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# Journal of Pyrotechnics

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# Copper in Pyrotechnics

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**Abstract:** *Copper compounds play a key role in the development of “greener” pyrotechnics by substitution of noxious barium compounds from green colored effects. The application of many copper(II) compounds in pyrotechnics is limited because of their noble and often hygroscopic character. We have investigated nitratocuprates(II) as well as basic copper(II) nitrate as potential combined oxidizers and (green) coloring agents. A formulation based on ammonium nitratocuprate(II) nitrate and boron has promising properties for civilian fireworks. Copper-based high-nitrogen compounds show good flame colors as pure compounds. However, the implementation of ready-for-use pyrotechnics from these substances proved to be much more challenging. A promising candidate for civil pyrotechnic applications would be a mixture based on copper(II) nitrate pentahemihydrate and 5-aminotetrazole.*

**Keywords:** *cuprates, pyrotechnics, fireworks, green color, pollution*

## Introduction

Fireworks are no longer the only application of pyrotechnics, since the number of civilian and military applications of pyrotechnics is constantly increasing. Pyrotechnics are used in technological fields such as matches, fire extinguishers, airbags, propellants, all kinds of flares, military counter-measures (acoustic and optical decoy devices), delusion devices and igniters.

In contrast to explosives, pyrotechnics are traditionally mixtures of several compounds. The characteristics of pyrotechnics are consequently dependent on the ingredients and their formulation, which is often determined just by trial and error. Most pyrotechnic reactions are solid–solid state reactions, and the vast number of chemical reactions taking place are not always understood. The basic parts of any pyrotechnic device are the oxidizer and the reductant (fuel). The most common oxidizers are nitrates and perchlorates of alkali and alkaline earth metals. A variety of metals, metalloids or non-metals can be used as a fuel: magnesium, aluminium, magnalium alloy (Mg–Al 50 : 50), titanium, iron, silicon, charcoal, boron, sulfur and many more including

organic compounds and natural products. A binder is usually used to inhibit segregation of the homogeneous, fine-grained mixtures. Coloring agents are used in fireworks and flares.

Colors in pyrotechnics are obtained by the addition of substances with the desired flame color. A yellow flame color is achieved by the addition of sodium compounds, usually cryolite ( $\text{Na}_3\text{AlF}_6$ ) or sodium oxalate. The main light-emitting species is atomic sodium. Compounds such as sodium nitrate or sodium chloride are less often used due to their hygroscopic character. In general, compounds used in pyrotechnics should not be hygroscopic nor contain water of crystallization, because water might inhibit the desired reactions or initiate hazardous reactions. Emission of red light is achieved by the addition of strontium nitrate, which simultaneously acts as oxidizer and coloring agent. The same is true for barium nitrate, which is added for green colors. The main emitting species are the monochlorides,  $\text{SrCl}$  and  $\text{BaCl}$ , and the monohydroxides,  $\text{SrOH}$  and  $\text{BaOH}$ , respectively. Since the above-mentioned chlorides are characterized by a high volatility and satisfactory color emission, such pyrotechnic

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compositions need a chlorine donor: usually perchlorates, PVC powder or other organic or inorganic chlorides. The blue color in pyrotechnics is caused by a copper–chlorine species. There has been a controversy in the literature about the emitting species:  $\text{Cu}_3\text{Cl}_3$ , as suggested in ref. 1 or, more likely,  $\text{CuCl}$ .<sup>2</sup> Copper-based coloring agents include metallic copper, copper(I) chloride, basic copper(II) carbonate (azurite and malachite, respectively), copper(II) oxide and copper(II) sulfide. Basic copper(II) nitrate,  $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ , is known as an additive for gas generating compositions with metal complexes of nitrogen-rich ligands: see the patents in ref. 3–6. However, because of its positive oxygen balance, we investigated its properties as a pyrotechnic oxidizer and colorant. Basic copper(II) nitrate contains both copper and hydroxide which might help form the green light-emitting species  $\text{CuOH}$ .

Copper compounds sometimes show problematic features that complicate their application in pyrotechnics. In this study, we discuss these features and present an outline of some of the many aspects of copper compounds in pyrotechnics and their role in the recent efforts toward environmentally benign compositions.

## Environmental aspects

In several environmental analytical studies as well as medical studies, pyrotechnic applications and fireworks have been identified as potential sources of environmental pollution.<sup>7</sup> Increasingly rigorous environmental legislation in the industrialized world thus puts pyrotechnicians and the producers of fireworks under pressure to develop alternatives. The environmental legislation may be regarded as exaggerated; however, environmental concerns should be taken seriously and explain recent efforts toward the development of “green” pyrotechnics. Any improvement in this respect will definitely be appreciated by both pyrotechnicians and environmentalists.

The main (potential) pollutants in pyrotechnics are heavy metals (especially barium from green-colored fireworks), perchlorate (which is teratogenic and disturbs the iodine metabolism in the thyroid gland), polychlorinated dibenzo-*p*-dioxines (PCDD) and dibenzofurans (PCDF), gaseous pollutants (mainly the oxides of sulfur,

nitrogen and carbon;  $\text{SO}_x$ ,  $\text{NO}_x$  and  $\text{CO}$ ), smoke and particulate matter.<sup>7</sup>

Combustion of organic matter in the presence of chlorine always leads to the formation of traces of toxic and teratogenic PCDD and PCDF. Therefore, pyrotechnics are potential sources of both poisons as well.<sup>8,9</sup> Interestingly, copper plays a key role in the formation and decomposition of these organohalogen compounds.<sup>10</sup> From this point of view, blue-colored pyrotechnics have been the principal object of investigation in previous environmental studies, since they combine all three factors – organic materials (e.g., the binder), chlorine and copper compounds. In the literature, there is controversy about the significance of pyrotechnics as sources of PCDD/F: Fleischer et al.<sup>8</sup> conclude that fireworks contribute only marginally to the total output of PCDD/F and can hence be regarded as harmless in this respect (complete absence of the most toxic 2,3,7,8-TCDD), whereas Dyke and Coleman<sup>9</sup> found a fourfold increase of PCDD/F concentration in ambient air in the course of a night of fireworks and bonfires and believe that fireworks could be a “significant source of dioxins”. Fireworks may not contribute to the total PCDD/F output like an industrial waste incinerator; however, the teratogenic character of these substances should be reason enough to not neglect these concerns.

In a study from India, Kulshrestha et al.<sup>11</sup> found the barium concentrations in street dust increased by a factor of 1000 immediately after the Diwali festival (the Indian Festival of Lights, which is traditionally accompanied by firecrackers and fireworks), compared to the average value. More than fireworks up in the sky, hand-held flares or indoor fireworks exhibit a severe health-risk for persons standing in the heavy-metal-rich smoke cloud of a green pyrotechnic device. Inhalation of significant amounts of barium aerosols has cardiotoxic and bronchoconstrictor effects.

The development and implementation of barium-free pyrotechnics is a major challenge for chemists and a field of recent research. Chavez et al.<sup>12</sup> tested green pyrotechnic compositions based on boric acid for application in indoor fireworks. However, they admit that the flame color is of lower quality than in traditional pyrotechnics or barium-containing high-nitrogen compounds. Apart from barium and

boric esters, the only elements with a noteworthy green flame color are thallium (one of the most toxic heavy metals) and copper. Of these elements, copper is the least toxic. Occasionally, copper powder or copper compounds like malachite or azurite are added in minor concentrations to green-colored, barium nitrate-based fireworks. Even though many copper compounds are somewhat noxious, their implementation as a substitute for barium compounds can be regarded as an environmental improvement.

## Copper-based oxidizers

According to Jennings-White and Kosanke,<sup>13</sup> the  $\text{Cu}^{2+}$  ion is incompatible with magnesium, zinc and aluminium in pyrotechnics, especially in a moist environment. This is the reason why the readily available copper nitrate hydrates  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  cannot be used in pyrotechnics as oxidizers. Indeed we observed a violent reaction including the emission of brown nitrogen dioxide ( $\text{NO}_2$ ) gas or even self-ignition when grinding  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  and magnesium powder in a mortar. The anhydrous covalent copper(II) nitrate, however, is extremely hygroscopic and requires a time consuming synthesis, which makes it unacceptable in pyrotechnics. At the same time, copper(II) compounds do cause problems in pyrotechnics because of their noble character (standard electrode potential for  $\text{Cu}^{2+}_{\text{aq}} + 2\text{e}^- \rightarrow \text{Cu}_\text{s}$ :  $E^0 = +0.34 \text{ V}$ ), e.g. when applied as a coloring agent or as a high-nitrogen fuel copper salt in combination with metal fuels. Thus  $\text{Cu}^{2+}$  ions act as oxidizers – so why not make use of this trait? The application of water-free, copper(II) oxidizers could be an interesting alternative in the development of green and “green” pyrotechnics.

Tetranitratocuprates(II),  $[\text{Cu}(\text{NO}_3)_4]^{2-}$ , have recently been described as suitable pyrotechnic oxidizers.<sup>14</sup> In this patent, the use of cobalt(III)hexaammine nitratocuprate(II),  $[\text{Co}(\text{NH}_3)_6]_2[\text{Cu}(\text{NO}_3)_4]_3$ , as the oxidizer for the inflation of airbags is described. We investigated the applicability of nitratocuprates as both oxidizer and coloring agent for green-colored

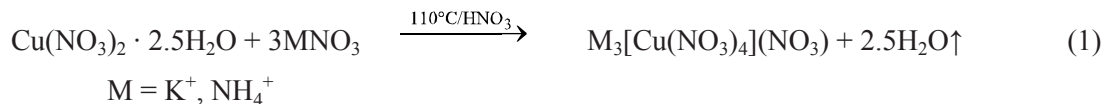
pyrotechnics.

The first structurally fully characterized nitratocuprate(II) was the nitrosylium compound,  $\text{NO}[\text{Cu}(\text{NO}_3)_3]$ , previously misinterpreted as the dinitrogen tetraoxide adduct of copper(II) nitrate. Crystal structure analysis confirmed the absence of molecular  $\text{N}_2\text{O}_4$ .<sup>15,16</sup> In this anion, the  $\text{Cu}^{2+}$  ions are coordinated by six nitrate ions, where each bridging  $\text{NO}_3^-$  ligand links two copper atoms in an octahedral environment. Later, several tetranitratocuprates were structurally characterized.<sup>17</sup> Some nitratocuprate compounds cocrystallize with one additional metal nitrate moiety, following the general formula  $\text{M}_3[\text{Cu}(\text{NO}_3)_4](\text{NO}_3)$ , where  $\text{M} = \text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ . The  $\text{M} : \text{Cu}$  ratio is thus 3 : 1.

## Experimental

Two nitratocuprates(II) were investigated in the course of this study: the potassium salt ( $\text{K}_3[\text{Cu}(\text{NO}_3)_4](\text{NO}_3)$ , KNC) and the corresponding ammonium salt ( $(\text{NH}_4)_3[\text{Cu}(\text{NO}_3)_4](\text{NO}_3)$ , ANC). In a previous study, single crystals of both compounds were obtained from the salt melts at elevated temperatures with a large excess of potassium nitrate and ammonium nitrate, respectively.<sup>18</sup> Since this preparation was not practicable for large scale syntheses, we developed an improved synthesis using stoichiometric amounts of  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  and the corresponding potassium or ammonium nitrate as solutions in a minimum of concentrated nitric acid ( $\text{HNO}_3$ , 65%). The excess of nitrate ions inhibits hydrolysis of the  $[\text{Cu}(\text{NO}_3)_4]^{2-}$  complex, following the principle of Le Chatelier. From this solution, water and nitric acid have been evaporated at  $110^\circ\text{C}$  in an oil bath, residual moisture has been removed by heating under high vacuum for 6 hours. A pure product with a yield of 100% was obtained in this simple and straightforward synthesis [see equation (1)].

The resulting product is slightly hygroscopic, but when handled quickly in ambient air, no significant hydrolysis takes place. However, the salts should be stored in air-tight containers and,





when applied in a pyrotechnic mixture, covered with a non-water-based binder as soon as possible. We mixed pyrotechnic formulations by grinding the constituents in a mortar in the glove box.

Characterization of ANC (as the more promising compound) was performed by single crystal X-ray diffraction via the identification of the crystallographic cell:<sup>18</sup> monoclinic, space group  $P21/c$ ,  $a = 8.271(3)$ ,  $b = 14.658(4)$ ,  $c = 12.105(3)$  Å,  $\beta = 90.92(3)^\circ$ ,  $V = 1467.4(8)$  Å<sup>3</sup>; IR (diamond-ATR, cm<sup>-1</sup>): 3240 (vs), 3071 (sh), 1468 (sh), 1399 (s), 1300 (sh), 1271 (s), 1022 (m), 828 (w), 802 (w), 753 (w); Raman (25 °C, green and blue laser, cm<sup>-1</sup>, relative intensities given in percent): 1493 (11), 1427 (8), 1337 (5), 1051 (84), 1041 (100), 765 (15), 720 (14), 294 (14), 230 (13); melting point 144 °C (first changes in the crystal morphology), 151–152 °C (true mp). Determination of the melting point was found to be the most practicable way of determining the purity of the water-free product.

## Pyrotechnic performance

KNC and ANC were tested in pyrotechnic mixtures with several fuels, additives and vinyl alcohol acetate resin (VAAR) as a binder. The performance was compared to the barium nitrate-based US Army green flare composition # 125A1: 50% BaNO<sub>3</sub>, 30% Mg; 15% PVC; 5% VAAR (mass percent). The performance has been evaluated with respect to the following categories:

- color emission (subjective impression)

- smoke generation
- morphology and amount of solid residues
- thermal stability
- moisture sensitivity
- toxicity of the constituents or reaction products.

## Results

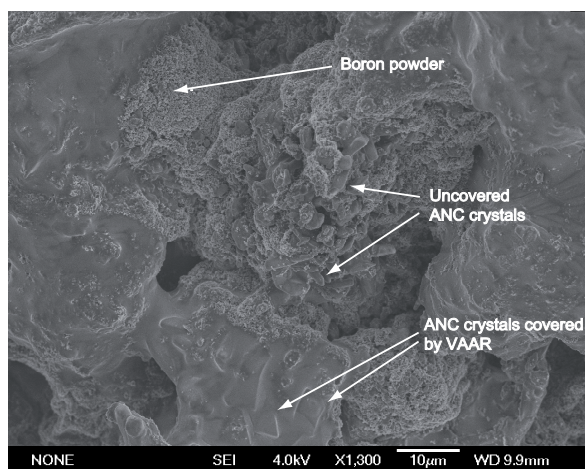
The emission of green light is much more intense with ANC-based mixtures than with KNC mixtures. The latter obviously lack a sufficient amount of hydrogen to form CuOH, which is the emitting species for the green copper spectrum. ANC mixtures show variable performance, depending on the fuel (see Table 1). Some compositions are very promising for applications in civilian fireworks.

