abide with conventional wisdom regarding the preference for choosing potassium perchlorate or barium nitrate over potassium chlorate.

With Magnesium and Zinc:

Like aluminum, magnesium and zinc form energetic mixtures with chlorates, and similar considerations apply. However, because of the lack of a cohesive oxide coating on these metals, the activation energy for their ignition is much lower than it is for aluminum. The combination of both the fuel and oxidizer contributing to a low activation energy, together with high energy output, provides these mixtures the potential to be particularly dangerous.

With Acids:

The predecessor of the modern match was a wooden splint tipped with a chlorate pyrotechnic composition. This was ignited by allowing the composition to come in contact with concentrated sulfuric acid (which was sometimes absorbed on asbestos wool for relative safety). Use outside the home obliged one to carry a vial of sulfuric acid in one's pocket! Apparently, Alfred Nobel invented a mine for use in naval warfare based on this principle. A ship hitting the mine would break a glass tube of sulfuric acid, which then triggered the potassium chlorate and sugar igniter.

The high ignition sensitivity of chlorate compositions in the presence of acids is thought to involve the formation of chloric acid.[5]

$$KClO_3 + H^+ \rightarrow HClO_3 + K^+ \qquad (1)$$

Ignition may occur because chloric acid is capable of spontaneous ignition of organic fuels, or through its decomposition into highly reactive and unstable chlorine dioxide.[6–8]

One can therefore appreciate the necessity for keeping acidic materials away from chlorate compositions. However, if the acid is sufficiently weak, such as stearic acid, it is probably incapable of displacing sufficient chloric acid from the chlorate to induce spontaneous ignition. Moreover, the greasy nature of stearic acid helps lubricate the composition, thereby reducing its friction sensitivity.

With Ammonium Salts:

Ammonium ions are capable of acting as an acid (proton donor).

$$NH_4^+ \rightarrow NH_3 + H^+ \qquad (2)$$

Accordingly, most ammonium salts, such as ammonium perchlorate, are acidic in aqueous solution and potentially lead to the problems discussed above.

In addition, a mixture of a chlorate oxidizer and an ammonium salt may form ammonium chlorate through a double decomposition reaction.[9]

$$NH_4^+ + ClO_3^- \rightarrow NH_4ClO_3 \qquad (3)$$

This is problematic because ammonium chlorate is a substance which explosively decomposes at 102 °C, and is probably capable of undergoing a true detonation.[7,10a]

With Copper(II) [Cupric] Salts:

Like the ammonium ion, the cupric ion (Cu^{2+}) has an acidic reaction in aqueous solution. In addition, in common with other transition metals, copper ions catalyze the decomposition of some oxidizers by lowering their activation energy. For these reasons soluble copper(II) salts with an acidic reaction, such as the sulfate, should not be used with chlorates. In practice, experience has shown that such potential problems can be overcome by using a copper(II) compound which is insoluble and/or has a counter anion with a basic reaction (e.g., carbonate, oxide, etc.). Note also that copper(I) [cuprous] salts (Cu^+) do not have an acidic reaction and therefore engender a relatively minor increase in sensitivity, unless they contain sulfur, such as copper(I) thiocyanate (CuCNS).

With Sulfur:

The combination of sulfur with chlorates is historically the most famous cause of accidental ignitions in pyrotechnics due to “incompatible” chemicals. Such mixtures have long since been banned in some countries (e.g., England). One possible mechanism for the high sensitivity of such mixtures may begin with the formation of polythionic acids on the surface of sulfur grains, and ultimately producing sulfuric acid[5] (see comments above about acids). To some extent, during mechanical action sulfur reacts with oxygen in the air to form sulfur dioxide.[11] It is thought that a chain reaction involving the gases sulfur dioxide and chlorine dioxide may be implicated in cases of spontaneous ignition of potassium chlorate and sulfur mixtures.[5]

$$2\ KClO_3 + SO_2 \rightarrow K_2SO_4 + 2\ ClO_2 \qquad (4)$$

$$4\ S + 2\ ClO_2 \rightarrow 2\ SO_2 + S_2Cl_2 \qquad (5)$$

It can be seen from the equations that one molecule of sulfur dioxide ends up generating two molecules of sulfur dioxide, and the cycle potentially repeats at twice the rate; and so forth until the ignition temperature may be reached. Further, sunlight is thought to exacerbate this problem as well as the use of sublimed sulfur (flowers of sulfur) rather than sulfur flour.[5,12]

It is probable that the bad reputation this mixture acquired in the past was due, in part, to impurities in the materials formerly available.[13] For example, the presence of chlorite in the chlorate, or various sulfur acids in the sulfur, could serve to initiate the chain reaction. Notwithstanding this proviso, it is clear that even with pure materials the sensitivity of a chlorate and sulfur mixture to friction and impact is too high to justify its use.[14]

With Sulfides:

Similar considerations apply to mixtures of chlorates with sulfides as for mixtures with sulfur described above. For example, the mixture of arsenic sulfide with potassium chlorate is even more impact sensitive than the mixture of sulfur with potassium chlorate.[3c] However, different sulfides may vary in the degree and type of hazard involved. While the sulfides of antimony and copper were those most commonly used with chlorates in the past, it would be wise to assume that any sulfide so used represents a significant hazard.

Perchlorates

Perchlorates have a substantially higher activation energy towards decomposition than do chlorates as evidenced by their energies of decomposition, see Table 4. Therefore it can be inferred that any given material is likely to form a "safer" mixture with a perchlorate than with a chlorate. However, ammonium perchlorate is incompatible with many materials because of the ammonium ion. Perhaps more important than these considerations is the observation that, in perchlorate compositions, additives are sometimes specifically used to restore the favorable burning properties present in the corresponding chlorate composition. While it has not been well researched, there is the potential for this to increase the hazard, possibly approaching that of the chlorate composition. Thus, one can by no means make a valid generalization, "perchlorate compositions are safer than chlorate compositions." Much of the advantage of perchlorates lies with less stringent compatibility considerations, rather than its inherent safety.

Table 4. Decomposition Energies for Some Common Oxidizers.[3d]

Oxidizer	Product	Decomposition Energy (kcal/mole)
Fe_3O_4	Fe	–266
KNO_3	K_2O	–151
$Ba(NO_3)_2$	BaO	–104
$Sr(NO_3)_2$	SrO	–89
$KClO_4$	KCl	+1.2
$KClO_3$	KCl	+10

With Aluminum:

The combination of potassium perchlorate with aluminum has quite a large activation energy and generally causes no problem. However, when the aluminum is a very fine powder, in the context of a flash powder, the consequence of accidental ignition is so devastating that such mixtures should be handled with extreme caution and avoided when possible. Mixtures containing relatively small percentages of potassium perchlorate or fine aluminum tend not to be a problem.

With Magnesium:

As with aluminum, there is generally no direct problem with the combination of potassium perchlorate and magnesium. However, as will be discussed below, the presence of water with this mixture is problematic. Further, with fine magnesium powder, the combination of lower activation energy and high energy output do make for a substantial hazard. Small percentages of either potassium perchlorate or fine magnesium in these mixtures do not seem to pose a problem.

Substances Hazardous with Chlorates but not with Perchlorates:

Zinc is not a particular hazard with perchlorates because, despite zinc having a lower activation energy than aluminum, it is not a sufficiently high energy fuel to form a dangerous flash powder with these oxidizers (see Table 5). It is important to note, however, that the combination of zinc with ammonium perchlorate is exceptionally hazardous because of its incompatibility with the ammonium ion (discussed below).