Mixtures of ANC with magnesium and boron powder show the best color performance. Both are even greener than the conventional barium nitrate-based composition (subjective impression when using comparable amounts). Magnesium-fueled compositions (“GST63”: 27.3% Mg; 64.5% ANC; 8.2% VAAR), however, offer two major drawbacks – **CAUTION!** – the lack of sufficient thermal stability (self-ignition at 50 °C) and a high moisture sensitivity, which causes self-ignition upon storing the pyrotechnic star in moist air or after contact with water. The water-mediated exothermic redox-reaction with magnesium, as described above, is the reason for this undesired

**Table 1.** General summary of ANC-based pyrotechnic compositions, in comparison to the conventional, barium nitrate-based formulation 125A1.

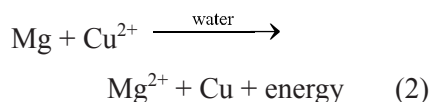
ANC + ...	Color emission	Smokeless combustion	Amount of solid residues	Thermal stability	Moisture stability	Environmental compatibility
... Mg	+++	+	+	---	---	++
... Al	--	+	+	n.d.	n.d.	++
... B	+++	+++	+++	-	++	+
... Ti	--	+	+	n.d.	n.d.	++
... Si	---	+++	+++	n.d.	n.d.	++
... magalium	-	+	+	n.d.	n.d.	++
125A1	++	--	--	+++	+++	---

Key to symbols: +++ outstanding (or large amount of solid residue); ++ good; + fair; - poor; -- bad; --- unacceptable (or very little solid residue); n.d. not determined.



**Figure 1.** SEM image of GST90, a boron and ANC-based pyrotechnic formulation.

self-ignition [equation (2)]. This observation is in good agreement with the warnings of Jennings-White and Kosanke.<sup>13</sup>



However, compositions based on the use of ANC and boron powder (“GST90”: 73.7% ANC; 13.1% boron powder, 325 mesh; 11.3% VAAR; 1% urea; 1% quartz powder), are characterized by a much higher stability. Even in a moist atmosphere, no self-ignition takes place. The quartz powder in the mixture reduces the hygroscopicity of ANC and urea increases the thermal stability to approximately 80 °C. This value may not be enough for military purposes, but is enough for civilian applications, like less toxic indoor fireworks.

This composition burns with a brilliant green flame and generates only very little smoke. The flame color is much more intense compared to the

barium-based 125A1 composition. In experiments with flame-color-neutral oxidizers, we observed that the contribution of boron fuel to the green flame color is negligible. Most of the combustion products of GST90 remain as a solid residue in the place of combustion and they keep the shape of the pyrotechnic star before ignition. Water in the composition slightly reduces the combustion velocity. However, the flame color of a star which had been stored in a moist atmosphere for several hours can be described as even more intense than with the very dry product. We believe that the presence of a little water in the mixture facilitates the formation of the emitting species: CuOH. However, the storage of such pyrotechnics in a moist atmosphere should be avoided because of the slightly hygroscopic character of ANC. In the reaction with water, ANC decomposes by the inverse reaction of equation (1), forming copper(II) nitrate pentahemihydrate and ammonium nitrate. Figure 1 shows an SEM image of the composition. One can see that not all grains are covered by the binder, which allows direct contact of some ANC crystallites with the surrounding air. The binder not only suppresses segregation but also, to a certain extent, acts as water sealant of the pyrotechnic. The very dry product is not friction sensitive (>360 N, BAM friction test), but considerably impact sensitive (approximately 2 J, BAM drop hammer).<sup>19</sup> The GST90 composition is less friction sensitive than previously published flash compositions using barium nitrate or potassium perchlorate and metal fuels (60–160 N) and slightly more impact sensitive than those pyrotechnic formulations (5–15 J).<sup>20</sup> However, the impact sensitivity of the ANC-boron-based pyrotechnics can be noticeably reduced by a certain amount of moisture in the formulation. So we suggest exposing it to ambient air for approximately 12 hours, before further processing. The dry composition can be ignited by

**Table 2.** Comparison of the LD<sub>50</sub> values (oral uptake) of some pyrotechnic ingredients and possible combustion products.

Chemical	LD <sub>50</sub> value/mg kg <sup>-1</sup>	Chemical	LD <sub>50</sub> value/mg kg <sup>-1</sup>
B	650 (rat)	Ba(NO <sub>3</sub> ) <sub>2</sub>	355 (rat)
B <sub>2</sub> O <sub>3</sub>	3163 (mouse)	BaCl <sub>2</sub> · 2H <sub>2</sub> O	118 (rat)
B(OH) <sub>3</sub>	2660 (rat)	BaO	50 (mouse)
Cu(NO <sub>3</sub> ) <sub>2</sub> · 2.5H <sub>2</sub> O	794 (rat)		
CuO	470 (rat)		

**Table 3.** General summary of BCN-based pyrotechnic compositions.

$\text{Cu}_2(\text{OH})_3(\text{NO}_3) + \dots$	Color emission	Smokeless combustion	Amount of solid residues	Thermal stability	Moisture stability	Environmental compatibility
... Mg	+	++	-	++	+++	++
... Al	---	--	+++	n.d.	n.d.	++
... B	-	++	+	n.d.	n.d.	+
... Ti	--	-	++	n.d.	n.d.	++
... Si	---	--	++	n.d.	n.d.	++
... magnalium	-	-	-	n.d.	n.d.	++
... S <sub>8</sub>	---	-	+++	n.d.	n.d.	+

electrostatic stimuli only after very intense spark spraying, so this can probably be regarded as a minor threat.

Boron powder is only slightly noxious (hazard symbol Xn – harmful). According to the Material Safety Data Sheet (MSDS), it is an irritant substance and may cause disturbances of the central nervous system. Table 2 summarizes the lethal concentration 50 percent death rate (LD<sub>50</sub>) for oral uptake of chemicals used in green-colored pyrotechnics and their combustion products.

ANC–boron compositions should not contain chlorine compounds which would cause the emission of blue rather than green light. From environmental point of view, the lack of chlorine offers the advantage that it makes the (potential) formation of toxic polychlorinated organic compounds such as PCDD and PCDF impossible.

Basic copper nitrate ( $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ , BCN) is known as the rare mineral gerhardtite. The natural mineral is orthorhombic, whereas the synthetic compound crystallizes mostly in the monoclinic crystal system.<sup>21</sup> BCN offers high thermal stability and low hygroscopicity and can be prepared from low cost materials. Furthermore, it is an oxidizer that contains both copper and hydroxide which makes it interesting as a potential coloring agent for pyrotechnic applications for the same reasons mentioned above.

## Experimental

$\text{Cu}_2(\text{OH})_3(\text{NO}_3)$  was prepared according to literature.<sup>22</sup> To a solution of 80 g (1 mol)  $\text{NH}_4\text{NO}_3$  in 100 mL  $\text{H}_2\text{O}$ , firstly 2.8 g (12 mmol) of  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  in 24.4 mL  $\text{H}_2\text{O}$  were added, secondly 12.5 mL of 1.5 M aqueous ammonia solution and lastly 325 mL  $\text{H}_2\text{O}$ . The solution

was stirred at a temperature of 65 °C for more than 48 hours. During that time it became turbid due to the precipitation of BCN. The light green powder obtained was washed with water and ethanol and dried under high vacuum. Yield: 66%.

IR (diamond-ATR,  $\text{cm}^{-1}$ ): 3540 (s), 3411 (s), 2837 (w), 2739 (w), 2465 (w), 2343 (w), 1762 (w), 1415 (vs), 1349 (s), 1321 (s), 1046 (m), 871 (m), 807 (m), 775 (m), 717 (m), 669 (m); Elemental analysis  $\text{Cu}_2\text{H}_3\text{NO}_6$  (240.12 g mol<sup>-1</sup>): calc.: H, 1.26; N, 5.83; found: H, 1.63; N, 5.88%.

## Results

BCN was combined with several fuels and the binder VAAR. The performance was evaluated with respect to the same categories as before (see Table 3).

All compositions with BCN show a poor green flame color. The mixture with magnesium (71.1% BCN; 15.1% Mg; 13.8% VAAR) is comparably the best. Its flame color can be described as pale green. The combustion is almost smokeless and produces only little solid residue. In Differential Scanning Calorimetry (DSC) measurements, the composition starts to decompose at temperatures above 240 °C (heating rate 5 °C min<sup>-1</sup>). It is also moisture stable.

The flame color achieved in combination with boron powder (53.3% BCN; 26.7% boron powder 325 mesh; 20.0% VAAR) is surprisingly yellow. All other fuels did not yield any flame color. These mixtures were quite hard to ignite and then burned down glowing. Thereby the formation of much smoke and a huge amount of solid residues were observed. For this reason, their stabilities toward temperature and moisture were not determined.

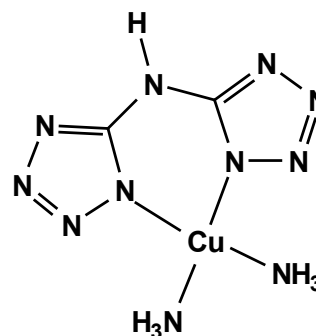
Due to these disappointing results we conclude



that BCN, despite its theoretically good properties, cannot serve as both coloring agent and oxidizer. A mixture of BCN and 5-aminotetrazole fuel verified the applicability of BCN as a gas generant, since we observed no flame but a lot of smoke during its combustion.<sup>3</sup>

## High-nitrogen copper compounds

Nitrogen-rich energetic materials are a rapidly expanding scientific field in the development of new and potentially environmentally benign pyrotechnics.<sup>7,23</sup> These materials are mostly derivatives of tetrazole and tetrazine. Very often, metal salts and complexes of these substances show a deep flame color of the respective cation (green for  $\text{Cu}^{2+}$ , in the absence of chlorine) in the flame of a Bunsen burner. However, in many cases, it is difficult to implement these substances in pyrotechnic formulations ready-for-use, because they often drastically forfeit their good coloring performance when pressed into pellets or in combination with a binder or a metal fuel like magnesium. Moreover, they often need an external oxidizer for self-sustaining combustion. It appears that the energetic materials community in many cases ignored these problems related to practical use and settled for the desired flame color of their compounds in the flame of a Bunsen burner. A noteworthy exception is the substantial work of Chavez et al.<sup>12</sup> and Chavez and Hiskey.<sup>24</sup> In their investigations, Chavez et al. found that copper(II) compounds in such formulation can exhibit disadvantageous characteristics. A mixture of copper(II) salts in dihydrazino tetrazine (DHT) lacks the long-term stability that is necessary for storage. Furthermore, copper drastically increases the burn rate of DHT and, therefore, should not be used in combination with DHT.



**Scheme 1.** Structure of the copper(II) bis(tetrazolyl)amine diammine complex,  $[\text{Cu}(\text{BTA})(\text{NH}_3)_2]$ .

## Experimental

We investigated formulations based on the use of copper(II) bis(tetrazolyl)amine diammine ( $[\text{Cu}(\text{BTA})(\text{NH}_3)_2]$ , see Scheme 1), a compound that has been developed in our research group.<sup>25</sup> The ligand's free acid bis(tetrazolyl)amine hydrate ( $\text{H}_2\text{BTA} \cdot \text{H}_2\text{O}$ ) is synthesized from sodium dicyanamide and sodium azide in diluted hydrochloric acid, ethanol and water.

$[\text{Cu}(\text{BTA})(\text{NH}_3)_2]$  was prepared according to the literature.<sup>25</sup> To a solution of 16.4 g (96 mmol)  $\text{H}_2\text{BTA} \cdot \text{H}_2\text{O}$  in 500 mL  $\text{H}_2\text{O}$  and 125 mL of concentrated aqueous ammonia solution, 8.2 g (48 mmol)  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 50 mL  $\text{H}_2\text{O}$  were added at 70 °C. A blue solid started to precipitate while cooling to 4 °C. The solid was washed several times with ethanol. Yield: 94%.

IR (diamond-ATR,  $\text{cm}^{-1}$ ): 3373 (w), 3321 (s), 3254 (m), 3127 (m), 3053 (m), 2915 (m), 2826 (w), 2656 (vw), 1612 (vs), 1545 (s), 1497 (vs), 1463 (w), 1445 (m), 1327 (w), 1232 (s), 1161 (vw), 1141 (vw), 1123 (w), 1093 (vw), 1017 (vw), 853 (vw), 806 (vw), 746 (m), 723 (m), 675 (w), 620 (vw); Elemental analysis  $\text{C}_4\text{H}_7\text{CuN}_{11}$  (248.70 g  $\text{mol}^{-1}$ ):

**Table 4.** General summary of  $[\text{Cu}(\text{BTA})(\text{NH}_3)_2]$ -based pyrotechnic compositions.

$[\text{Cu}(\text{BTA})(\text{NH}_3)_2] + \dots$	Color emission	Smokeless combustion	Amount of solid residues	Thermal stability	Moisture stability	Environmental compatibility
... $\text{Mg} + \text{MnO}_2$	+	+	--	+++	+++	++
... $\text{Si} + \text{MnO}_2$	---	-	+++	n.d.	n.d.	++
... $\text{KMnO}_4$	--	+	+	n.d.	n.d.	++
... $\text{KNO}_3$	--	+	+	n.d.	n.d.	++
... $\text{S}_8 + \text{KClO}_3$	++	--	-	+	++	+

calc.: C, 9.66; H, 2.84; N, 61.95; found: C, 9.79; H, 3.00; N, 61.40%.

## Results

Due to the fact that  $[\text{Cu}(\text{BTA})(\text{NH}_3)_2]$  does not contain any oxygen, the addition of an oxidizer for application in pyrotechnics is essential. Therefore, the performance of potassium permanganate, potassium nitrate and manganese dioxide was investigated. In addition to these mixtures, a composition with potassium chlorate and sulfur was prepared to check the potential of this complex as a blue flame colorant.

Despite the fact that pure  $[\text{Cu}(\text{BTA})(\text{NH}_3)_2]$  powder burns with a beautiful, deep green flame color in the Bunsen burner, the compositions with the potassium salts yielded a bright violet flame color. However, during ignition with a pocket lighter, a green emission could be observed for a short time. The addition of retardant chemicals for lowering the flame temperature, like  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  or  $\text{Cu}(\text{SO}_4) \cdot 5\text{H}_2\text{O}$ , did not improve the results. Either the same color could be observed as before or the mixture was glowing only. Combinations of  $[\text{Cu}(\text{BTA})(\text{NH}_3)_2]$  with potassium nitrate or permanganate and different fuels like magnesium, silicon and sulfur (all powdered) were disappointing with respect to the emission of green light as well.

Furthermore,  $[\text{Cu}(\text{BTA})(\text{NH}_3)_2]$  was combined with the oxidizer manganese dioxide and the fuels silicon or magnesium powder, respectively. The first mixture burned down by glowing, without any visible flame in any ratio of the constituents. It has long been known that silicon burns with mostly infrared emission only.<sup>26</sup> With magnesium fuel and manganese dioxide (24.3%  $[\text{Cu}(\text{BTA})(\text{NH}_3)_2]$ ; 66.2%  $\text{MnO}_2$ ; 2.3% Mg; 7.2% VAAR), a spectacular combustion with golden and partly blue sparks could be observed. For this effect, the addition of  $[\text{Cu}(\text{BTA})(\text{NH}_3)_2]$  is essential to obtain a good sparkling result. With an increased amount of magnesium powder, a very bright colorless flame will be obtained. The combustion takes place without generating much smoke; the solid residue is a small amount of brown powder. One major advantage of this pyrotechnic formulation is its stability in a moist environment and at high temperature – it decomposes at temperatures above

250 °C. Furthermore, it is not impact sensitive (>40 J, BAM drop hammer) nor friction sensitive (>360 N, BAM friction test).

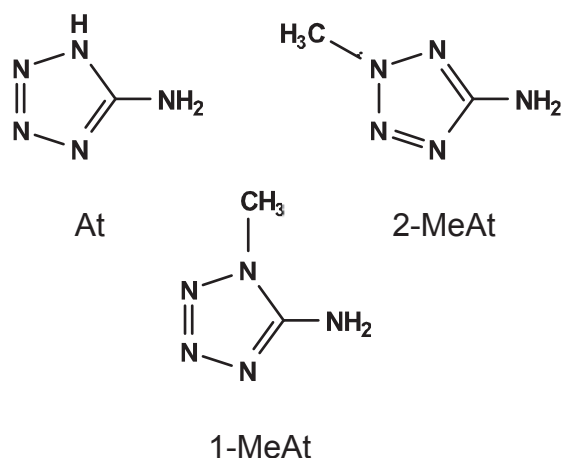
The composition containing  $[\text{Cu}(\text{BTA})(\text{NH}_3)_2]$ , sulfur and potassium chlorate produces an intense blue flame. Unfortunately, during the combustion much smoke is produced. Furthermore, it is very sensitive toward impact (<2.5 J, BAM drop hammer) and friction (>80 N, BAM friction test). This fact was expected for a mixture containing sulfur and potassium chlorate. Decomposition occurs at temperatures above 170 °C (DSC, heating rate 5 °C min<sup>-1</sup>).

For lowering the flame temperature, several mixtures with 5-aminotetrazole fuel were prepared. Copper(II) nitrate pentahemihydrate and bis(2-methyl-5-aminotetrazole)copper(II) nitrate were used as colorant agents and oxidizers and VAAR as a binder. The copper complex diaqua-bis(1-methyl-5-aminotetrazole)copper(II) nitrate was combined with magnalium alloy and VAAR (for the structures of the tetrazole derivatives, see Scheme 2).

## Experimental

The chemicals  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  and 5-aminotetrazole were used as purchased from SigmaAldrich. 1- and 2-methyl-5-aminotetrazole were prepared according to the literature.<sup>27</sup>

Bis(2-methyl-5-aminotetrazole)copper(II) nitrate  $[\text{Cu}(\text{2-MeAt})_2(\text{NO}_3)_2]_2$  was prepared according



**Scheme 2.** Structures of 5-aminotetrazole (At), and 1- and 2-methyl-5-aminotetrazole (1-MeAt and 2-MeAt, respectively).

**Table 5.** General summary of 5-aminotetrazole-based pyrotechnic compositions.

5-Aminotetrazole + ...	Color emission	Smokeless combustion	Amount of solid residues	Thermal stability	Moisture stability	Environmental compatibility
... $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O} + \text{urea}$	+++	+++	--	+	+	++
... $[\text{Cu}(2\text{-MeAt})_2(\text{NO}_3)_2]_2$	++	++	-	+	++	++
$[\text{Cu}(1\text{-MeAt})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2] + \text{magnalium}$	+	+	++	++	n.d.	++

to Radies.<sup>28</sup> A solution of 2.8 g (12 mmol)  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  in 10 mL  $\text{H}_2\text{O}$  was added to a solution of 1.2 g (12 mmol) 2-methyl-5-aminotetrazole in 25 mL  $\text{H}_2\text{O}$  at 60 °C. When the dark green solution was allowed to cool down to room temperature, green crystals formed which were washed with ethanol and diethyl ether. After powdering in a crucible, the green powder was dried under high vacuum. Yield: 88.6%.

IR (diamond-ATR,  $\text{cm}^{-1}$ ): 3453 (m), 3352 (s), 3313 (s), 3250 (m), 3173 (m), 2749 (vw), 2357 (vw), 2331 (vw), 1633 (s), 1562 (m), 1536 (m), 1488 (vs), 1458 (s), 1442 (s), 1375 (w), 1295 (s), 1267 (vs), 1198 (w), 1153 (vw), 1124 (vw), 1070 (vw), 1022 (m), 916 (vw), 813 (w), 742 (w), 718 (vw), 647 (w); Elemental analysis  $\text{C}_4\text{H}_{10}\text{CuN}_{12}\text{O}_6$  (385.79 g  $\text{mol}^{-1}$ ): calc.: C, 12.45; H, 2.61; N, 43.57; found: C, 12.74; H, 2.71; N, 43.12%.

Diaqua-bis(1-methyl-5-aminotetrazole)copper(II) nitrate  $[\text{Cu}(1\text{-MeAt})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]$  was prepared according to Radies.<sup>28</sup> A solution of 2.8 g (12 mmol)  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  in 10 mL  $\text{H}_2\text{O}$  was added to a solution of 1.2 g (12 mmol) 1-methyl-5-aminotetrazole in 15 mL  $\text{H}_2\text{O}$  at 60 °C. The dark blue solution was cooled down to ambient temperature. The blue crystals obtained were washed with ethanol and diethyl ether. Yield: 71.3%.

IR (diamond-ATR,  $\text{cm}^{-1}$ ): 3456 (m), 3398 (vs), 3313 (m), 3261 (m), 3203 (m), 3166 (s), 2443 (vw), 1760 (vw), 1647 (m), 1597 (w), 1497 (w), 1420 (m), 1326 (s), 1237 (w), 1139 (vw), 1079 (w), 1050 (w), 984 (vw), 818 (w), 784 (w), 739 (vw), 718 (vw), 689 (w); Elemental analysis  $\text{C}_4\text{H}_{14}\text{CuN}_{12}\text{O}_8$  (421.78 g  $\text{mol}^{-1}$ ): calc.: C, 11.39; H, 3.35; N, 39.85; found: C, 11.24; H, 3.29; N, 39.25%.

## Results

The results of this investigation are listed in Table 5. Only the most promising formulations are listed. The mixture with copper(II) nitrate pentahemihydrate as oxidizer and colorant (43.7%  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ , 43.7% At, 1% urea, 11.6% VAAR) yields the deepest green flame color. It combusts without smoke generation and produces a small amount of solid residues. Urea was added to increase the thermal stability. The mixture decomposes in DSC measurements at temperatures above 130 °C with a heating rate of 5 °C  $\text{min}^{-1}$ . The stability toward moisture is better than expected. There is no loss in performance after storing it in an open vial for one month.

CAUTION! No magnesium or magnalium alloy should be added to this composition! This causes an explosion even at temperatures as low as 60 °C.

The composition with  $[\text{Cu}(2\text{-MeAt})_2(\text{NO}_3)_2]_2$  as a colorant (45%  $[\text{Cu}(2\text{-MeAt})_2(\text{NO}_3)_2]_2$ ; 45% 5-aminotetrazole; 10% VAAR) shows a good performance as well. The emitted light is yellowish-green. Only a small amount of smoke and little solid residue (but more than with the  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  mixture) are formed in the course of combustion. According to DSC measurements (heating rate 5 °C  $\text{min}^{-1}$ ), the mixture decomposes at 148 °C. It is stable toward moisture, but sensitive toward impact (>2.5 J, BAM drop hammer) and friction (>240 N, BAM friction test).

From the observations, we can conclude that 5-aminotetrazole seems to be a good alternative as a fuel if low flame temperature are desirable. This is confirmed by our observations during the investigation of the following pyrotechnics.

A composition containing  $[\text{Cu}(1\text{-MeAt})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]$  and magnalium alloy (68.4%  $[\text{Cu}(1\text{-MeAt})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]$ , 17.1%

magnalium, 14.5% VAAR) produces a deep green flame with red spots and no smoke. The red color arises from the formation of CuO in the gas phase which is an indication of a flame temperature too high for the formation of the green light emitter CuOH. One drawback is the afterglow and partial reignition of the solid residue. Surprisingly,  $[\text{Cu}(\text{1-MeAt})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]$ , containing water of crystallization, decomposes in combination with magnalium alloy in DSC measurements at temperatures above 152 °C. Sensitivities toward shock, friction and moisture were not determined.

## Conclusion

Beyond blue luminescence, copper plays a key role in the development of environmentally benign green-colored pyrotechnics. The noble character and the high hygroscopicity are responsible for the somewhat troublesome features of copper and many copper compounds in pyrotechnics. Until now, copper and copper compounds have been applied almost exclusively as a fuel or as a coloring additive (primarily for blue colors) to a distinct pyrotechnic formulation. To our knowledge, the pyrotechnic composition GST90 presented in this paper (boron + ammonium nitratocuprate(II) nitrate + binder) is the first including a copper-based combined oxidizer and coloring agent that has been investigated and tested successfully. We could not find a promising composition based on the use of basic copper(II) nitrate to act as both oxidizer and green colorant. High-nitrogen compounds of copper(II), with BTA or derivatives of 5-aminotetrazole as ligands, offer a field for new pyrotechnic investigations. However, it is hard to maintain the good colorant quality of the pure compound in the flame of a Bunsen burner in the course of the production of a material suitable for pyrotechnic applications. Unfortunately, some recent studies on new nitrogen-rich pyrotechnics focused rather on academic problems than on possible applications and problems related to practical use. However, some promising candidates for the application in civilian fireworks (like the mixture of copper(II) nitrate pentahydrate and 5-aminotetrazole) have been presented and discussed in this paper.

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# The Debris Hazard from Fireworks Held in Steel ISO Containers

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**Abstract:** *A number of serious accidents in European Union countries involving explosions of fireworks stored in steel ISO freight containers has shown that the hazards associated with bulk-stored fireworks might be greater than previously thought. To address this problem an EU research programme was initiated, part of which involved field trials with fireworks packed in ISO freight containers. In a few of these trials a mass explosion effect was observed. This prompted a number of questions, including whether the current quantity-distances applying to fireworks storage under such conditions offer adequate protection to the public. We consider this issue in the current paper by looking at the debris hazard from just one of the mass exploding trials, and show that for that particular firework the inhabited building distance specified in MSER is more than adequate to ensure that members of the public are not exposed to unacceptably high risks.*

**Keywords:** *Explosives, quantity–safety distances, fireworks, storage, risks*

## Introduction

In an earlier paper<sup>1</sup> we presented the results of two propriety explosives steel-magazine trials and discussed how these results could be used to evaluate the adequacy of UK quantity–distance (QD) prescriptions from a risk perspective. The results of these and other small quantities trials on stores built of brick and concrete suggested that the quantity of debris generated in an explosion and the distance to which it would be thrown could be considerably greater than had previously been thought; and that in certain cases, distances set primarily to protect against the effects of blast might not offer sufficient protection against flying debris. The trials were part of a program of work whose aim was to review and revise the QD prescriptions applied to explosives stores.

Following on from this, models were developed to estimate the risks both to an individual living near an explosives store and of an explosion involving multiple fatalities, and to prescribe new QD tables. These tables were subsequently introduced in the UK when the Manufacture and Storage of

Explosives Regulations (MSER) came into force in 2005.

More recently some large-scale trials work on fireworks held in steel ISO containers has produced a range of hazardous effects including mass explosions with associated fireball, blast, cratering and fragmentation effects. The purpose of this paper is to test the adequacy of our “new” MSER QD’s for fireworks held in steel ISO containers which mass explode. For such situations, QDs are directed by the blast and debris/fragmentation effects.

## Hazards associated with bulk stored fireworks

A number of serious accidents<sup>2</sup> in European Union countries involving explosions in the large-scale storage of fireworks have shown that we did not have an adequate understanding of the hazards posed by pyrotechnic articles (especially display fireworks) during transport and bulk storage. To address this problem an EU research programme was initiated entitled ‘Quantification and control

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of the hazards associated with the transport and bulk storage of fireworks (CHAF)'. The work was undertaken by three partners: The Health and Safety Laboratory (United Kingdom), TNO Prins Maurits Laboratory (The Netherlands) and Bundesanstalt für Materialforschung und -prüfung (Germany) and coordinated by the former.

To gain a better understanding of the hazards posed by fireworks in transport and storage, part of the CHAF project involved full-scale testing of ignition of fireworks in 20 ft steel ISO containers. Nine such trials were carried out and in three cases a mass explosion effect was observed. The trials producing a mass explosion involved (1) stickless rockets, (2) waterfalls and (3) 150 mm coloured shells. In the latter trial an extra degree of confinement was achieved by placing the ISO container in the ground to a depth of around 1.5 m and covering it with at least 1 m of sand in all directions. Of these three trials, only that involving

the stickless rockets have sufficient information for analysis of the associated fragment/debris effects.

### **Trials on stickless rockets**

The trials on stickless rockets involved 720 boxes (86400 articles) with a net explosives content of 5011 kg, packed inside a 6.1 m (20 ft) ISO container. Almost immediately after ignition a violent explosion of the contents of the container was observed along with the associated ground shockwave, see Figure 1.

The container was fragmented into small pieces, typically 5–70 cm wide and 5–200 cm long. The mass of the fragments varied between 0.1 and 30 kg. The largest distance where a fragment was recovered was 462 m. In total about 560 kg of fragments were recovered, representing about 25% of the total mass of the container. The blast data at 400 m distance corresponded to a detonation of 3367 kg TNT; i.e. an equivalence of 0.67 (based



**Figure 1.** Full-scale ISO container testing of stickless rockets.

on peak pressure). Full details of the large scale ISO container fireworks trial and results are given in the CHAF 'Work Package 9' report.<sup>3</sup>

### Debris-throw distribution

The debris-throw data were analyzed<sup>4</sup> by dividing the debris field into 20 m deep sectors and counting the number of pieces of potentially lethal debris found in each. For example, five fragments were found between 20 and 40 m of the container (mid range 30 m) and 16 fragments were found between 40 and 60 m of the container (mid range 50 m). The complete results are summarized in Table 1 below.

### Basis of current QD prescriptions

The UK QD prescriptions do not guarantee members of the public complete immunity against the effects of an accident on a licensed explosives

site, for which aim impractically large distances would be required. Rather the prescriptions are designed to offer members of the public a high level of protection should an accident occur and to limit property damage to an acceptable level (typically broken windows and other easily repairable damage). This qualification notwithstanding, the QD prescriptions can be said to have stood the test of time: in the last 60 years there have been almost 100 incidents of major accidental explosion on licensed explosives sites in the UK, not one of which has caused fatal injury off site.