Table 5. Heats of Reaction for the Complete Combustion of Various Fuels.[15,16]

Fuel	Heat of Reaction (kcal/mole) (a)
Aluminum	–401
Titanium	–225
Silicon	–218
Magnesium	–144
Shellac	–131 (b)
Stearic acid	–109 (b)
Lactose	–108 (b)
Carbon (c)	–94
Zinc	–84
Sulfur	–71

a) Note that negative values correspond to exothermic reactions.

b) This value is per mole of carbon in the compound.

c) Carbon is in the form of graphite.

Acids (typically encountered in pyrotechnics), ammonium salts, or copper(II) salts present little or no problems with perchlorates for two reasons. Firstly, perchloric acid is a significantly stronger acid than chloric acid and so is less susceptible to displacement from its salts. Secondly, perchloric acid is a stable acid, in marked contrast with chloric acid which spontaneously decomposes at 40 °C (104 °F).[10b]

With Sulfur:

The combination of sulfur with a perchlorate is generally believed to be substantially less hazardous than the combination with a chlorate. However, with respect to impact sensitivity (see Table 3), the difference is barely worth mentioning. It has been speculated that to some extent the bad reputation of sulfur and chlorate mixes came about because earlier supplies of materials were contaminated.[13] If this was the case, that might explain the wisdom about perchlorate and sulfur mixtures being substantially less hazardous. That may have been true at one time, but not for high purity materials.

Obviously potassium perchlorate and sulfur mixes have a low activation energy barrier, are quite sensitive to accidental ignition, and must be avoided if possible.

With Sulfides:

Similar considerations apply to mixtures of perchlorates with sulfides as for mixtures with sulfur.

Aluminum

The burning of aluminum metal produces the greatest amount of energy of the fuels in common use in fireworks, see Table 5. Nonetheless, aluminum can be one of the safest high energy metal fuels, because of the cohesive and nonporous oxide coating which engenders a high activation energy barrier for both combustion (see Tables 2 and 3) and corrosion. However, there are certain circumstances in which the oxide coating may be disrupted, potentially creating a hazard.

With Water:

Water is widely used to activate binders of pyrotechnic compositions, and must therefore be considered a temporary ingredient of such compositions. Any active metal has the capability for a reaction with water to produce hydrogen gas. One example is the simple mixture of aluminum metal powder and pure water.

$$2\ \mathrm{Al} + 6\ \mathrm{H_2O} \rightarrow 2\ \mathrm{Al(OH)_3} + 3\ \mathrm{H_2} \qquad (6)$$

Because this is an exothermic reaction, there is the potential for generating sufficient heat to reach the ignition temperature of a pyrotechnic composition. (Even if the ignition temperature is not reached, the metal can corrode and the pyrotechnic composition becomes useless.) In Figure 2, note the relatively sudden onset of the exothermic reaction after a prolonged latency (see Table 6).

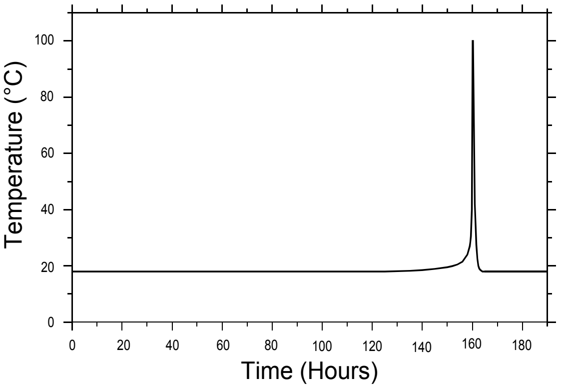

Figure 2. An example of an aluminum and water exothermic reaction.[17]
[See Table 6 for Experimental Conditions.]

The water reactivity of aluminum rises in particular with nitrate compositions, wherein the following exothermic decomposition can take place:

$$6\ \mathrm{KNO_3} + 16\ \mathrm{Al} + 9\ \mathrm{H_2O} \rightarrow 6\ \mathrm{KAlO_2} + 6\ \mathrm{NH_3} + 5\ \mathrm{Al_2O_3} \qquad (7)$$

Aluminum oxide is amphoteric, meaning that not only can it dissolve in acids to form aluminum salts but it can also dissolve in alkalis to form aluminates (such as the potassium aluminate formed in the reaction above). Consequently, the alkaline nature of the ammonia produced in

Table 6. Aluminum and Water Reactivity Data at 18 °C (64 °F) unless Otherwise Stated.[17]

Conditions for Test	Average Time to Exotherm
Aluminum, 12 micron atomized, 2 g Distilled water, 2 g	159 hours
Aluminum, 12 micron atomized, 1 g Potassium nitrate, 1 g Distilled water, 2 g	10 hours
Aluminum, 12 micron atomized, 1 g Potassium nitrate, 1 g Boric acid, 0.04 g Distilled water, 2 g	>500 hours
Aluminum, 12 micron atomized, 1 g Copper(II) oxide, 1 g Distilled water, 2 g	15 hours
Aluminum, 12 micron atomized, 2 g Distilled water, 2 g Temperature of 43 °C (109 °F)	1 hour

this reaction (equation 7) can enable it to dissolve not only some of the aluminum oxide produced in the reaction, but also some of the oxide coating of the aluminum. The aluminum so activated can then go on to react directly with water, generating more heat. Another series of tests similar to that shown in Figure 2 was performed; however, half of the aluminum was replaced with potassium nitrate (see Table 6). In this case a slightly higher temperature was reached as the water was consumed, and the reaction peaked after only 10 hours. At least one plant explosion, is believed to have been caused by such an aluminum, nitrate, and water reaction, when it occurred in 12 kg (26 lb) of a pyrotechnic mixture left partially submerged in water.[18]

In practice, many of these water and aluminum reactions do not appear to be a serious problem when atomized or coarse flake aluminum is used. Presumably this is because the wetted compositions are cut or rolled into relatively small stars, from which heat readily escapes. Also the amount of water present is relatively small and drying is fairly fast.

If for some reason it is desired to use fine aluminum with a nitrate present, or if it is anticipated that the drying time will be prolonged, a small amount of boric acid can be used to counteract the incipient alkalinity and prevent decomposition. This is partly because the protective oxide coating of aluminum is much more resistant to mild acids than it is to alkali. Moreover, aluminum borate formed[19] on the surface of the aluminum is very insoluble and therefore improves the protection. For example, when as little as 0.2% boric acid was added to an aluminum and potassium nitrate mixture, there was no detectable reaction with water even after 500 hours, see Table 6. (Note that using 0.5% boric acid would provide a more reliable safety margin.)

With Copper(II) [Cupric] Salts:

A metal will react with the salt of a more electronegative (less reactive) metal in what is called a displacement reaction. Such a reaction is exothermic and has the potential to produce enough heat to raise a pyrotechnic composition to ignition temperature. A classic example of this is the silver nitrate and magnesium flash powder which is initiated by a mist of water droplets:[6]

$$Mg + 2\,AgNO_3 \rightarrow Mg(NO_3)_2 + 2\,Ag \quad \text{Displacement Reaction} \qquad (8)$$

$$6\,Mg + 2\,AgNO_3 \rightarrow 6\,MgO + 2\,Ag + N_2 \quad \text{Flash Reaction} \qquad (9)$$

The activation energy of the displacement reaction is lowered so much by the presence of water that the reaction proceeds at ambient temperature, generating sufficient heat to initiate the pyrotechnic flash reaction.

Displacement reactions can occur with copper salts and aluminum, but in practice this is seldom a problem because of the large activation energy engendered by the oxide layer on aluminum. However, problems can arise when the copper salt is significantly soluble. Although most copper salts used in pyrotechnics are poorly soluble, it should be borne in mind that the presence of ammonia substantially enhances the solubility of the copper salts.[20] Consequently, situations with the potential for generating ammonia, such as described in the previous section, can be exacerbated by the presence of a copper compound.