In 2005 the Health & Safety Executive (HSE) introduced MSER.<sup>5</sup> These regulations (through an associated Approved Code of Practice<sup>6</sup>) included, amongst many other things, revised and increased QDs for relatively small quantities of mass exploding explosives held in steel and brick magazines. The revised QD prescriptions

**Table 1.** *Fragment data for stickless rockets trial*

Radius/m	Annulus/m	No. of fragments	No. of fragments per m <sup>2</sup>
30	20–40	5	$1.326 \times 10^{-3}$
50	40–60	16	$2.546 \times 10^{-3}$
70	60–80	24	$2.728 \times 10^{-3}$
90	80–100	15	$1.326 \times 10^{-3}$
110	100–120	46	$3.328 \times 10^{-3}$
130	120–140	70	$4.285 \times 10^{-3}$
150	140–160	102	$5.411 \times 10^{-3}$
170	160–180	83	$3.885 \times 10^{-3}$
190	180–200	90	$3.769 \times 10^{-3}$
210	200–220	145	$5.495 \times 10^{-3}$
230	220–240	54	$1.868 \times 10^{-3}$
250	240–260	76	$2.419 \times 10^{-3}$
270	260–280	38	$1.120 \times 10^{-3}$
290	280–300	13	$3.567 \times 10^{-4}$
310	300–320	11	$2.824 \times 10^{-4}$
330	320–340	8	$1.929 \times 10^{-4}$
350	340–360	9	$2.046 \times 10^{-4}$
370	360–380	2	$4.301 \times 10^{-5}$
390	380–400	4	$8.162 \times 10^{-5}$
410	400–420	4	$7.764 \times 10^{-5}$
430	420–440	0	0
450	440–460	3	$5.305 \times 10^{-5}$
470	460–480	2	$3.386 \times 10^{-5}$
490	480–500	0	0
510	500–520	0	0

were designed to ensure that the individual risk to members of the public would be kept to a level judged to be broadly acceptable (i.e. a risk of fatal injury no greater than  $10^{-6}$ , or 1 in one million per year). In cases where licensed facilities are located near to areas of high population density ('urban'), more restrictive distances apply; these are designed to ensure that the chance of an accident causing 10 or more fatalities would be less than  $10^{-5}$  per year, in addition to ensuring that no one person would be exposed to an individual risk greater than  $10^{-6}$ .

### Adequacy of quantity distances against trials results

The CHAF large scale ISO container trial on 5011 kg of stickless rockets produced debris out to 462 m. The TNT equivalence for this configuration of fireworks was measured as 3367 kg, and the MSER inhabited building distance (IBD) for this mass of TNT is 362 m. The question then is whether the MSER prescriptions are adequate, given that debris was thrown beyond the currently prescribed IBD. This is now examined first in regard to individual risk.

The individual risk (IR) for a person living at the IBD from an explosives facility is given by:

$$IR = PE \times FE \times (T_O \times L_O + T_I \times L_I)$$

where

PE is the likelihood of accidental explosion, expressed as an annual probability;

FE is the individual's fractional exposure, i.e. the fraction of time per year that the individual is present at the IBD;

$T_O$  is the fraction of time the individual spends outdoors at the location;

$L_O$  is the conditional probability that the individual would be killed in the event of an explosion, given that the person is outdoors;

$T_I$  is the fraction of time the individual spends indoors at the location;

$L_I$  is the conditional probability that the individual would be killed in the event of an explosion, given that the person is located indoors.

PE for UK commercial explosives magazines has been estimated<sup>7</sup> to be  $10^{-4}$  per magazine-year.

FE is conservatively assumed to be unity, i.e. the

person is constantly exposed to risk.

$T_O$  and  $T_I$ , the fraction of time each individual resident is assumed to spend both outdoors and indoors at the location, are 0.11 and 0.89 respectively (these figures are typically used by HSE in studies of the risks arising from industrial activities).

$L_O$  and  $L_I$  express lethality from the combined effects of both debris and blast. The overall level of lethality for population outdoors ( $L_O$ ) and indoors ( $L_I$ ) is then given by:

$$L_O = F_{D_O} + F_{B_O} - F_{D_O} \times F_{B_O}$$

and

$$L_I = F_{D_I} + F_{B_I} - F_{D_I} \times F_{B_I}$$

where

$F_{D_O}$  is the outdoor probability of fatal injury due to debris effects,

$F_{D_I}$  is the indoor probability of fatal injury due to debris effects,

$F_{B_O}$  is the outdoor probability of fatal injury due to blast effects,

$F_{B_I}$  is the indoor probability of fatal injury due to blast effects,

and the products  $F_{D_O} \times F_{B_O}$  and  $F_{D_I} \times F_{B_I}$  prevent double counting.

Thus:

$$IR = 0.0001 \times 1 \times [0.11 \times (F_{D_O} + F_{B_O} - F_{D_O} \times F_{B_O}) + 0.89 \times (F_{D_I} + F_{B_I} - F_{D_I} \times F_{B_I})]$$

### Lethality due to debris effects

Outdoor lethality,  $L_O$ , is effectively determined by debris effects (blast effects to people outdoors are negligible except at very close range) and is dependent on both the density of lethal debris at the given range and the target area presented by the exposed person, viz.

$$L_O = 1 - e^{-D \times A}$$

where

$D$  is the lethal debris density, and

$A$  is the effective target area of the exposed person

This Poisson distribution equation gives the



probability that a given person at the range will be struck by at least one piece of potentially lethal debris. If a value can be assumed for the target area presented by an average person to incoming debris, then values of  $L_O$  can be computed using the debris density measurements derived from the analysis of the magazine trial data.

Target areas will, of course, be dependent on the size and shape of the exposed person and the angle of descent of the incoming debris. Ballistic calculations suggest that debris landing in the mid to far field, where the IBD will be located, will mostly impact the ground at angles between  $49^\circ$  and  $76^\circ$ , giving an average target area of  $0.22 \text{ m}^2$ . For debris projected out horizontally and passing the range below head height an average target area of  $0.56 \text{ m}^2$  is appropriate.

### Determination of lethal debris densities

In the next stage of analysis values were computed for the density of lethal debris produced at various distances from the explosion. Two possible procedures were considered, the first producing “pseudo trajectory normal” (PTN) debris densities and the second producing “modified pseudo trajectory normal” (MPTN) debris densities<sup>4</sup>.

The PTN method assumes that a person at a particular range is at risk of being struck not only by debris landing at that range but also by all the debris that travels beyond the range. This implies that fragments which pass over the range do so at head height or below. In practice many of these fragments are likely to pass at heights significantly greater than head height.

The MPTN method provides an alternative, less conservative procedure for analyzing the data. This assumes that only one-third of the debris passing beyond a given range poses a risk to anyone located at that range; in other words two-thirds of the debris passes above head height.

As with the previous analysis for the MSER QDs, the less conservative MPTN method has been adopted in this study. This is largely in consideration of the fact that steel ISO containers can be expected to balloon somewhat before fragmenting, resulting in a more even distribution of debris launch angles than would be the case with brick stores holding a small NEQ – where the roof of the buildings lifts off vertically and where the

walls move out more or less horizontally towards any exposed sites.

Applying this methodology to the data presented in Table 1 allows the data in Table 2 to be constructed.

A regression analysis of these data produces the following lethality function:

$$L_{Do} = -6.780171583533 \times 10^{-16} R^6 \\ - 1.423336053601 \times 10^{-12} \times R^5 \\ + 2.540655404929 \times 10^{-9} \times R^4 \\ - 1.275797107962 \times 10^{-6} \times R^3 \\ + 2.568501531817 \times 10^{-4} \times R^2 \\ - 2.687365853920 \times 10^{-2} \times R \\ - 7.830518274706 \times 10^{-1}$$

where  $R$  is the range (m) within the limits 30–490 m.

There is, of course, no underlying physical reason why lethality for people located in the open should be related to the 6th power of the range; the regression analysis is simply a convenient way of providing a continuous function.

In general, people indoors would be afforded a certain amount of protection from flying debris by the walls and roof of the building. Clearly the degree of protection will increase the smaller the area of glazing and the greater the thickness and strength of the walls and roof. The approach adopted in this study is to assume that occupants will only be at risk from those pieces of debris that strike an area of glazing (this assumption was also applied in the derivation of the MSER QD tables). Taking account of typical debris descent angles and dimensions for modern housing, indoor lethality probabilities are assumed to be one-twelfth of those derived for outdoor population.

### Lethality due to blast effects

Two well-established blast models were available to the study: the ESTC Outdoor Blast Model<sup>8</sup> (for population located in the open) and the ESTC Indoor Blast Model<sup>9</sup> (for population located inside buildings of conventional construction). These models are described briefly below.

#### The ESTC Outdoor Blast Model



**Table 2.** *Lethality for persons outdoors ( $L_{Do}$ ) as a function of range from ISO container*

Range/m	Area/m <sup>2</sup>	No. of fragments	MPTN Density	$L_{Do}$
30	3770	5	$7.3447 \times 10^{-2}$	$3.9863 \times 10^{-2}$
50	6283	16	$4.4970 \times 10^{-2}$	$2.4024 \times 10^{-2}$
70	87976	24	$3.2122 \times 10^{-2}$	$1.6916 \times 10^{-2}$
90	11310	15	$2.3746 \times 10^{-2}$	$1.2764 \times 10^{-2}$
110	13823	46	$2.0562 \times 10^{-2}$	$1.0329 \times 10^{-2}$
130	16336	70	$1.7439 \times 10^{-2}$	$8.2745 \times 10^{-3}$
150	18850	102	$1.5008 \times 10^{-2}$	$6.5430 \times 10^{-3}$
170	21363	83	$1.1058 \times 10^{-2}$	$4.8594 \times 10^{-3}$
190	23876	90	$8.9304 \times 10^{-3}$	$3.7125 \times 10^{-3}$
210	26389	145	$8.3493 \times 10^{-3}$	$2.7949 \times 10^{-3}$
230	28903	54	$3.8289 \times 10^{-3}$	$1.5078 \times 10^{-3}$
250	31416	76	$3.4165 \times 10^{-3}$	$1.0915 \times 10^{-3}$
270	33929	38	$1.6701 \times 10^{-3}$	$5.5433 \times 10^{-4}$
290	36442	13	$7.5004 \times 10^{-4}$	$2.9870 \times 10^{-4}$
310	38956	11	$5.5619 \times 10^{-4}$	$2.1543 \times 10^{-4}$
330	41469	8	$3.8583 \times 10^{-4}$	$1.5046 \times 10^{-4}$
350	43982	9	$3.1831 \times 10^{-4}$	$1.0867 \times 10^{-4}$
370	46496	2	$1.3621 \times 10^{-4}$	$6.1653 \times 10^{-5}$
390	49009	4	$1.4283 \times 10^{-4}$	$5.2234 \times 10^{-5}$
410	51522	4	$1.0999 \times 10^{-4}$	$3.5195 \times 10^{-5}$
430	54035	0	$3.0844 \times 10^{-5}$	$1.7273 \times 10^{-5}$
450	56549	3	$6.4841 \times 10^{-5}$	$1.8273 \times 10^{-5}$
470	59062	2	$3.3863 \times 10^{-5}$	$7.4498 \times 10^{-6}$
490	61575	0	0	0

The ESTC Outdoor Blast Model is designed to estimate the likelihood of blast-induced fatality for persons in the open following an explosion of Hazard Type 1 (mass exploding) material. It is based on a review of the available literature on primary and tertiary blast effects, and gives a single prediction of fatality probability as a function of scaled distance. Fatality probability, range and NEQ are related by equation (1):

$$F_{Bo} = \frac{e^{\left(-5.785 \times \left(\frac{R}{Q^{1/3}}\right) + 19.047\right)}}{100} \quad (1)$$

where  $F_{Bo}$  is the fatality probability,  $R$  is the range (m) and  $Q$  is the NEQ (kg).

The model is applicable to population in the open between a scaled distance (actual distance/ $Q^{1/3}$ ) of 2.5 and 5.3 m kg<sup>-1/3</sup>.

A fatality probability of unity is assumed for

scaled distances less than 2.5 m kg<sup>-1/3</sup> while a zero fatality probability is assumed for scaled distances greater than 5.3 m kg<sup>-1/3</sup>.

### The ESTC Indoor Blast Model

The ESTC Indoor Blast Model is designed to estimate likelihood of blast-induced fatality for persons within a conventional UK brick building following an explosion of Hazard Type 1 material external to the structure. This model is based on an analysis of casualty data collated from records of a number of major incidents of accidental explosion. It is worth noting that the fatality data on which the model is based do not differentiate between those killed by blast and those killed by fragments; it is assumed that blast effects were responsible for most of the fatalities recorded, but the model implicitly makes some allowance for fragment/debris effects. Fatality probability, range and NEQ are related by equation (2):

$$\text{Log}(F_B) = 1.827 - 3.433 \cdot \text{Log}\left(\frac{R}{Q^{1/3}}\right) - 0.853 \cdot \left(\text{Log}\left(\frac{R}{Q^{1/3}}\right)\right)^2 + 0.356 \cdot \left(\text{Log}\left(\frac{R}{Q^{1/3}}\right)\right)^3 \quad (2)$$

where

$F_{Bi}$  is the fatality probability,  $R$  is the range (m),  
 $Q$  is the NEQ (kg)

The model is applicable to population inside buildings of conventional construction and for scaled distances in the range 3.06 to 55 m kg<sup>-3</sup> and has been applied within these limits. A fatality probability of unity is assumed for scaled distances less than 3.06 m kg<sup>-3</sup> while a zero fatality probability is assumed for scaled distances greater than 55 m kg<sup>-3</sup>.

#### Possible IBD based on individual risk criterion

The individual risks at distance from the large scale stickless rockets trial can now be calculated using the earlier formula:

$$\text{IR} = 0.0001 \times 1 \times [0.11 \times (F_{Do} + F_{Bo} - F_{Do} \times F_{Bo}) + 0.89 \times (F_{Di} + F_{Bi} - F_{Di} \times F_{Bi})]$$

The results of these calculations are shown in Table 3.

This shows that at a distance around 142 m the individual risk of fatality is  $1 \times 10^{-6}$ .