As part of the testing of aluminum's reactivity with water (Table 6), a series of tests were conducted wherein a mixture of atomized aluminum and copper(II) oxide were used. Despite the low solubility of copper(II) oxide, a reaction similar to that shown in Figure 2 occurred. The time interval before the peak (exotherm) was 15 hours, nearly as fast as it occurred when testing aluminum with potassium nitrate.

Magnesium

The activation energy for the reaction of magnesium is substantially less than for aluminum. As a result, the associated chemical reactivity problems are generally similar in kind but much greater in degree.

With Acids:

Magnesium is extraordinarily reactive towards acids and so even mild acids, such as boric acid, must be avoided.

$$Mg + 2\,H^+ \rightarrow Mg^{2+} + H_2 \qquad (10)$$

With Ammonium Salts:

The ammonium ion is sufficiently acidic to react with magnesium:

$$Mg + 2\,NH_4^+ \rightarrow Mg^{2+} + 2\,NH_3 + H_2 \qquad (11)$$

The only known way of preventing this reaction is by conversion coating the metal. Traditionally, the only effective coating was obtained by treatment with a dichromate.[21] This, however, may be considered an extreme solution because of the carcinogenicity of dichromates. Recently, a report of a conversion coating that may be superior to that of dichromate has appeared.[22] That coating is based on treatment with a low toxicity ammonium metamolybdate and ammonium dihydrogen phosphate solution.

With Water:

The reactivity of magnesium with water is so great that aqueous binding is generally considered to be incompatible with the presence of magnesium. In fact, reactions occur with unprotected magnesium and many (most?) salts in the wet state. For example, Shimizu[21] reports that active or violent reactions occur between magnesium and the list of wet salts listed in Table 7.

Table 7. Some Wet Salts Invoking Active or Violent Reactions with Magnesium.

Barium nitrate	Potassium chlorate
Potassium nitrate	Potassium perchlorate
Sodium oxalate	Sodium chloride
Sodium bicarbonate	Sodium carbonate
Strontium nitrate	

With Copper Salts:

The reactivity of magnesium with copper salts (both cupric and cuprous) is so great that such mixtures are generally considered to be incompatible. This is because of an exothermic displacement reaction.

$$Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu \qquad (12)$$

Copper metal or copper(II) oxide should be used when combinations with magnesium are desired. Copper metal works because both it and magnesium metal are in the same oxidation state, zero or neutral, thus displacement is not possible. However, because of magnesium's intrinsic water reactivity and because copper and magnesium metals form an electrochemical couple, non-aqueous binding is essential. When drying times are fairly short, copper(II) oxide seems to be acceptable, because of its low solubility. However, there may be problems similar to that when mixed with aluminum (see above and Table 6).

With Sulfur:

Sulfur can act as an oxidizer for active metal fuels. A metal associated with low activation energies, such as magnesium, can react spontaneously with sulfur leading at least to corrosion, and perhaps to ignition under some circumstances. Even aluminum and sulfur mixtures can present a problem under rare circumstances. For example, it has been reported that when a mixture of aluminum and sulfur was ball milled, an explosion resulted.[23] Presumably this was partly the result of physical abrasion removing enough of the protective aluminum oxide layer to lower the activation energy to unsafe levels for ball milling.

Zinc

Despite being a substantially less energetic fuel than magnesium, zinc also has a somewhat low activation energy barrier, and so generally shares similar compatibility concerns.

With Acids:

Zinc reacts readily with acids, and the combination is best avoided. (See equation 10 for a similar reaction.)

$$Zn + 2\ H^+ \rightarrow Zn^{2+} + H_2 \qquad (13)$$

With Ammonium Salts:

Like magnesium, zinc is incompatible with ammonium salts. The reaction is exacerbated in this case because zinc oxide is dissolved by aqueous ammonia.

$$ZnO + H_2O + 4\ NH_3 \rightarrow [Zn(NH_3)_4]^{2+} + 2\ OH^- \qquad (14)$$

Thus, the ammonia formed in the reaction is able to solubilize the partly protective zinc oxide layer on the zinc particles, thereby accelerating its decomposition. A classic demonstration of spontaneous combustion is the mixture of zinc with ammonium nitrate, which is initiated with a drop of water. Under conditions of high humidity, because of the hygroscopicity of the ammonium nitrate, the mixture will spontaneously heat up.

With Water:

In its behavior with water, zinc more closely resembles aluminum than magnesium. Usually there is no problem, even with nitrates present. However, on occasion, such mixtures have been known to heat up. Ammonia, the water reaction product of nitrates and zinc (see equation 7 for a similar reaction) dissolves the protective zinc oxide layer, leading to a self-accelerating reaction.

With zinc metal, because of its acid sensitivity, anything but a neutral pH composition must be avoided. Thus, in practice, nitrate and zinc mixtures can generally be used with aqueous binding only if there are no acidic or alkaline ingredients present to initiate its decomposition. However, it is well to be aware of this potential problem.

With Copper Salts:

Like magnesium, zinc is incompatible with copper salts due to exothermic displacement reactions as discussed above.

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \qquad (15)$$

With Sulfur:

The mixture of zinc and sulfur is a traditional model rocket fuel.

$$Zn + S \rightarrow ZnS \qquad (16)$$

However, it is not generally recognized that this mixture has a quite low activation energy for ignition, and is significantly sensitive to both friction and impact. According to Partington[24] "... the mixture may detonate on percussion." As with magnesium, this combination is best avoided, even though it probably is not capable of a true detonation.[25]

Addendum for Magnalium

In general, the properties of an alloy are somewhat intermediate between those of its constituent metals. This is not necessarily the case however; for example, the hardness of magnalium (magnesium/aluminum alloy) is significantly greater than that of either of its constituent metals. Nevertheless, its chemical sensitivity is more often intermediate than resembling a mixture containing particles of the individual metals.[21] Of particular interest are hazardous combinations that are not exactly predictable from the properties of the constituent metals. (For the purpose of this discussion, magnalium refers specifically to the 50:50 alloy. Other magnalium alloys may be expected to have properties more or less intermediate between this alloy and the major constituent metal.)

With Chlorates and Perchlorates:

It is not expected for there to be a significant deviation from intermediate properties here; namely significantly hazardous with chlorates, less so with perchlorates. (See below for ammonium perchlorate.)

With Acids:

Here again the properties are intermediate. Magnalium is more acid sensitive than aluminum, but less so than magnesium. However, it is still sufficiently acid sensitive so as to preclude its use even with mild acids such as boric acid.[21,26] There are a number of published formulations containing boric acid with magnalium, or even with magnesium. However, such compositions are almost always used with non-aqueous binding, which minimizes the danger. If such formulations are developed for use with aqueous binding, the boric acid content should be deleted in the interest of safety.

With Ammonium Salts:

Magnalium is more reactive than aluminum, but less reactive than magnesium, towards moist ammonium perchlorate.[21] Boric acid does not prevent this reactivity and should not be used, because of magnalium's reaction with acids. In practice the problem can be avoided with the use of non aqueous binding.

With Water:

Magnalium does not usually present any problem with aqueous binding. However, the potential for decomposition exists and it is well to be aware of this possibility when conducting formulation development. Certain substances seem able to trigger the reactivity of magnalium towards water. Examples are lampblack and alkali metal oxalates.[21,27] The reasons are not obvious and do not necessarily depend on any acidic or alkaline reaction. For example, aqueous lithium oxalate has a pH of 7 (neutral), yet is able to trigger such exothermic decomposition.