**Table 3.** Individual risks at distance from the large scale stickless rockets trial.

Radius/ m	No. of fragments	Outdoor blast lethality	Outdoor fragment lethality	Indoor blast lethality	Indoor fragment lethality	Overall individual risk of fatality (per year)
30	5	$1.00 \times 10^0$	$4.07 \times 10^{-2}$	$1.00 \times 10^0$	$3.39 \times 10^{-3}$	$1.00 \times 10^{-4}$
50	16	$7.78 \times 10^{-3}$	$2.35 \times 10^{-2}$	$7.05 \times 10^{-1}$	$1.96 \times 10^{-3}$	$6.31 \times 10^{-5}$
70	24	$3.45 \times 10^{-6}$	$1.64 \times 10^{-2}$	$1.79 \times 10^{-1}$	$1.37 \times 10^{-3}$	$1.62 \times 10^{-5}$
90	15	0	$1.28 \times 10^{-2}$	$6.39 \times 10^{-2}$	$1.07 \times 10^{-3}$	$5.92 \times 10^{-5}$
110	46	0	$1.04 \times 10^{-2}$	$2.80 \times 10^{-2}$	$8.70 \times 10^{-4}$	$2.68 \times 10^{-6}$
130	70	0	$8.53 \times 10^{-3}$	$1.41 \times 10^{-2}$	$7.10 \times 10^{-4}$	$1.41 \times 10^{-6}$
150	102	0	$6.75 \times 10^{-3}$	$7.86 \times 10^{-3}$	$5.63 \times 10^{-4}$	$8.24 \times 10^{-7}$
170	83	0	$5.09 \times 10^{-3}$	$4.73 \times 10^{-3}$	$4.24 \times 10^{-4}$	$5.15 \times 10^{-7}$
190	90	0	$3.62 \times 10^{-3}$	$3.02 \times 10^{-3}$	$3.02 \times 10^{-4}$	$3.36 \times 10^{-7}$
210	145	0	$2.44 \times 10^{-3}$	$2.03 \times 10^{-3}$	$2.03 \times 10^{-4}$	$2.25 \times 10^{-7}$
230	54	0	$1.56 \times 10^{-3}$	$1.41 \times 10^{-3}$	$1.30 \times 10^{-4}$	$1.54 \times 10^{-7}$
250	76	0	$9.69 \times 10^{-4}$	$1.02 \times 10^{-3}$	$8.07 \times 10^{-5}$	$1.08 \times 10^{-7}$
270	38	0	$5.90 \times 10^{-4}$	$7.52 \times 10^{-4}$	$4.93 \times 10^{-5}$	$7.78 \times 10^{-8}$
290	13	0	$3.60 \times 10^{-4}$	$5.70 \times 10^{-4}$	$3.00 \times 10^{-5}$	$5.74 \times 10^{-8}$
310	11	0	$2.23 \times 10^{-4}$	$4.41 \times 10^{-4}$	$1.86 \times 10^{-5}$	$4.34 \times 10^{-8}$
330	8	0	$1.43 \times 10^{-4}$	$3.48 \times 10^{-4}$	$1.19 \times 10^{-5}$	$3.36 \times 10^{-8}$
350	9	0	$9.53 \times 10^{-4}$	$2.78 \times 10^{-4}$	$7.94 \times 10^{-6}$	$2.65 \times 10^{-8}$
370	2	0	$6.61 \times 10^{-4}$	$2.26 \times 10^{-4}$	$5.50 \times 10^{-6}$	$2.13 \times 10^{-8}$
390	4	0	$4.71 \times 10^{-4}$	$1.86 \times 10^{-4}$	$3.92 \times 10^{-6}$	$1.74 \times 10^{-8}$
410	4	0	$3.37 \times 10^{-5}$	$1.54 \times 10^{-4}$	$2.81 \times 10^{-6}$	$1.44 \times 10^{-8}$
430	0	0	$2.33 \times 10^{-5}$	$1.30 \times 10^{-4}$	$1.94 \times 10^{-6}$	$1.20 \times 10^{-8}$
450	3	0	$1.47 \times 10^{-5}$	$1.10 \times 10^{-4}$	$1.22 \times 10^{-6}$	$1.01 \times 10^{-8}$
470	2	0	$7.79 \times 10^{-6}$	$9.39 \times 10^{-5}$	$6.49 \times 10^{-7}$	$8.50 \times 10^{-9}$

## Possible IBD based on group risk criterion

The criteria against which the revised and current QD prescriptions were fixed, were (1) to limit the level of individual risk of fatality to any identifiable person to  $10^{-6}$  per year, and (2) to ensure that the chance of an accident causing 10 or more fatalities would be less than  $10^{-5}$  per year. This latter criterion is somewhat stricter than that advocated in the first report of the Advisory Committee on Major Hazards (ACMH), which recommended that the chance of a serious accident (involving the death of 10 or more people) at any one major non-nuclear plant should be less than  $10^{-4}$  per year.<sup>10</sup> In practice the group risk criterion only takes effect in the case of stores located near to areas of urban population density (4210 persons per km<sup>2</sup>).<sup>11</sup> Given that the generic rate of accidental explosion has been assessed as  $10^{-4}$  per storehouse-year,<sup>7</sup> it can be shown<sup>11</sup> that the group risk criterion is met when the average number of fatalities expected in the event of an accident does not exceed 6.225<sup>12</sup>. From this it follows that the minimum IBD conforming to the group risk criterion can be obtained from the following equation:

$$6.225 = A \times d \times (L_O \times T_O + L_I \times T_I)$$

where

$A$  is the area of the danger zone

$d$  is the population density in the danger zone,

$L_O$ ,  $T_O$ ,  $L_I$  and  $T_I$  are defined as before.

The danger zone is defined as that area between the inhabited building distance (IBD) already determined by the individual risk criterion, and the range where the effects of any potential explosion would decay to a level that could be considered, for all practical purposes, sub lethal. The latter range is defined as the distance at which lethality falls to  $10^{-4}$ , as predicted by the explosion consequence models. This range corresponds to an individual risk of  $10^{-8}$ , a value generally regarded as negligible. The model involves iterative calculations in which the IBD is extended by 1 m at a time until the group risk criterion is met. In this instance whilst the outer radius of the danger area is 450 m, the group risk criterion is met at a distance of 198 m.

## Conclusions

The furthest distance of debris travel from the large-scale stickless-rocket fireworks ISO container trial was just over 450 m. The TNT equivalent of the associated explosion was measured to be 3367 kg, which if stored inside an unmounted metal magazine, would be required under MSER to have an IBD of 362 m. From an analysis of the debris distribution data from the fireworks trial and, based on the individual risk criteria of  $1 \times 10^{-6}$  outlined above, an IBD prescription of 142 m would be appropriate. If a person were permanently located at the MSER IBD of 362 m the individual risk to that person would be  $3 \times 10^{-8}$ . This is an exceptionally low level of risk and is very much below the overall background level of risk to which people are exposed in their daily lives. A further analysis of the trials debris data based on the group risk criteria outlined above, indicates that an IBD prescription of 198 m would be appropriate. Clearly this distance is well within the current IBD. Thus based both on the individual and group risk criteria, the existing MSER IBD prescription is more than adequate to ensure a high level of safety for persons living, working or travelling near an area where an ISO container packed with mass-exploding fireworks of the type described in this paper is located.

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# Movement Dynamics Of Firework Shells Fired From Mortars

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**Abstract:** *Experimental investigations were carried out using 125 and 310 mm firework shells. The pressures in a mortar during firing were measured. A mathematical model of the firing action concerning low pressure in the space behind the shell was developed. Here it is supposed that non-simultaneous processes of ignition and combustion of black powder particles as well as outflow of combustion materials through the gap between the shell and mortar walls limit the pressure increase. We determined the usage limit of zero-dimensional mathematical models of firing, defined kinetic characteristics for the process of flame spreading through black powder particles, analyzed the results and carried out a comparison between the calculated and experimental results of shots for firework shells of 125 and 310 mm. The calculation results were used to design 2A85 self-propelled mountings for launching shells with integral lifting charge and for the improvement of 2A30 self-propelled mountings for launching shells with integral lifting charge.*

**Keywords:** *Mathematical model, firework, ignition, combustion, flame, powder, muzzle velocity, self-propelled launcher, shell, self-propelled mounting*

## Introduction

In this work we report the experimental results and the simulation of firework movement in firing from a mortar. It is supposed that the pressure is produced in the process of non-simultaneous ignition and combustion of black powder particles and this is followed by outflow of combustion materials through the gap between the shell and the mortar walls. In this case the pressure does not exceed several tens of bars. In firing fireworks from mortars, approaches developed for artillery are usually used. This problem differs from the traditional problems of firing artillery shells. In weapons, where charge density is rather high, the conditions for momentary ignition of powder particles arise. Under the conditions of fast increasing pressure (to about several thousand bar) powder particles burn down the space behind a shell more quickly than the shell comes out from the barrel. Nevertheless, for analysis of the problem under present consideration a traditional statement of the problem of artillery shells is used as a rule with the introduction of some factors that allow fitting theoretical results to the experimental data. To obtain experimentally based results the definition and solution of the problem regarding fireworks fired from a mortar must be considered

taking into consideration the basic features of the processes going on during firing. The necessity of its fulfillment is mainly defined by the practical value of results for understanding the ongoing physical processes and for making soundly based decisions for the development of firework shells and mortars for launching them.

## Definition of the problem of artillery firing

Reasonable usage of this or that model is worth evaluating to determine the limits of application of different approaches to solving the problem posed. So, the theoretical study of the artillery firing process is supposed to use a traditional model. One of such models describing the shot process in a thermodynamic approximation is represented.<sup>1</sup> According to this model the kinetic characteristics of the shell can be found from the solution of the following combined equations, including the fundamental equation of pyrodynamics (1), the charge burning law (2), gas formation law (3), and the equation of shell motion (4):

$$PS(l_{\psi} + x) = f m \psi - \frac{k-1}{2} \phi M V^2 \quad (1)$$

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$$\frac{de}{dt} = a_1 P \quad (2)$$

$$\psi = \chi z + \lambda z^2 \quad (3)$$

$$\varphi M \frac{dV}{dt} = PS \quad (4)$$

where  $x$  = firework path inside the barrel,  $V$  = shell velocity,  $P$  = pressure of combustion materials in the space behind the shell,  $\frac{de}{dt}$  = speed of black

powder combustion,  $S$  = barrel cross-section area,  $M$  = shell mass,  $m$  = lifting charge mass,

$$l_\psi = \frac{1}{S} \left( W - \frac{(1-\psi)m}{\rho} - \alpha m \psi \right) = \text{free}$$

reduced length of space behind the shell,  $\psi$  = proportion of the powder that becomes gas,  $m\psi$  = gas mass,  $\alpha$  = covolume,  $\rho$  = powder density,  $W$  = chamber volume,  $f$  = powder force,  $k = c_p/c_v$ ,  $c_p$  and  $c_v$  = specific heat capacities under constant pressure and volume,  $a_1$  = combustion rate of powder under  $P = 1$  bar,  $\varphi = 1.05$  to  $1.1$  = factor experimentally determined in other work,  $z = e/e_0$  = thickness ratio of powder,  $e$ ,  $e_0$  = current and initial thickness of powder,  $e\chi$ ,  $\lambda$  = factors characterizing the form of powder particles. The adequacy of the proposed model was proved<sup>1</sup> by comparison of the shell velocity on exiting the barrel and the maximum pressure of combustion materials in the barrel with the appropriate values obtained experimentally. Under conditions of low pressure in the space behind the shell in combined equations (1)–(4), as a rule an additional factor  $\phi$  is used with the help of which one attempts to take into consideration the non-simultaneity of powder particle ignition and outflow of combustion materials through the gap between the shell and the mortar walls. At that point the factor of outside forces becomes:  $\phi = \phi \times (1.05 \text{ to } 1.1)$ . The value of  $\phi$  in each individual case is found from comparison of the experimental data on pressure measurement in the barrel with the calculation results. And if it is possible to achieve satisfactory coincidence of the pressure values with the experimental results in the middle of the process in terms of time, then during the initial moments the calculated values greatly exceed the data obtained in the course of

the experiment. The use in practice of such estimated values for firing results particularly in an inevitable weight increase and rise in price of mortars for fireworks, the impossibility of calculating the lifting charge mass for shells, and as a consequence difficulty in achieving the necessary burst height of the shell.

One of the possible reasons for the disagreement between the values obtained in the course of calculation and those determined by experiment lies in the averaging methods that were used in the definition of the problem. The pressures included in equations (1) and (4) are considered to be equal although in equation (1) it is a value that was averaged over the volume of the space behind the shell, and in equation (4) it is a value that is effective at the boundary between the space behind the shell and the volume occupied by the shell. The use of equations (1) and (4) together indirectly implies homogeneity of pressure in the space behind the shell, i.e. some average of medium parameters.

There are detailed discussions<sup>2</sup> on the use of average processes in solving problems of gas dynamics. It is indicated there that “by every average, i.e. by reducing of parameter number characterizing the flow, not all the properties of considerably uneven flow can be retained; some of these properties are lost during average, therefore in some cases average is impossible at all, in other cases the number of parameters describing average flow can differ”. Under these constraints the evaluation of pressure inhomogeneity in the space behind the shell is carried out. The gas flow equation (gaseous combustion materials of powder and oxide particles are considered to be so small that they have the speed and temperature of the gas) has the appearance:

$$\rho \frac{dv}{dt} = - \frac{\partial P}{\partial x} \quad (5)$$

Here  $\rho$  = gas and particle flow density,  $v$  = its speed,  $x$  = longitudinal coordinate,  $t$  = time. For the velocity of sound the following relation is used:<sup>5</sup>  $a^2 = kP/\rho$ ; from which the density is found and substituted into the equation of motion (5). The equation becomes of the form:

$$\frac{dv}{dt} = -\frac{a^2}{kP} \cdot \frac{\partial P}{\partial x} \quad (6)$$

In order to get the final expression the resulting equation can be written:

$$\frac{P_2 - P_1}{P_0} \approx -k \frac{v_e^2}{a^2} \quad (7)$$

Here  $P_0$ ,  $P_1$ ,  $P_2$  = average pressure in the space behind the shell, in the base of the barrel and on the surface of the shell,  $v_e$  = average velocity of the gas flow in the cross-section of the barrel near to the shell. For an artillery shell  $v_e$  is the movement velocity of the shell.

It follows from the ratio (7) that pressure inhomogeneity in the mortar is proportional to the square of the speed of the shell and inversely proportional to the speed of sound in the combustion materials. The equation (7) actually establishes the limits of applicability of zero-dimensional problems of gas dynamics in mathematical modeling of a shot from a mortar or from an artillery barrel. The essence of these restrictions lies in the finite nature of the rate of information in the volume of gas. A shell that moves through the barrel at supersonic speed is not affected by pressure changes in the base of the barrel.

Since the muzzle velocity of a firework is less than  $200 \text{ m s}^{-1}$ , the error in pressure determination in equation (4) does not exceed 4–6%. Thus the disagreement between experimental data and calculated results is determined by:

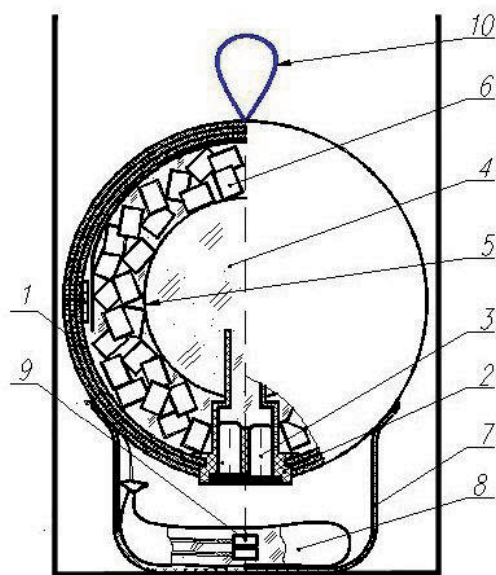
- 1 the non-simultaneous nature of ignition of the powder particles in the space behind the shell;
- 2 the outflow of powder combustion materials through the gap between the shell and mortar walls.

This article is devoted to the analysis and detailed description of the processes accompanying firework shots under specified conditions.

### **Problem of powder combustion polydisperse mode**

The investigation relates to mortars that consist of a metal pipe with a welded bottom. The shell with an attached container where the lifting charge in the form of a powder sack is situated is inserted in the mortar (see Figure 1). After actuation of the ignition device, ignition and combustion of some part of the powder particles on reaching destruction pressure inside the container, the combustion action spreads in the space under the shell. As a result of the pressure from the combustion of the lifting charge, the firework moves along the mortar barrel till the moment it emerges into the atmosphere. After leaving the barrel the shell does not accelerate any further.