In general, magnalium is more stable in an alkaline rather than an acidic environment, in contrast with aluminum. Thus, lithium carbonate, with an alkaline reaction, presents no problem with magnalium, although it is incompatible with aluminum.[27]

With Copper Salts:

Copper salts, both copper(I) and copper(II), should be avoided with magnalium unless the counter anion has a basic reaction. Fortunately many of the copper salts used in pyrotechnics, such as the carbonate or benzoate, fall into the latter category and normally present no problem. A danger can arise when conditions allow the production of ammonia, which has the ability to solubilize otherwise poorly soluble copper compounds.[20] Ammonium perchlorate in combination with alkaline materials, such as hexamine, can produce sufficient ammonia to cause a solubilization effect with certain copper salts.[28] Thus, the fourfold combination of ammonium perchlorate, hexamine, copper(II) carbonate, and magnalium is incompatible despite the fact that any of the binary combinations cause no problem.[29] Certain copper compounds, such as copper(II) benzoate, seem to be less problematic for unknown reasons.[29,30]

With Sulfur:

Magnalium does not cause any particular problems with sulfur, and resembles aluminum in this respect.

Exercise for the Reader

As a test, the reader is invited to consider all of the combination hazards associated with the hypothetical blue star formulation in Table 8. Any experimentation with this composition is definitely not advised.

Table 8. Hypothetical Blue Star Formulation.

(Consider what is wrong with this blue star formulation!)	
Ammonium perchlorate	30
Potassium chlorate	30
Sulfur	20
Copper(II) sulfate	10
Zinc	10
(Dampen with water.)	

Closing Remarks

The discussion of some particularly hazardous combinations and the listings in Table 1 should not be interpreted too rigidly. They should serve only as guidelines. Some combinations listed as generally hazardous can be used by knowledgeable and skilled pyrotechnists in certain circumstances with reasonable safety, provided appropriate precautions are taken. Conversely, the list is not all inclusive, with other hazardous combinations existing.

Knowledge of hazardous combinations has been acquired through more than a century of observations by pyrotechnists. The explanations given in this article should be seen as post facto rationalizations rather than as theoretical predictions. Consequently, formulation development should be guided by cautious experimentation. For example, it is not obvious that titanium is compatible with ammonium salts whereas manganese is not, despite the two metals having almost identical electronegativities.

New star compositions containing active metal fuels should be dampened with water (if at all) only as a small sample. Such stars should be checked periodically for the occurrence of an exothermic reaction or other indication of an adverse reaction (e.g., an ammonia or a hydrogen sulfide odor).

Great care must be taken when working with new formulations, especially if there is any known potential for an adverse reaction. It is always appropriate to start working with very small quantities, to store those materials separate from other pyrotechnic materials and in a manner such that an accidental ignition would be less than disastrous.

Only after small batches have been successfully prepared, should larger batches be attempted. It must, however, be recognized that the fact that small batches did not experience adverse reactions, is not a guarantee that problems will not appear when batch sizes are scaled up. Mostly this is because increasing temperature generally has a powerful effect on the rate of chemical reactions. As an example, consider the two experiments with aluminum and water reactions in Table 6. Note that while in the first case at 18 °C the reaction peaked only after 159 hours. However, the same reaction at 43 °C peaked in only 1 hour. When large batches are prepared, any heat produced will generally escape more slowly (i.e., the temperature will rise to higher levels). This in turn accelerates chemical reaction rates and the rate of heat production. Such a thermal run-away may well lead to a catastrophe for a large batch while a small batch may show no signs of a problem.

In the event an adverse reaction is detected, it may be necessary to take more or less immediate safety measures. If the reaction is mild, the amount of material is small and it is in an isolated location, it may be possible to monitor the situation and hopefully wait it out. Actual ignitions of compositions undergoing adverse reactions are not common; nonetheless, disposal is probably the best way to terminate the potential problem.

The only certain way to eliminate a pyrotechnic hazard is to consume the material, generally by burning. While such disposal may constitute unlicensed hazardous waste disposal, it may also be a safety imperative. Great care must be taken when materials under going adverse reactions are handled or moved, such as in preparation for disposal by burning. Consideration must always be given to the possibility that the material may enflame at any time. If the temperature of the composition has risen (as will almost always be the case), combustion of the material will probably be especially violent and could be explosive. When burning pyrotechnic materials, always be extremely careful. Even under the best of conditions unexpectedly large or violent output is possible. Some limited guidance on the subject that may be useful can be found in references 31 and 32. In cases where immediate disposal by burning is not possible and when the amount of material is relatively small, it will generally be possible to limit the buildup of heat in the materials by their immersion in a large amount of water. This will preclude the ignition of the material, but often will not terminate the adverse reactions such as the production of flammable (potentially explosive) hydrogen gas. If such treatment is necessary, as soon as possible the pyrotechnic composition should be separated from the water and disposed of by burning. Obviously, the best course of action is studiously to avoid those potentially hazardous combinations that might lead to adverse chemical reactions!

Acknowledgments

The authors wish to acknowledge the published works of the many pyrotechnists that have shared the information on which this article is based. In addition, the authors wish to acknowledge Arno Hahma, Per Alenfelt, and Bonnie Kosanke for their technical and editorial assistance in preparing this article.

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Bullet Impact Sensitivity Testing of Class B Fireworks and Ingredients and Detonability Testing of Flash Powders

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Introduction

The Treasury Department's Bureau of Alcohol, Tobacco and Firearms (BATF) requested the Bureau of Mines to perform bullet impact sensitivity tests on a selection of class B (display) fireworks shells and some ingredients thereof (flash powder, "stars"), and also to establish that the flash powder used in salute shells is a detonable material, something which is widely presumed but apparently not documented.

The fireworks and ingredients to be tested were procured by BATF from two different domestic suppliers and included a variety of foreign as well as domestic shells, two different flash powder compositions, and two different kinds of "stars."

Suppliers of the shells and ingredients are designated in this report as Manufacturer K and Manufacturer M.

In most cases, there was only one shell of each kind; where more than one shell of the same kind was available, the shell was impacted in two different orientations: through the center of the lateral surface when seated vertically, and through the center of the bottom when lying on its side. In a very few cases there were more than two shells, and in these cases a replicate shot using the shell in one or the other of these orientations was performed. Manufacturer K supplied shells in both the "lifted" and "unlifted" form. "Lifted" refers to the inclusion of a small charge (several grams to a few ounces depending on the size of the shell) of coarse black powder which serves as the propellant charge to eject the shell from the mortar for aerial displays.

Description of Tests/Results

Bullet Impact Tests

The bullet impact sensitivity test used was that implied in Institute of Makers of Explosives (IME) Safety Library Publication No. 3 ("Suggested Code of Regulations for the Manufacture, Transportation, Storage, Sale, Possession and Use of Explosive Materials"): the sample is subjected to the impact of a 150 gr, .30 caliber ball ammunition having a nominal muzzle velocity of 2700 ft per second (i.e., .30-06 M2 ammunition) fired from a distance of 100 ft, with the sample against a 0.5 in. steel backing plate.

The charge stand was made from 8 in. × 8 in. × 24 in. oak lumber; for most of the firings, in addition to the backing plate behind the sample the sample was set on a 6 in. × 6 in. × 0.125 in. mild steel witness plate to serve as additional diagnostic for the violence of the reaction. A sketch of the charge stand is shown in Figure 1.

No instrumentation was used in the bullet impact sensitivity tests except that all firings were recorded by color video camera and tape recorder.