The area where the parameters of the problem are determined is the volume (Figure 1) bounded by the inner surface of the barrel, the lower surface of the firework shell and the cross section of the barrel axis that has minimum clearance between the firework shell and the barrel (critical section). One or two electric matches activate the black powder in the lifting charge. At the initial moment only some part of the powder charge ignites. With time the flame spreads along the whole powder charge involving more and more powder particles



**Figure 1.** 1 – Firework shell; 2 – Pipe; 3 – Delay mechanism; 4 – Ignition-bursting charge (IBC); 5 – Casing of IBC; 6 – Pyroelements; 7 – Lifting charge container; 8 – Lifting charge (LC); 9 – Electric match; 10 – Loop.

in combustion. Gaseous and condensed products of powder combustion are formed. The mass fraction of condensed material is quite substantial – 0.56 – and it must be considered in the process of analysis. It is suggested that the particles in the condensed phase are of a size at which it is possible to assume that both gas and condensed phases have the same temperature and velocity. Under the pressure influence of the gaseous products of powder combustion the firework moves and is ejected into the atmosphere. At that point a proportion of the combustion products emerge into the atmosphere through the gap between the firework shell and the inner surface of the barrel, reducing the pressure level in the space behind the shell. The parameters of the suggested model are defined from the solution of the following combined equations consisting of the mass change equation (8), energy equation (9), equation of firework motion (10) and equation of state (11):

$$\frac{dm}{dt} = \dot{\psi} - G \quad (8)$$

$$\frac{d(mu)}{dt} = -P \frac{dv}{dt} + \dot{\psi} u_0 - Gu \quad (9)$$

$$M \frac{dV}{dt} = PS_u \quad (10)$$

$$P = (1 - \varepsilon)(m/v)(Ru/c_{vg}) \quad (11)$$

Here  $m$  = mass of powder combustion products,  $\varepsilon$  = fraction of powder combustion products in the condensed phase,  $\dot{\psi}$  = mass input of powder combustion products per unit of time,  $G$  = mass flow of powder combustion products through the surface of critical section,  $u$  = internal energy per mass unit of combustion products,  $u_0 = c_v T_{\text{comb}}$ ,  $c_v$  = specific heat of combustion products under constant volume,  $T_{\text{comb}}$  = combustion temperature of powder,  $v$  = the volume occupied by powder combustion products, defined by the relation:  $v = W - m_p/\rho_p + Sx$ ;  $W$  = volume under the shell at initial time,  $m_p$  – mass of unburnt powder,  $\rho_p$  = powder density,  $S$  = cross-section area of the barrel,  $x$  = firework path inside the barrel,  $S_u$  = cross-section area of firework shell,  $P$  = pressure in the space behind the shell,  $R$  = gas constant in gas phase of powder combustion products,  $c_{vg}$  =

specific heat in the gas phase of combustion products at constant volume.

In order to define the function  $\dot{\psi}$  a number of assumptions were made. It is supposed that powder particles are of spherical form, with a particle diameter of  $2r = 1$  mm. After actuation of ignition initiators some part  $N_0$  of the powder particles is ignited. From the burning powder the flame spreads to the rest of the particles. It is supposed that the burning and unburnt powder particles are evenly distributed within the space behind the shell and the volume occupied by the particles is relatively small in comparison with the volume where powder combustion occurs. The mechanism of flame spreading through the particles is represented in the form:

$$\frac{dN}{dt} = \alpha_1 \cdot N \cdot (P/P_0)^{\alpha_2} \quad (12)$$

*i.e.* the number of inflammable particles per unit volume is proportional to the number of burning particles per unit volume and pressure of combustion products. Here  $\alpha_1$  and  $\alpha_2$  are constants determined in the course of the experiment. At the initial moment all the particles are of the same size. The mixture is monodisperse. As the flame spreads some particles are ignited, others cease burning. Therefore for the treatment of powder particle combustion it is necessary to use the polydisperse medium model. Equation (12) determines the mechanism of formation of particles of burning powder. Here the function  $\delta_i$  is introduced for different fractions of powder. This function is equal to one if the fraction is burning and equal to zero if the burning has not yet begun or is already finished. The number of fraction  $i$  of particles being ignited is found by integration of equation (12) with respect to time  $[t_i, t_{i+1}]$ :

$$N_i = \alpha_1 \int_{t_i}^{t_{i+1}} \left( \sum_{j=0}^{i-1} (\delta_j \cdot N_j) \right) (P/P_0)^{\alpha_2} dt \quad (13)$$

Here  $i = 1 \dots J_k$ ,  $t_i = i\Delta$ ,  $t_k = J_k\Delta$ ,  $t_k$  is the time at the

end of the process. Equation (13) is true if  $\sum_{j=0}^{i-1} N_j$

is less or equal to particle number, otherwise  $N_i = 0$ . Following Nigmatulin<sup>3</sup> we consider that unitary fuels to which powder and explosive substances refer contain within them not only “fuel” in particular but also an oxidizing agent “mixed” with the fuel on a molecular level; so they represent a condensed solid homogeneous mixture of “fuel” and oxidizing agent. The linear combustion velocity of powder and other types of unitary fuel depends on the pressure. The corresponding empirical dependence has the form as stated by Zeldovich:<sup>4</sup>

$$\frac{dr_i}{dt} = -b_1 (P / P_0)^{b_2} \quad (14)$$

where  $b_1$  and  $b_2$  are empirical constants, individual for each type of fuel.

For the powder involved:  $b_1 = 12.1 \text{ mm s}^{-1}$ , and  $b_2 = 0.24$ , under  $P < 60 \text{ MPa}$ .

At particle combustion of fraction  $i$  the value of  $r_i$  becomes zero. At the same instant the function  $\delta_i$  becomes zero as well. For the function  $\psi$  the following expression can be written:

$$\dot{\psi} = 4\pi\rho \cdot \sum_i \delta_i \cdot N_i \cdot r_i^2 \cdot \left| \frac{dr_i}{dt} \right| \quad (15)$$

where the sum is carried out on all the fractions.

The function  $G$  is found according to Abramovich<sup>5</sup> the solution about combustion materials outflow from supersonic nozzle. A similar problem is examined by Weinman.<sup>6</sup> A supersonic nozzle must consist of convergent (subsonic) and divergent (supersonic) parts. In the narrowest section of a supersonic nozzle (critical section) the flow velocity is equal to the sonic velocity in the combustion materials. The flow of gas or gas mixture through the critical section is determined from the relation:

$$G = \frac{PF_{kp}}{\sqrt{T}} \left( \frac{2}{k+1} \right)^{\frac{k+1}{2(k-1)}} \left( \frac{k}{R} \right)^{0.5} \quad (16)$$

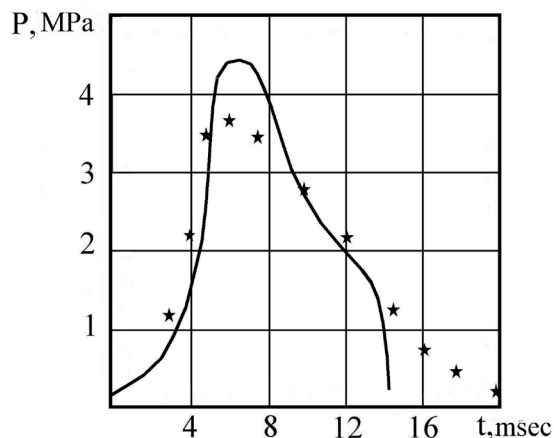
Here  $F_K$  is the critical section between firework product and barrel wall,  $P$ ,  $T$  = pressure and temperature of the gas in the space outside the shell,  $R$  is the gas constant. The constant for the mixture of powder combustion products is  $k \approx 1.1$ . From Zeldovich<sup>4</sup> it follows that supersonic flow of powder combustion products begins at  $P > 1.63 P_0$ . In practice under the conditions of the shot this value is achieved immediately.

Combining equations (8)–(16) allows the solution of the problem of a shell fired from a gun barrel taking into consideration the non-simultaneity of powder particle ignition and combustion, and the outflow of powder combustion products through the gap between the shell and the inner wall of the gun during the shot.

## Practical use of the solution method developed

The solution of this problem was used for the study of firework shells fired from a mortar barrel and for the design of shells. High-altitude firework shells manufactured in the Russian Federation are subdivided into two groups. One group includes shells of caliber 195 and 310 mm operating at a height of 250–500 m and capable of creating large figures in the sky from several types and sizes of pyro elements. The other group includes shells of caliber 60 mm and 105 mm with operational heights up to 150 m, and these may be equipped with only one type of pyro element because of the size of the shells. In order to make firework displays more attractive it is necessary to have shells that can operate at a height of 150–250 m and form very large figures. The public corporation “Piro-Ross” has developed a firework shell that can achieve this sort of result. The relevance of the development of shells of caliber 125 mm is also determined by the fact that mortars of this caliber can be used for firing existing shells from self-propelled mountings 2A30 for launching shells with integral lifting charge without any change in the main structural features of the shells. Before shell development began, calculation research was carried out. For that the constants including



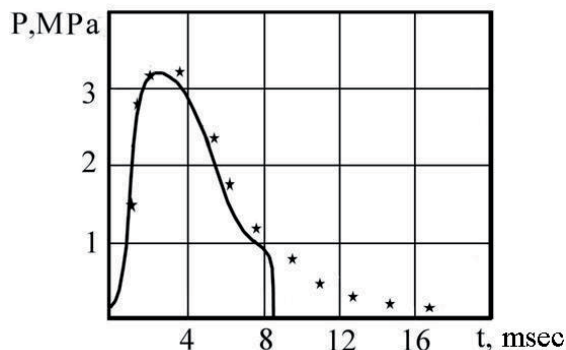


**Figure 2.** Pressure measured in the lower part of the mortar for a 310 mm shell. Asterisks indicate experimental results and the solid line indicates calculated values.

in equation (12) were found at the initial stage. The product with a caliber of 310 and 125 was experimentally more thoroughly examined. Experimental results were used to determine the constants  $N_0$ ,  $\alpha_1$  and  $\alpha_2$  which were determined by the gradient method from the solution created with the help of the model equations (8) – (16).

Figure 2 shows the results of measuring combustion product pressure in the bottom part of the barrel for a 310 mm firework. Asterisks show the experimental results. The solution showed that ~68 g powder out of the total mass of 700 g is ignited by the electric match at the initial moment. The values  $\alpha_1$  and  $\alpha_2$  are respectively equal to 22 and 1.95. The calculation for a firework of 125 mm caliber presented in Figure 3 shows that the kinetic constants retain their values whereas the mass of powder being ignited at the initial moment depends on the caliber of the shell. The mass is equal to 35 g out of the total mass 70 g for a 125 mm firework. The kinetics of ignition and combustion of powder particles represent those during the firing process for a 310 mm firework ~90% of the lifting charge is burnt off. The rest of the burning powder particles and combustion products fly out into the atmosphere from the mortar barrel after the firework shell and create a burning smoky cloud.

## Conclusion



**Figure 3.** Pressure measured in the lower part of the mortar for a 125 mm shell. Asterisks indicate experimental results and the solid line indicates calculated values.

We developed a model for firing of fireworks from mortar barrels under conditions of low pressure in the space outside the shell which originates from the non-simultaneity of powder particle ignition and combustion and the outflow of powder combustion products through the clearance between the firework and the inner wall of the mortar barrel. Comparison of the results of the calculation with the experimental data showed that the model could be applied to a wide variety of firework shells used in civilian pyrotechnics. In particular the calculation results from the research allow the conclusion that for functioning of a 125 mm firework at a height of 150–250 m it is enough to use a lifting charge with 72 g powder and a mortar of barrel length 450 mm in the firework setup. The experimental results demonstrated the adequacy of mass of powder used for the lifting charge of the 125 mm firework and the parameters of the launcher. The use of this product will offer the chance to create more colorful and varied firework pictures in the night sky using improved 2A30 self-propelled mountings and new 2A85 self-propelled mountings without increasing the danger areas or changing the foundations of 2A30 self-propelled mountings.

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# Comparison of 6-DOF Trajectory Model with Modified Linear Theory for Bullets

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**Abstract:** *A modified linear model is proposed for fast and accurate prediction of short and long-range trajectories of spin-stabilized bullets via atmospheric flight to a final impact point. This model is compared with a full 6-DOF trajectory model. The computational flight analysis takes into consideration the Mach number and total angle of attack effects by means of the variable aerodynamic coefficients.*

**Keywords:** *Low and high pitch angles, projectile trajectory, variable aerodynamic coefficients*

## Introduction

External ballistics<sup>1</sup> deals with the behavior of a non-powered projectile in flight. Several forces act upon the projectile during this phase including gravity and air resistance.

Various authors have extended the projectile model for lateral force impulses,<sup>2</sup> as well as aerodynamic jump extending analysis due to lateral impulses<sup>3</sup> and aerodynamic asymmetry,<sup>4</sup> instability of controlled projectiles in ascending or descending flight.<sup>5</sup> Costello's modified linear theory<sup>6</sup> has also been applied recently for rapid trajectory projectile prediction.

The present work proposes several modifications to the full six degrees of freedom (6-DOF) theory that significantly improve the accuracy of impact point prediction of short and long range trajectories with variable aerodynamic coefficients of spin-stabilized bullets. For the purposes of the analysis, linear interpolation has been applied from the tabulated database of McCoy's text.<sup>1</sup>

## Projectile model

The present analysis considers a 0.30 caliber

(0.308 inch diameter), 168 grain (~10.9 g) Sierra International bullet used by National Match M14 rifle and loaded into 7.62 mm M852 match ammunition for high power rifle competition shooting, as shown in Figure 1. This bullet is not for combat use. The basic physical and geometrical characteristic data of the above mentioned 7.62 mm bullet are illustrated briefly in Table 1.

## Trajectory flight simulation model

A six degrees of freedom rigid-projectile model<sup>7-10</sup> has been employed in order to predict the "free"



**Figure 1.** 7.62 mm match ammunition with a diameter of 0.30 caliber: representative small bullet types.

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**Table 1.** Physical and geometrical data of 7.62 mm bullet type.

Characteristics	7.62 mm M852 bullet
Reference diameter/mm	7.62
Total length/mm	71.88
Total mass/kg	0.385
Axial moment of inertia/kg m <sup>2</sup>	$7.2282 \times 10^{-8}$
Transverse moment of inertia/kg m <sup>2</sup>	$5.3787 \times 10^{-7}$
Center of gravity from the base/mm	12.03

nominal atmospheric trajectory to final target area without any control practice runs. The six degrees of freedom in the flight analysis comprise the three translation components ( $x$ ,  $y$ ,  $z$ ) describing the position of the projectile's center of mass and three Euler angles ( $\varphi$ ,  $\theta$ ,  $\psi$ ) describing the orientation of the projectile body as shown in Figure 2. Two main coordinate systems are used for the computational approach of the atmospheric flight motion. The one is a plane fixed (inertial frame, IF) at the firing site. The other is a no-roll rotating coordinate system on the projectile body (no-roll-frame, NRF,  $\varphi = 0$ ) with the  $X_{\text{NRF}}$  axis along the projectile axis of symmetry and  $Y_{\text{NRF}}$ ,  $Z_{\text{NRF}}$  axes oriented so as to complete a right hand orthogonal system. If the independent variable is changed from time  $t$  to dimensionless arc length  $l$  measured in calibers of travel:

$$l = \frac{1}{D} s = \frac{1}{D} \int_0^t V_T dt \quad (1)$$

Equations (2)–(13) are the 6-DOF atmospheric equations of motion expressed in the no-roll frame.

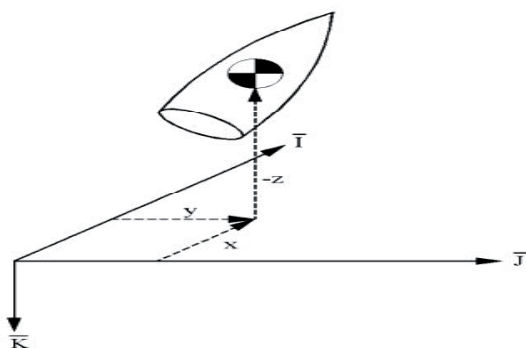
The aerodynamic coefficients  $C_D$ ,  $C_{L\alpha}$ ,  $C_{MPA}$ ,  $C_{MQ}$ ,  $C_{MA}$  used in this model are projectile-specific functions of the Mach number and total angle of attack variations.

The projectile dynamics trajectory model consists of twelve non-linear first order ordinary differential equations, which are solved simultaneously by resorting to numerical integration using a 4th order Runge–Kutta method and with regard to the 6-D nominal atmospheric motion.

### Modified trajectory model

Modified linear theory<sup>10,15</sup> makes several assumptions regarding the relative size of different quantities to further simplify the analysis: the Euler angle  $\psi$  is small so  $\sin \psi \approx \psi$ ,  $\cos \psi \approx 1$ . The axial velocity  $\tilde{u}_{\text{NRF}}$  is replaced by the total velocity  $V_T$  because the side velocities  $\tilde{v}_{\text{NRF}}$  and  $\tilde{w}_{\text{NRF}}$  are small. The aerodynamic angles of attack  $\alpha$  and sideslip  $\beta$  are small for the main part of the atmospheric trajectory.

The projectile is mass-balanced such that  $I_{XY} = I_{YZ} = I_{XZ} = 0$ ,  $I_{YY} = I_{ZZ}$ . Quantities  $V_T$  and  $\varphi$  are large compared to  $\psi$ ,  $\tilde{q}_{\text{NRF}}$ ,  $\tilde{r}_{\text{NRF}}$ ,  $\tilde{v}_{\text{NRF}}$  and  $\tilde{w}_{\text{NRF}}$ , such that products of small quantities and their derivatives are negligible. In projectile linear theory, the Magnus forces in equations (9) and (10) are typically regarded as small and dropped. Magnus moments are due to the fact that a cross



**Figure 2.** No-roll (moving) and earth-fixed (inertial) coordinate systems for the projectile trajectory analysis.

$$x'_{\text{IF}} = \frac{D}{V_T} \cos \psi \cos \theta \tilde{u}_{\text{NRF}} - \frac{D}{V_T} \sin \psi \tilde{v}_{\text{NRF}} + \frac{D}{V_T} \cos \psi \sin \theta \tilde{w}_{\text{NRF}} \quad (2)$$

$$y'_{\text{IF}} = \frac{D}{V_T} \cos \theta \sin \psi \tilde{u}_{\text{NRF}} + \frac{D}{V_T} \cos \psi \tilde{v}_{\text{NRF}} + \frac{D}{V_T} \sin \psi \sin \theta \tilde{w}_{\text{NRF}} \quad (3)$$

$$z'_{\text{IF}} = -\frac{D}{V_T} \sin \theta \tilde{u}_{\text{NRF}} + \frac{D}{V_T} \cos \theta \tilde{w}_{\text{NRF}} \quad (4)$$

$$\varphi' = \frac{D}{V_T} \tilde{p}_{\text{NRF}} + \frac{D}{V_T} \tan \theta \tilde{r}_{\text{NRF}} \quad (5)$$

$$\theta' = \frac{D}{V_T} \tilde{q}_{\text{NRF}} \quad (6)$$

$$\psi' = \frac{D}{V_T \cos \theta} \tilde{r}_{\text{NRF}} \quad (7)$$

$$\tilde{u}'_{\text{NRF}} = -\frac{D}{V_T} g \sin \theta - L_1 V_T C_D + \tilde{v}_{\text{NRF}} \frac{D}{V_T} \tilde{r}_{\text{NRF}} - \tilde{q}_{\text{NRF}} \frac{D}{V_T} \tilde{w}_{\text{NRF}} \quad (8)$$

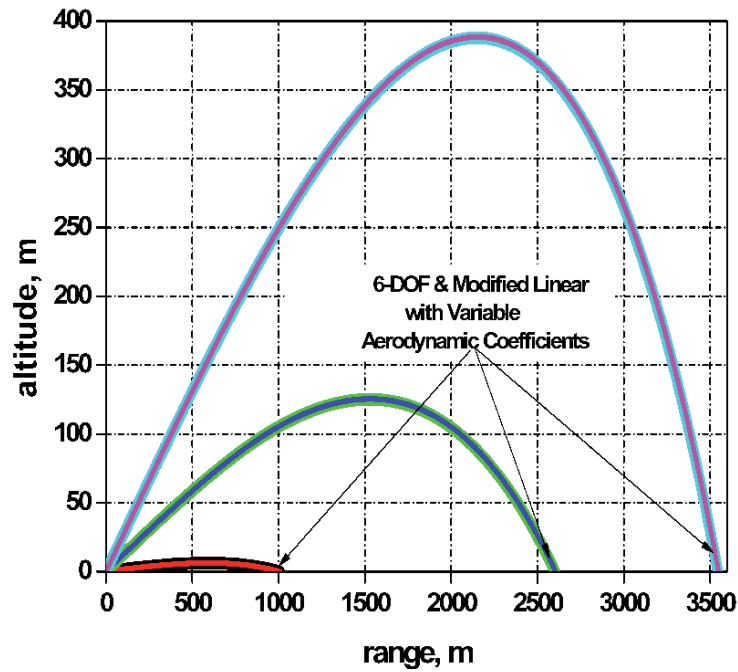
$$\tilde{v}'_{\text{NRF}} = -L_1 (C_{\text{La}} + C_D) \tilde{v}_{\text{NRF}} - \frac{D}{V_T} \tilde{r}_{\text{NRF}} \tilde{w}_{\text{NRF}} \tan \theta - \frac{D}{V_T} \tilde{u}_{\text{NRF}} \tilde{r}_{\text{NRF}} \quad (9)$$

$$\tilde{w}'_{\text{NRF}} = \frac{D}{V_T} g \cos \theta - L_1 (C_{\text{La}} + C_D) \tilde{w}_{\text{NRF}} + \tilde{u}_{\text{NRF}} \frac{D}{V_T} \tilde{q}_{\text{NRF}} + \tan \theta \frac{D}{V_T} \tilde{r}_{\text{NRF}} \tilde{v}_{\text{NRF}} \quad (10)$$

$$\tilde{p}'_{\text{NRF}} = D^5 \frac{\pi}{16 I_{XX}} \tilde{p}_{\text{NRF}} \rho C_{\text{LP}} \quad (11)$$

$$\begin{aligned} \tilde{q}'_{\text{NRF}} = & 2L_2 (C_{\text{La}} + C_D) \tilde{w}_{\text{NRF}} L_{\text{CGCP}} + D \frac{L_2}{V_T} C_{\text{MPA}} \tilde{p}_{\text{NRF}} \tilde{v}_{\text{NRF}} L_{\text{CGCM}} + \\ & + D^2 L_2 C_{\text{MQ}} \tilde{q}_{\text{NRF}} + 2D L_2 C_{\text{MA}} - \frac{D}{V_T} \tilde{r}_{\text{NRF}} \frac{I_{XX}}{I_{YY}} \tilde{p}_{\text{NRF}} - \frac{D}{V_T} \tilde{r}_{\text{NRF}}^2 \tan \theta \end{aligned} \quad (12)$$

$$\begin{aligned} \tilde{r}'_{\text{NRF}} = & -2L_2 (C_{\text{La}} + C_D) \tilde{v}_{\text{NRF}} L_{\text{CGCP}} + D \frac{L_2}{V_T} \tilde{p}_{\text{NRF}} C_{\text{MPA}} \tilde{w}_{\text{NRF}} L_{\text{CGCM}} + \\ & + D^2 L_2 C_{\text{MQ}} \tilde{r}_{\text{NRF}} - 2D L_2 C_{\text{MA}} + \frac{D}{V_T} \tilde{p}_{\text{NRF}} \tilde{q}_{\text{NRF}} \frac{I_{XX}}{I_{YY}} + \frac{D}{V_T} \tilde{q}_{\text{NRF}} \tilde{r}_{\text{NRF}} \tan \theta \end{aligned} \quad (13)$$



**Figure 3.** Flight paths of 7.62 mm bullet at pitch angles of 1, 7 and 15 degrees for 6-DOF and modified linear models.

product between the Magnus force and its respective moment arm is not necessarily small. With the aforementioned assumptions, the above expressions results in equations (2i)–(13i):

The equations 5, 6, 7 and 11 remain invariable.

The modified linear trajectory model runs at faster time with variable aerodynamic coefficients than the corresponding full 6-DOF analysis. On the other hand 6-DOF gives results of high accuracy trajectory prediction.

$$x'_{\text{IF}} = D \cos \theta \quad (2\text{i})$$

$$y'_{\text{IF}} = D \cos \theta \psi \quad (3\text{i})$$

$$z'_{\text{IF}} = -D \sin \theta \quad (4\text{i})$$

$$V'_T = -\frac{D}{V_T} g \sin \theta - L_1 V_T C_D \quad (8\text{i})$$

$$\tilde{v}'_{\text{NRF}} = -L_1 (C_D + C_{\text{La}}) (\tilde{v}_{\text{NRF}} - \tilde{v}_w) - D \tilde{r}_{\text{NRF}} \quad (9\text{i})$$

$$\tilde{w}'_{\text{NRF}} = \frac{D}{V_T} g \cos \theta - L_1 (C_D + C_{\text{La}}) (\tilde{w}_{\text{NRF}} - \tilde{w}_w) + D \tilde{q}_{\text{NRF}} \quad (10\text{i})$$



$$\begin{aligned}\tilde{q}'_{\text{NRF}} = & 2L_2 (C_D + C_{La})(\tilde{w}_{\text{NRF}} - \tilde{w}_w)L_{\text{CGCP}} + \\ & + D \frac{L_2}{V_T} C_{\text{MPA}} \tilde{p}_{\text{NRF}} (\tilde{v}_{\text{NRF}} - \tilde{v}_w)L_{\text{CGCM}} + \\ & + D^2 L_2 C_{\text{MQ}} \tilde{q}_{\text{NRF}} + 2DL_2 C_{\text{MA}}\end{aligned}\quad (12i)$$

$$\begin{aligned}\tilde{r}'_{\text{NRF}} = & -2L_2 (C_D + C_{La})(\tilde{v}_{\text{NRF}} - \tilde{v}_w)L_{\text{CGCP}} + \\ & + D \frac{L_2}{V_T} \tilde{p}_{\text{NRF}} C_{\text{MPA}} (\tilde{w}_{\text{NRF}} - \tilde{w}_w)L_{\text{CGCM}} + \\ & + D^2 L_2 C_{\text{MQ}} \tilde{r}_{\text{NRF}} - 2DL_2 C_{\text{MA}}\end{aligned}\quad (13i)$$

## Atmospheric model

Atmospheric properties of air, like density  $\rho$ , are being calculated based on a standard atmosphere from the International Civil Aviation Organization (ICAO).

## Computational simulation

The flight dynamic model of a 7.62 mm bullet involves the solution of the set of twelve first order ordinary differentials for two trajectories with variable aerodynamic coefficients, first the full 6-DOF and second with simplifications for the modified trajectory, Equations (2)–(13), which are solved simultaneously by resorting to numerical integration using a 4th order Runge–Kutta method. The six-degrees-of-freedom and the modified linear model numerical trajectories were computed by using a time step size of  $10 \times 10^{-3}$  s. Initial flight conditions for both dynamic flight simulation models are illustrated in Table 2 for the test cases examined.

## Results and Discussion

The flight path of 6-DOF trajectory motion<sup>1</sup> with variable<sup>11</sup> and no constant<sup>12</sup> aerodynamic coefficients of the 7.62 mm projectile with initial firing velocity of  $792.48 \text{ m s}^{-1}$ , rifling twist rate 1 turn in 12 inches (30 cm), at  $1^\circ$ ,  $7^\circ$  and  $15^\circ$ , are indicated in Figure 3. The calculated impact points of the above no-wind trajectories with the proposed variable aerodynamic coefficients are compared with accurate estimations of modified linear trajectory analysis and provide quite good prediction of the entirety of the atmospheric flight

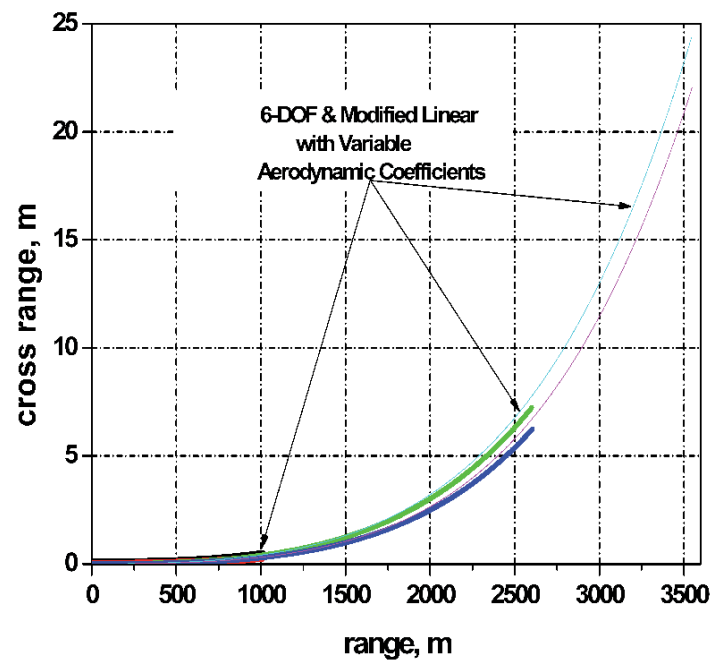
motion for the same initial flight conditions.

Figure 4 shows the crossrange flight path of a 7.62 mm bullet downrange distance for both methods with no big differences in low launch angle but differences in high angles. At 1, 7 and 15 degrees pitch angle for 6-DOF we have values of the crossrange as 3.94 cm, 7.2 m and 24.3 m, respectively. For the same initial conditions the modified theory has the values 3.9 cm, 6.9 m, and 22 m, respectively.