Those samples (i.e., the flash powders and "stars") that were provided in bulk were packed in 3.4 in. in diameter × 3.4 in. high (1 pint) cylindrical pasteboard cartons for the tests. (It may be noted here that manufacturer M's "stars" do

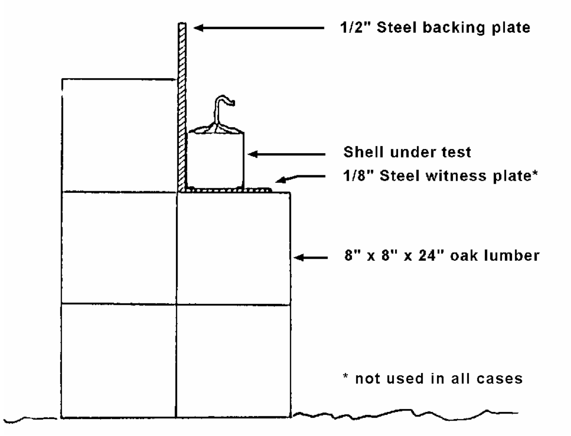

Figure 1. Test setup for bullet impact sensitivity.

not resemble the stars used by any other manufacturer within the authors' experience. They are approximately 1.3 in. outside diameter × 1.3 in. long cylindrical pellets with a 0.3 in. diameter axial hole, and look exactly like the black powder pellets from a cartridge of "pellet powder." They burn very slowly and neither brightly nor colorfully.)

All of the samples without exception were ignited by the impact of the bullet, and most exploded with greater or lesser violence. Detailed results are given in Table 1. (Note: in Table 1 the firing numbers are keyed to the numbering of the firings on the video tape.) Generally speaking, the results were not particularly violent except for the salute shells and flash powder. Table 1 includes a subjective impression of the intensity of the flash and report.

In a few cases, two shells were placed side by side, only one being impacted by the bullet, to determine whether the explosion of the first shell could propagate to its neighbors; in all cases the second shell exploded, but in the case of star shells there was a 1 to 2 s delay: evidently the explosion of the first shell merely lit the fuse of the second; with salute shells however, the explosion of the two shells was, as nearly as can be resolved by the human ear, simultaneous.

Damage to the witness plate, indicating a mode of reaction which either is or approximates detonation was observed only for salute shells, the flash powder ingredient of salute shells, or shells which contained a salute component.

Detonation Rate Determination: Flash Powder

Attempts were made to determine the detonation rate of each of the flash powder compositions supplied by manufacturers K and M. For this purpose a sample of the flash powder was placed in polymethylmethacrylate tube 2.5 in. in outside diameter and 12 in. long, having a wall thickness of 0.25 in., closed at the bottom end with a sheet of the same material 0.25 in. thick cemented to the tube bottom; a Hercules J-2 detonator was inserted through a hole in the center of the bottom plate. The flash powder was loaded to the density obtained by sharply tapping the container several times during filling. This density was approximately 0.8 g/cc. Two methods were used to determine the detonation rate. In one, a continuous rate probe[1] was inserted down the inner wall of the plastic tube. This probe contains an inner core of insulated resistance wire and an outer sheath of thin-wall aluminum tubing crimped to the core at the bottom. As a shock or detonation wave moves up the tubing, the latter crushes through the insulation of the wire—the effect is that one has a slide wire rheostat whose length and electrical resistance are proportional to the distance from the shock/ detonation wave to the upper end. If a constant current is applied between the tubing and the resistance wire, a voltage proportional to this distance is obtained and may be recorded oscillographically.

The other method used was to photograph the detonation with a high-speed framing camera operating at a known framing rate against a background containing distance markers.

Table 1. Results of Bullet Impact Sensitivity Tests.

Firing No.	Mfr.	Shell Type	Impact Model[1]	Shell Burst	Contents Ignited	Report
IA	K	3" Star, lifted	L	Yes	Yes	Mild
1B	K	3" Star, lifted	L	Yes	Yes	Mild
1C	K	3" Star, lifted	B	Yes	Yes	Mild
2A	K	3" Star, unlifted	L	Yes	Yes	Mild
2B	K	3" Star, unlifted	L	Yes	Yes	Mild
2C	K	3" Star, unlifted	L	Yes	Yes	Mild
3A	K	6" Star (yellow & green) lifted	L	Yes	Yes	Mild
3B	K	6" Star, red, lifted	L	Yes	Yes	Mild
3C	K	6" Star, variegated, lifted	B	Yes	Yes	Mild
4A	K	6" Star, unlifted	L	Yes	Yes	Mild
4B	K	6" Star, unlifted	L	Yes	Yes	Mild
4C	K	6" Star, unlifted	B	Yes	Yes	Mild
5A	K	Japanese 3" star, lifted	L	Yes	Yes	Mild
5B	K	Japanese 3" star, lifted	L	Yes	Yes	Mild
5C	K	Japanese 3" star, lifted	B	Yes	Yes	Mild
6A	K	Japanese 6" star, lifted	L	Yes	Yes	Violent
6B	K	Two Japanese 6" star, lifted	L[4]	Yes	Yes	Violent
7A	K	Chinese 3" star, lifted	L	Yes	Yes	Mild
7B	K	Chinese 3" star, lifted	L	Yes	Yes	Mild
7C	K	Chinese 3" star, lifted	B	Yes	Yes	Moderate
8A	K	Chinese 6" star, lifted	L	Yes	Yes	Mild
8B	K	Two Chinese 6" star, lifted	L[4]	Yes	Yes	Moderate
9A	K	3" Flash salute, lifted	L	Yes	Yes	Very loud
9B	K	Two 3" Flash salute, lifted	L[4]	Yes	Yes	Very loud
10A	K	3" Flash salute, unlifted	L	Yes	Yes	Very loud
10B	K	Two 3" Flash salute, unlifted	L[4]	Yes	Yes	Very loud
11A	K	(Cut stars)[5]	L	No	Yes	None
11B	K	(Cut stars)[4]	L	Yes	Yes	Loud
12A	K	(Flash powder)[5]	L	Yes	Yes	Violent
12B	K	(Flash powder)[5]	L	Yes	Yes	Violent
14	M	6" “R.W.S. Tit.”	L	Yes	Yes	Violent
15	M	6" Color change red-to-green	L	Yes	Yes	Loud
16	M	6" No markings	L	Yes	Yes	Mild
17	M	Taiwan 6" “Red-blue to Flash Chrysanthemum”	L	Yes	Yes	Loud
18A	M	5" “Wizzer”	L	Yes	Yes	Moderate
18B	M	5" “Wizzer”	B	Yes	Yes	Moderate
19	M	5" “#508 Red-to-Glittering Silver peony”	L	Yes	Yes	Very loud

NOTES:

1 L - lateral impact; B - bottom impact (shell lying on side)
2 witness plate not used
3 no visible stars produced
4 shells side by side, only one impacted by bullet
5 in 3.4 in.×3.4 in. cylindrical carton

Table 1. Results of Bullet Impact Sensitivity Tests (continued from opposite page).

Firing No.	Mfr.	Stars Thrown	Charge Stand Destroyed	Indentation of Witness Plate	Comments
IA	K	20'	No	—[2]	
1B	K	20'	No	—[2]	
1C	K	20'	No	—[2]	
2A	K	20'	No	—[2]	
2B	K	50'	No	—[2]	
2C	K	20'	No	—[2]	
3A	K	50'	No	—[2]	Brighter flash than firings 1 or 2
3B	K	75'	No	—[2]	Brighter flash than firings 1 or 2
3C	K	100'	No	—[2]	Brighter flash than firings 1 or 2
4A	K	50'	No	—[2]	Brighter flash than firings 1 or 2
4B	K	50'	No	—[2]	Brighter flash than firings 1 or 2
4C	K	20'	No	—[2]	
5A	K	35'	No	—[2]	
5B	K	35'	No	—[2]	
5C	K	100'	No	—[2]	
6A	K	[3]	Yes	None	No flash seen
6B	K	>100'	Yes	None	Second shell exploded after delay of 1 sec.
7A	K	20'	No	None	
7B	K	50'	No	None	Brighter flash than 7A
7C	K	40'	No	None	
8A	K	30'	No	None	Stars burned more slowly than previous shots
8B	K	50'	No	None	Brighter flash than most previous shots, 2nd shell delayed 2 sec. before exploding
9A	K	[3]	Yes	0.5"	
9B	K	[3]	Yes	0.75"	Both shells fired nearly simultaneously
10A	K	[3]	Yes	0.25"	
10B	K	[3]	Yes	0.75"	Both fired nearly simultaneously
11A	K	[3]	No	No	Top of container popped off, stars and container burned quietly
11B	K	100'	No	0.4"	
12A	K	[3]	Yes	1.25"	Bright flash
12B	K	[3]	Yes	1.0"	Bright flash
14	M	[3]	Yes	—[2]	Little flash
15	M	30'	No	None	Two small secondary reports
16	M	20'	No	None	Two small secondary reports
17	M	>100'	No	None	
18A	M	[3]	No	None	
18B	M	[3]	No	None	
19	M	>100'	No	None	

Table 1. Results of Bullet Impact Sensitivity Tests (continued).

Firing No.	Mfr.	Shell Type	Impact Model[1]	Shell Burst	Contents Ignited	Report
20	M	4" Red star	L	Yes	Yes	Moderate
21	M	4" Italian star	L	Yes	Yes	Moderate
22	M	4" #725A-2 Gold rippling Chrysanthemum with rising gold tail	L	Yes	Yes	Moderate
23A	M	3" (no markings-probably a salute)	L	Yes	Yes	Very loud
23B	M	3" (no markings-probably a salute)	B	Yes	Yes	Very loud
24	M	3" red-dot	L	Yes	Yes	Mild
25	M	3" "R & R"	L	Yes	Yes	Mild
26A	M	Flash Powder[5]	L	Yes	Yes	Violent
26B	M	Flash Powder[5]	B	Yes	Yes	Violent
27A	M	"stars" (see text)[5]	L	No	Yes	None
28A	M	"stars" (see text)[5]	B	No	Yes	None

NOTES: 1 L - lateral impact; B - bottom impact (shell lying on side)
2 witness plate not used
3 no visible stars produced
4 shells side by side, only one impacted by bullet
5 in 3.4 in.×3.4 in. cylindrical carton

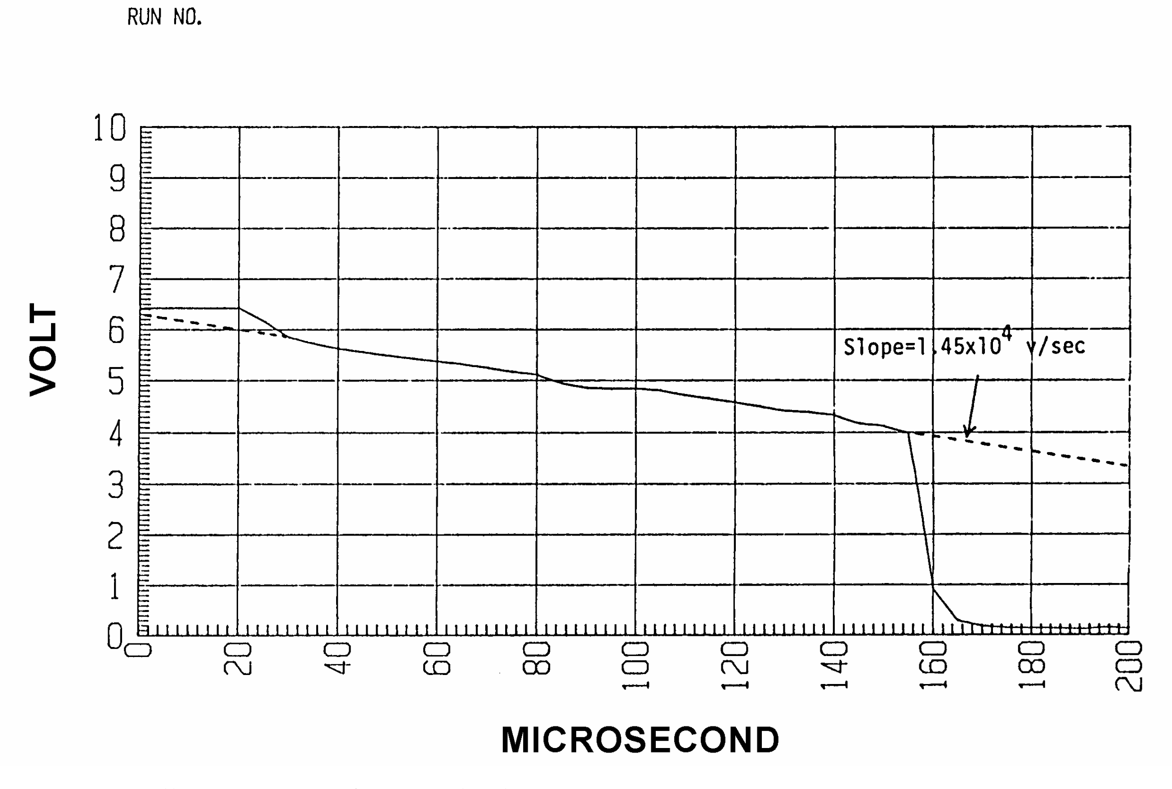

Figure 2. Oscilloscope trace of time and voltage.

Table 1. Results of Bullet Impact Sensitivity Tests (continued from opposite page).

Firing No.	Mfr.	Stars Thrown	Charge Stand Destroyed	Indentation of Witness Plate	Comments
20	M	30'	No	None	
21	M	30'	No	None	
22	M	[3]	No	No	
23A	M	[3]	Partly	0.4"	
23B	M	[3]	Partly	0.5"	
24	M	20'	No	None	
25	M	20'	No	None	
26A	M	[3]	Yes	1.8"	
26B	M	[3]	Yes	1.0"	Even backing plate was slightly bent
27A	M	[3]	No	None	some "stars" ignited and burned slowly with weak orange flame; some remained unburned
28A	M	[3]	No	None	as 27A

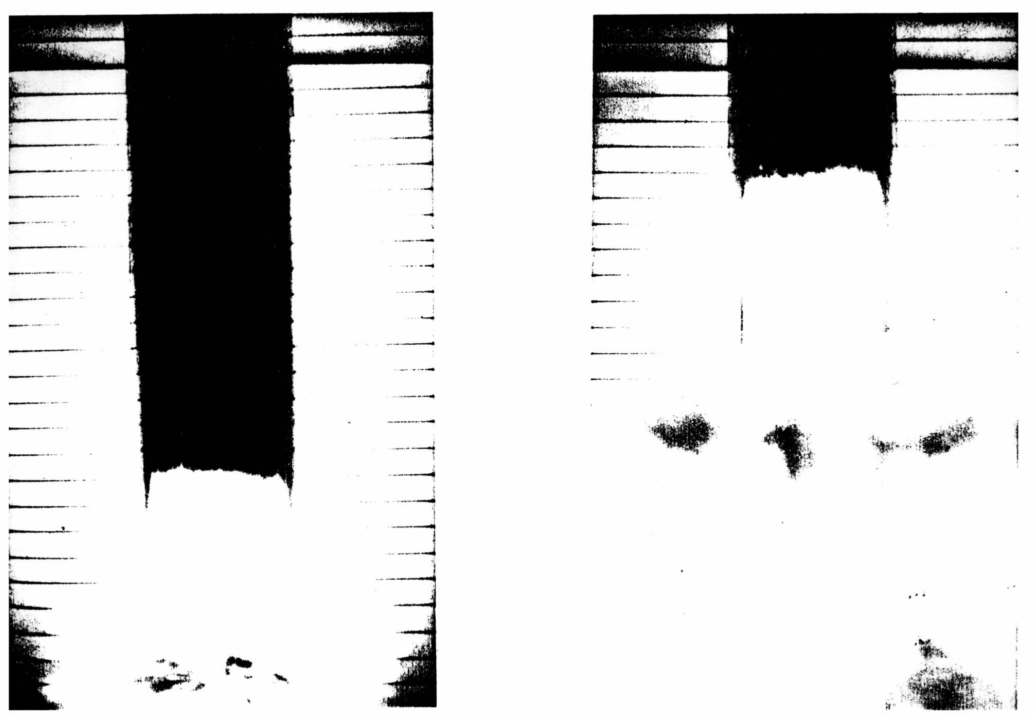

Figure 3. Selected frames from a high-speed framing camera sequence of manufacturer K's flash powder; background lines are 1 cm apart; frames shown are 90 microseconds apart. [Best available photo reproduction.]

The first method was tried using manufacturer K's flash powder. For reasons not exactly known in this test the rate probe short-circuited at its upper end 155 µs after the detonator fired. This may have been caused by high-velocity fragments or a shock wave in the plastic tube. In any case, before the probe ceased functioning, it recorded a relatively stable rate of ca 800 m/s. This trace is shown in Figure 2. To obtain the rate, the slope of the voltage/time trace must be

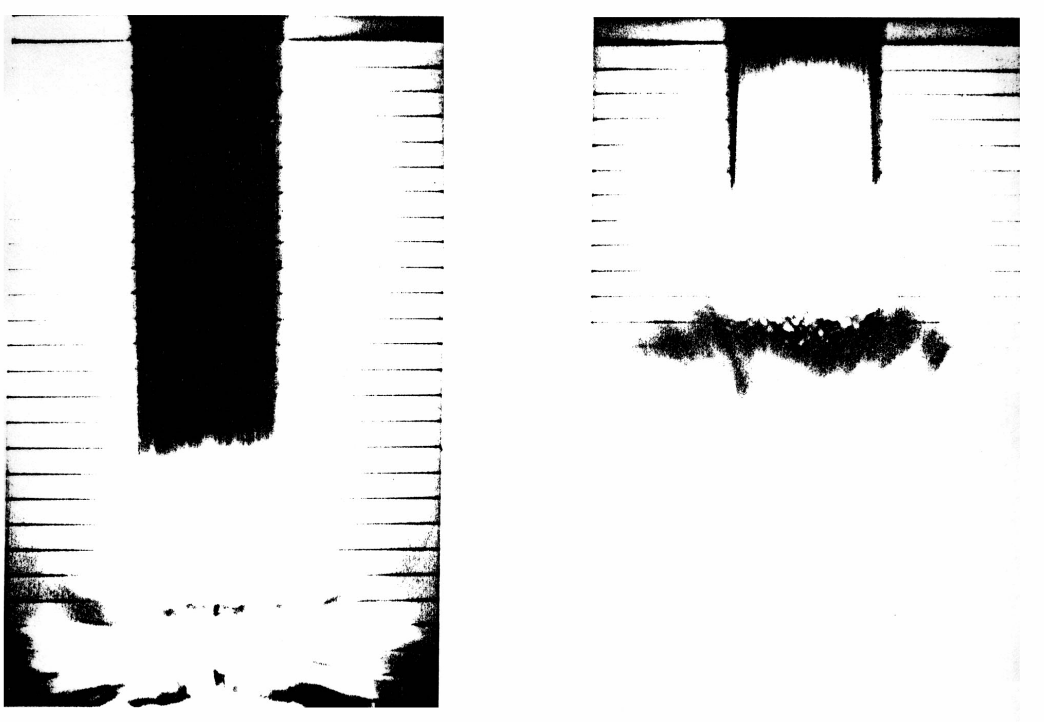

Figure 4. Selected frames from a high-speed framing camera sequence of manufacturer M's flash powder; background lines are 1 cm apart; frames shown are 70 microseconds apart. [Best available photo reproduction.]

divided by the product of the wire resistance/unit length (2.98 Ω/cm) and the applied current (0.06 milliamperes). The rate obtained is rather low for a detonation, even in a low-density powder, but results with the framing camera show definite evidence of a detonation.

Results obtained using the rotating-mirror framing camera are illustrated in Figures 3 and 4 for manufacturer K's and manufacturer M's flash powder, respectively. In both cases the flash powder was contained in an acrylic plastic tube of 2.5 in. outside diameter with 0.25 in. wall thickness and 12 in. long. Initiation was by a Hercules J-2 detonator. (Often such framing camera studies use an explosive booster for initiation, but the object here was to determine how detonation built up from a "weak" stimulus; it was not practical however to use a very weak stimulus such as an electric matchhead because the synchronization of the framing camera requires an initiator with a time "jitter" of only a few microseconds.) Based on the rate observed with the rate probe, the camera was run at a relatively slow speed of 10 µs/frame. Even at this low speed the light from the flash powder was found to be so persistent that in the first firing the film was washed out by exposures on successive revolutions of the mirror so that the use of a high-speed capping shutter was necessary.

Sample densities were those obtained by sharply tapping the plastic tube a few times after loading until no further perceptible settling occurred, and were 0.85 and 0.91 for manufacturer K's and manufacturer M's flash powder, respectively.

The frames shown in Figures 3 and 4 are 90 and 70 µs apart, respectively, giving a rate of 1.3 and 1.6 km/s, respectively, notably higher than the rate obtained with the rate probe using manufacturer K's flash powder. The most interesting thing about these pictures is that most of the frames (except for the earliest frames from the sequence using manufacturer M's flash powder) show a long zone of intense luminosity well in advance of any significant expansion of the tube walls, i.e., the development of high

Figure 5. Lead-block compressions obtained in D.O.T. cap sensitivity tests for (a) Manufacturer K's flash powder, (b) Manufacturer M's flash powder. [Best available photo reproduction.]

pressure lags far behind the development of luminosity, though this may not be too surprising in a material most of whose reaction products are expected to be nongaseous.

Department of Transportation (DOT) Cap Sensitivity Test

Following discussion of the results above with BATF and DOT personnel, it was decided to attempt to determine whether these flash powders were cap sensitive according to DOT specifications [Title 49 *Code of Federal Regulations* Part 173.53(c)]. Sufficient sample (703 g) remained of manufacturer K's flash powder to nearly fill the standard 3.38 in. diameter by 6.38 in. cylindrical fiberboard container used in this test. However, very little sample (216 g) remained of manufacturer M's powder and a much smaller container, viz., 2.0 in. diameter by 5.0 in. high, was used for this sample. The samples were set on a 4 in. long by 2 in. diameter lead block and primed with a No. 8 electric detonator and fired.

In both cases a compression of the lead block considerably in excess of the criterion value of 0.125 in. was obtained, viz., 0.450 in. and 0.586 in for manufacturer K's and manufacturer M's flash powder, respectively. Thus both are class A explosives according to DOT standards.

The mushrooming of the lead blocks is shown in Figure 5.

Summary

The Bureau of Mines was requested by the Treasury Departments' Bureau of Alcohol, Tobacco and Firearms (BATF) to conduct bullet impact sensitivity testing of a sampling of Class B (display) fireworks, and some ingredients thereof, and also to demonstrate that the flash powder used in salute shells is detonable, and to determine its detonation rate. All of the fireworks shells and ingredients were ignited/initiated by the impact of a bullet, though the violence of the resulting reaction varied greatly, from gentle burning to a violence which seemed characteristic of detonation. Both types of flash powder detonated, though at a very slow rate, and both exhibited cap sensitivity in the Department of Transportation cap sensitivity test.

Acknowledgment

The Bureau wishes to acknowledge the financial support and technical contributions of the Bureau of Alcohol, Tobacco, and Firearms towards successful completion of this program.

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Guide for Authors

Style Guide

The *Journal of Pyrotechnics* has adopted the *ACS Style Guide*. It is not necessary that authors have a copy; however, a copy can be purchased from the American Chemical Society, Distribution Office, Dept. 225, 1155 16th Street, NW, Washington, DC 20036, USA.

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General Writing Style

- The first time a symbol is used, it is preferred to write it out in full to define it [e.g., heat of reaction (ΔH_r) or potassium nitrate (KNO_3)].
- Avoid slang, jargon, and contractions.
- Use the active voice whenever possible.
- The use of third person is preferred; however, first person is acceptable where it helps keep the meaning clear.

Format

In addition to the authors' names, please include an affiliation for each author and an address for at least the first author.

A short abstract appears at the start of the article. (An abstract is a brief summary of the article, not a listing of areas to be addressed.)

Include 3 to 7 keywords to be used in a reference database: However, multi-word names and phrases constitute only one keyword (e.g., potassium nitrate and heat of reaction).

Use of SI units is preferred. If English units are used, please provide conversions to SI units.

Figures, Photos, and Tables are numbered consecutively. For submission, place them at the end of the text or as separate files. During page composition, they will be inserted into the text as appropriate. For graphs, please also submit "raw" X–Y data.

References cited in the text will be referred to by number (i.e., "Smith[1] states"; or "the research[2,3] shows ...") In the reference section, they will be ordered by usage and not alphabetically. It is preferred that a full citation, including author, title, book or journal, publisher for books, and volume and pages for journals, etc. be provided. Examples:

1) A.E. Smith, *Pyrotechnic Book of Chemistry*, XYZ Publishers (1993) [p nn optional].
2) A.E. Smith, R.R. Jones, "An Important Pyrotechnic Article," *Pyrotechnic Periodical*, Vol. 22, No. 3 (1994) [p n–n optional].

Editing

The *Journal of Pyrotechnics* is a refereed journal. However, the editing style is friendly, and the author makes the final decision regarding what editing suggestions are accepted.

More Information

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Events Calendar

Pyrotechnics

4th International Symposium on Special Topics in Chemical Propulsion

May 27 – 31, 1996, Stockholm, Sweden
Contact: Prof. Kenneth K. Kuo, Symp. Chair
140 Research Bldg. E, Bigler Road
Pennsylvania State University
University Park, PA 16802 USA
Phone: 814-863-6270
FAX: 814-863-3203
email: kkkper@engr.psu.edu

27th International Conf. of Inst. Chem. Tech.

June 25 – 28, 1996, Karlsruhe, Germany
Contact: Fraunhofer - Inst. für Chem. Tech.
P.O. Box 1240
D-76318 Pfinztal (Berghausen)
Germany
Phone: +49-721-4640-121
FAX: +49-721-4640-111

22nd International Pyrotechnics Seminar

July 15 – 19, 1996, Ft. Collins, Colorado, USA
Contact: IIT Research Institute
10 W. 35th Street
Chicago, IL 60616 USA
Phone: 312-567-4280
FAX: 312-567-4543

26th International Symp. on Combustion

July 28 – August 6, Naples, Italy
Contact: The Combustion Institute
5001 Baum Boulevard, Suite 635
Pittsburgh, PA 15213 USA
Phone: 412-687-1366
FAX: 412-687-0340
email: combust@telerama.lm.com

International Autumn Seminar on Propellants, Explosives and Pyrotechnics

October 7 – 10 1996, Beijing, China
Contact: Prof. Changgen Feng
Mechanics and Engineering Dept.
Beijing Institute of Technology
P.O. Box 327, Beijing 100081, China
Phone: +841-6688 ext. 2941 or 2764
FAX: +841-2889

23rd International Pyrotechnics Seminar

September 30 – October 4, 1997, Tsukuba, Japan
Contact: Prof. Tadao Yoshida
College of Engineering of Hosei University
3 – 7 – 2 Kajino–cho, Koganei–shi
Tokyo 184 Japan
Phone: +81-423-87-6132
FAX: +81-423-87-6381

Fireworks

Western Winter Blast

February 16 – 18, Lake Havasu, Arizona USA
Contact: Western Pyrotechnic Association
2230 Aralia Street
Newport Beach, CA 92660 USA
Phone/FAX: none listed

Benson & Hedges International Fireworks Competition in Montreal, Canada – 1996

Dates and Competitors:

June 15	Marutamaya Ogatsu, Japan
June 20	Sunny International, China
June 23	Pirotecnica Soldi, Italy
June 27	Kimbolton Fireworks, England
June 30	Weco Pyrotechniche Fab., Germany
July 4	Pirotechia Igual, Spain
July 7	Foti's International, Australia
July 11	Performance Pyro. Assoc., USA
July 14	Ampleman, Canada
July 18	Closing by Panzera of Spain

Contact: AMARC
Île Notre-Dame
Montreal, Quebec H3C 1A9 Canada
Phone: 514-872-6241
FAX: 514-872-8711

Symphony of Fire – Fireworks Displays

Toronto, Canada 1996 Schedule:

June 15	Concept Fiatlux, Canada
June 22	Ricardo Caballer, Spain
June 26	Martarello Fuochi, Italy
June 29	Maurel Pyrotechnie, France
July 3	Meijing Zhong Fa, China
July 6	Closing and Awards

(Continued on next page.)

Vancouver, Canada 1996 Schedule:

July 21	Pirotecnia Minhota, Portugal
July 31	Ricardo Caballer, Spain
August 3	Concept Fiatlux, Canada
August 7	Closing and Awards Show

Contact: Frank Furtado
3054 Lacombe
Montreal, Quebec H3T 1L4 Canada
Phone: 514-866-3335
FAX: 514-398-9287

Summer Fireworks Festival

July 15 – 19, 1996, Auburn, New York USA
Contact: Charles Hill
4533 Foster Valley Road
Endicott, NY 13760
Phone: 607-748-0667
FAX: 607-748-0899

Pyrotechnics Guild International Conv.

August 11 – 16, 1996, Muskegon, Michigan USA
Contact: Ed Vanasek, Secretary-Treasurer
18021 Baseline Avenue
Jordan, MN 55352 USA
Phone: 612-492-2061

3rd International Symposium on Fireworks

September 16 – 20, 1996, Walt Disney World, Lake Buena Vista, Florida, USA
Contact: Ettore Contestabile, Canadian Explosives Research Laboratory, CANMET
555 Booth Street
Ottawa, Ontario K1A 0G1 Canada
Phone: 613-995-1363
FAX: 613-995-1230

Florida Fall Fireworks Festival

November 1 – 3, 1996 site undetermined, but will be in Florida, USA
Contact: John Driver, Treasurer FPAG
2382 NW 30th Road
Boca Raton, FL 33431 USA
Phone: 407-483-7737
FAX: 407-483-4198
e-mail: 70233.1654@Compuserve.com

High Power Rocketry

LDRS

July 4 – 7, 1996; Orangeburg, So. Carolina USA
Contact: Jim Conn
Phone: 803-831-0979

Model Rocketry

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August 2 – 10, 1996, Evansville, Indiana USA
Contact: Chad Ring, Contest Director
RR 1 Box 7
Holland, IN 47541 USA
Phone: 812-536-5291

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