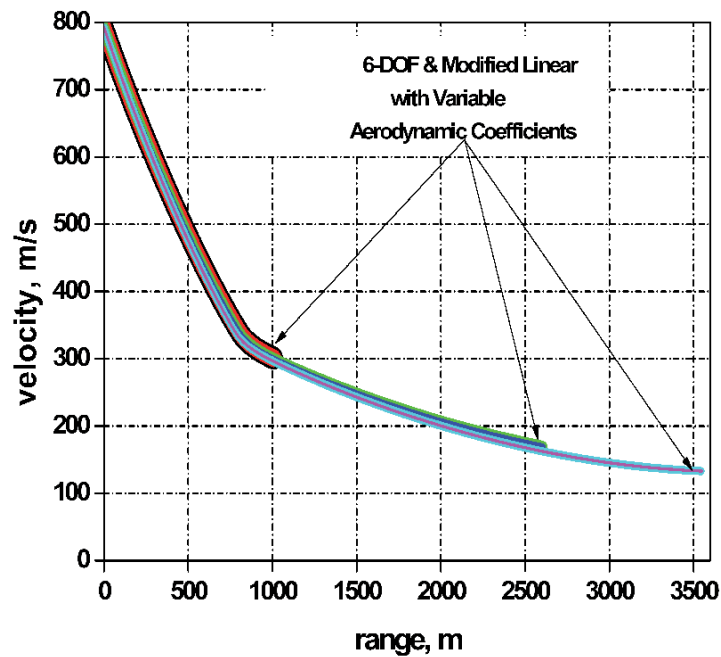
Figure 5 shows that the velocity *versus* range diagrams of the two methods, at initial pitch angles of 1, 7 and 15 degrees, have no differences. Figure 6 also shows that the trajectory analysis for the three roll rates is the same for the 7.62 mm

**Table 2.** Initial flight parameters of the bullet test case examined.

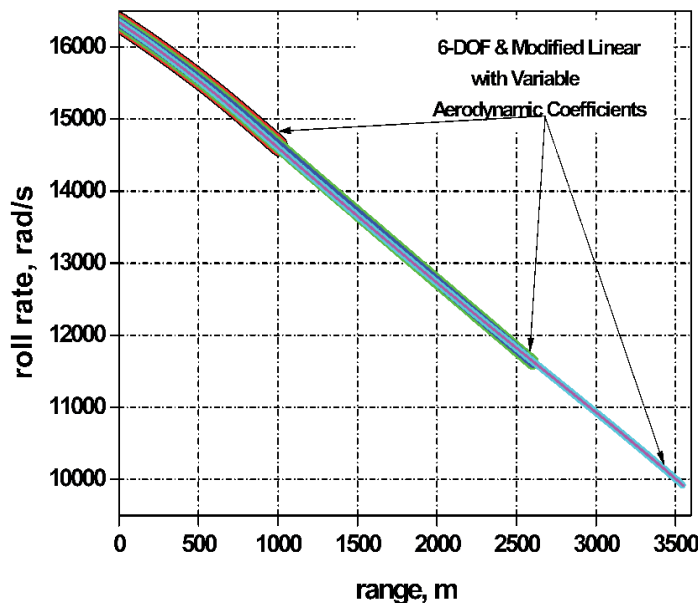
Initial flight data	7.62 mm M852 bullet
x/m	0.0
y/m	0.0
z/m	0.0
$\phi/\text{deg}$	0.0
$\theta/\text{deg}$	1, 7 and 15
$\psi/\text{deg}$	0.0
$u/\text{m s}^{-1}$	792.48
$v/\text{m s}^{-1}$	0.0
$w/\text{m s}^{-1}$	0.0
$p/\text{rad s}^{-1}$	16343.0
$q/\text{rad s}^{-1}$	0.0
$r/\text{rad s}^{-1}$	0.0



**Figure 4.** Crossrange versus downrange distance of 7.62 mm bullet for modified linear and 6-DOF models



**Figure 5.** Velocity versus range of 7.62 mm bullet for low and high pitch angles in the two trajectory models.



**Figure 6.** Roll rates versus range of 7.62 mm bullet for modified linear and 6-DOF models.

bullet with variable aerodynamic coefficients.

## Conclusion

The modified linear trajectory model was shown to provide reasonable impact predictions at short and long-range trajectories of high and low spin-stabilized bullets. Moreover, the modified model showed some differences at high pitch angles. However, the comparison between the 6-DOF and the modified trajectory model provided quite good results with the variable aerodynamic coefficients over the whole flight path. The computational results of the proposed synthesized analysis are in good agreement compared with other technical data and recognized exterior atmospheric projectile flight computational models.

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## Nomenclature

$C_D$	drag force aerodynamic coefficient
$C_{LP}$	lift force aerodynamic coefficient
$C_{La}$	roll damping moment aerodynamic coefficient
$C_{MQ}$	pitch damping moment aerodynamic coefficient
$C_{MA}$	overturning moment aerodynamic coefficient
$C_{MPA}$	Magnus moment aerodynamic coefficient
$x'_{if}, y'_{if}, z'_{if}$	projectile position coordinates in the inertial frame/m
$m$	projectile mass/kg
$D$	projectile reference diameter/m
$s$	dimensionless arc length
$V_T$	total aerodynamic velocity/m s <sup>-1</sup>
$\tilde{u}_{NRF}, \tilde{v}_{NRF}, \tilde{w}_{NRF}$	projectile velocity components expressed in the no-roll-frame/m s <sup>-1</sup>
$\tilde{u}_w, \tilde{v}_w, \tilde{w}_w$	wind velocity components in no-roll-body-frame/m s <sup>-1</sup>
$\tilde{p}_{NRF}, \tilde{q}_{NRF}, \tilde{r}_{NRF}$	projectile roll, pitch and yaw rates in the moving frame, respectively/rad s <sup>-1</sup>
$\rho$	density of air/kg m <sup>-3</sup>
$\varphi, \theta, \psi$	projectile roll, pitch and yaw angles, respectively/deg
$\alpha, \beta$	aerodynamic angles of attack and sideslip

$g$	gravity acceleration/m s <sup>-2</sup>
$I$	projectile inertia matrix
$I_{XX}$	projectile axial moment of inertia/kg m <sup>-2</sup>
$I_{YY}$	projectile transverse moment of inertia about y-axis through the center of mass/kg m <sup>2</sup>
$I_{XX}, I_{YY}, I_{ZZ}$	diagonal components of the inertia matrix
$I_{XY}, I_{YZ}, I_{XZ}$	off-diagonal components of the inertia matrix
$L_{CGCM}$	distance from the center of mass (CG) to the Magnus center of pressure (CM) along the station line/m
$L_{CGCP}$	distance from the center of mass (CG) to the aerodynamic center of pressure (CP) along the station line/m
$L_1, L_2$	dimensional coefficients, $\pi\rho D^3/8m$ and $\pi\rho D^3/16I_{YY}$ , respectively

# Metal–Fluorocarbon Pyrolants: VIII.<sup>1‡</sup> Behavior of Burn Rate and Radiometric Performance of two Magnesium/Teflon/Viton (MTV) Formulations upon Addition of Graphite§

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**Abstract:** The burn rate,  $u$  ( $\text{mm s}^{-1}$ ) of fuel rich magnesium/Teflon/Viton (MTV) is increased by 23–36 % upon addition of 5 wt% graphite whereas the spectral efficiency  $E_\beta$  ( $\text{J g}^{-1} \text{sr}^{-1}$ ) remains largely unaffected.

**Keywords:** Burn rate, graphite, magnesium, MTV, polytetrafluoroethylene, radiometry, Teflon<sup>TM</sup>, Viton<sup>TM</sup>

## Introduction

Magnesium/Teflon/Viton, better known as MTV, is the most widely used aerial infrared decoy flare material.<sup>1–4</sup> Its success is mainly based on the high spectral efficiency,  $E_\lambda$ , in both  $\alpha$  and  $\beta$  bands at sea level not reached by any other material. There have been numerous reports on the alteration of MTV combustion rate. Kuwahara has proposed applying zirconium as burn rate modifier to yield an increase in burn rate by factor  $\sim 1.4$  at 10 wt% Zr.<sup>5</sup> Nielson has proposed applying nanometric carbon fibres to enhance the burn rate by factor of  $\sim 1.11$  at 2 wt% fibres.<sup>6</sup> Shortridge and Wilharm reported the modification of MTV burn rate with nanometric aluminium (ALEX) and observed an increase in burn rate by factor of  $n \approx 1.44$  at  $\sim 27$  wt% ALEX.<sup>7</sup> All these methods have in common the application of very expensive materials thus restricting their use for small scale applications. Nadler has disclosed a method to improve the performance of MTV based flares by adding graphite to MTV but without further specifying the achieved rate of improvement.<sup>8</sup> Although based

on different chemistry the burn rate behaviour of magnesium sodium nitrate pyrolants is similar to MTV as they show the same dependency of burn rate on the weight fraction of magnesium.<sup>9,10</sup> Singh *et al.* have reported the influence of graphite on the burn rate of magnesium/sodium nitrate 70/30 pyrolant. They observed an increase in burn rate of  $\sim 1.15$  upon addition of 2 wt% graphite.<sup>11</sup>

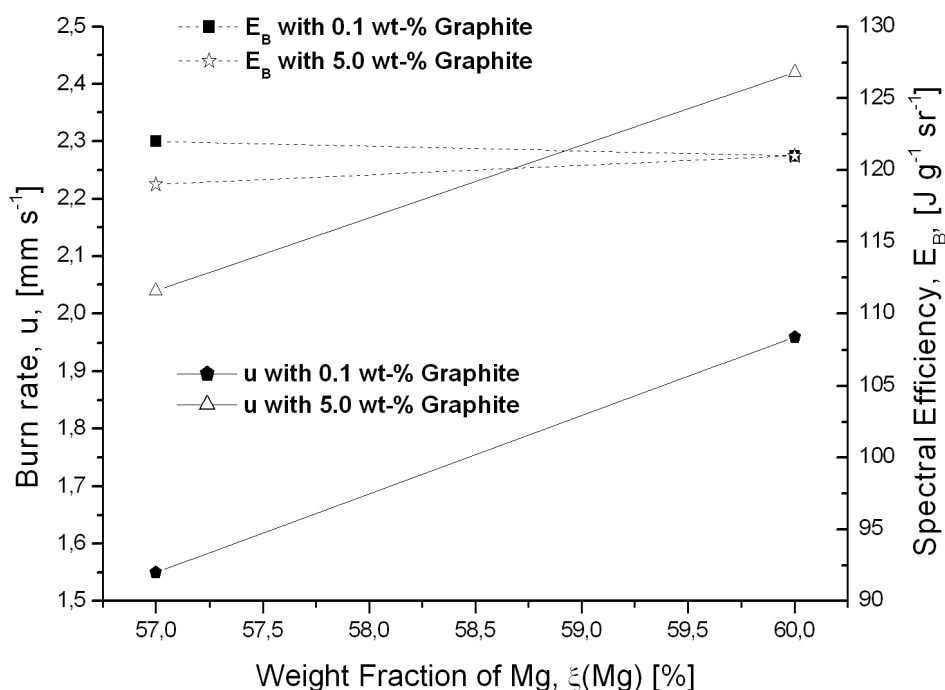
It was now decided to investigate the effect of addition of 5 wt% graphite on two fuel rich compositions having either 57 or 60 wt% magnesium, 10 wt% Viton binder and the remainder being polytetrafluoroethylene.

The compositions were prepared in 5 kg batches with conventional mixing in a 5 l planetary blender. Thus magnesium (non-ferrum Metallpulver, A-5111 St. Georgen, ECKA Mg-Pulver LNR-61, mean particle radius: 20  $\mu\text{m}$ ) and graphite (Edelgraphit GmbH, D-53175 Bonn, E 321) were wetted with acetone and mixed in a blender until a dark grey mass resulted. Addition of PTFE powder (Dyneon, D-84504 Burgkirchen, TF-9205, mean particle radius: 2  $\mu\text{m}$ ) and Viton (MACH I Inc, King of Prussia, USA, FC-2175) dissolved in acetone followed. Now the heating jacket of the blender was heated to  $\sim 40^\circ\text{C}$  and the mass was mixed until small granules had formed. These were spread on stainless steel drying pans and dried at reduced pressure at  $40^\circ\text{C}$  for 12 h.

<sup>‡</sup> For Part VII see ref. 1.

<sup>§</sup> This paper was presented as part of the lecture “Performance Modification of MTV” at the 6th Workshop on Pyrotechnic Combustion Mechanisms, July 12 2008, Fort Collins, USA.





**Figure 1.** Burn rate and spectral efficiency as a function of stoichiometry.

The compositions were pressed in a 22.4 mm cylindrical die with 100 MPa pressing pressure and 10 s hold time to give consolidated strands of 25 g mass. The lateral surfaces of the strands were wrapped in Kraft paper and the top face was applied with an ignition dip of boron, potassium nitrate, nitrocellulose (12/84/4) mix.

The pellets were placed between steel split pins on a brass cylinder and ignited by an electric igniter enhanced with a quickmatch fixed with adhesive tape on top of the strands.

The burn rate was measured with the timer of the video camera. The radiometric performance was determined in the  $\beta$ -band (3.5–4.8  $\mu\text{m}$ ) with an IR radiometric system (RM 6600 and un-cooled pyro-electric detector RkP 575 both from Laser Probe USA).

The burn rate of MTV generally is a function of stoichiometry and rises exponentially with increasing magnesium content between  $\xi(\text{Mg}) = 0.3\text{--}0.7$  as has been observed by Kuwahara,<sup>5</sup> Kubota<sup>12</sup> and Koch.<sup>1</sup> This behaviour is mainly

**Table 1.** Composition details.

Component	1	2	3	4
Magnesium	57	57	60	60
Polytetrafluoroethylene	28	32.9	25	29.9
Hexafluoropropene vinylidene fluoride copolymer	10	10	10	10
Graphite	5	0.1	5	0.1
Experimental density/ $\text{g cm}^{-3}$	1.75	1.76	1.71	1.73

**Table 2.** *Performance of compositions.*

Component	Unit	1	2	3	4
Burn rate	mm s <sup>-1</sup>	2.04	1.55	2.42	1.96
Increase factor	—	1.36	—	1.23	—
Spectral efficiency	J g <sup>-1</sup> sr <sup>-1</sup>	119	122	121	121

attributed to the increasing thermal conductivity of the pyrolant.<sup>13</sup> Hence it would seem logical to increase the condensed phase conductivity to achieve a higher burn rate.

Figure 1 shows burn rate and spectral efficiency as a function of stoichiometry. The burn rate observed for compositions **2** and **4** is significantly lower than those with equal magnesium content reported by the author earlier<sup>1</sup> (2–3 mm s<sup>-1</sup> versus 7–8 mm s<sup>-1</sup>). This is due to higher Viton content which is known to slow down the combustion rate<sup>14</sup> and due to the lower density of the latter samples.

The burn rate now increases by 36 and 23% upon addition of 5 wt% graphite. Interestingly the reduction in fluorine content due to the lower PTFE content affects neither burn rate nor spectral efficiency. This is in accord with findings that substitution of Viton binder for thermoplastic polystyrene does not decrease the performance of magnesium/PTFE pyrolants either.<sup>15</sup>

The burn rates and radiometric performances for the pyrolants are given in Table 2.

With the graphite modified Mg/NaNO<sub>3</sub> pyrolant Singh *et al.* speculated that graphite would oxidise at the surface of the strand and thus contribute to the heat of combustion and hence alter the burn rate.<sup>11</sup> In view of the negative oxygen balance of Mg/NaNO<sub>3</sub> (70/30),  $\Delta = -31.95\%$  oxidation of carbon directly at the strand surface appears very unlikely. Hence the underlying mechanism must be mainly physical in nature.

The spectral efficiency of a flare material,  $E_\lambda$ , generally can be written as follows:

$$E_\lambda = \frac{1}{4\pi} \cdot H_c \cdot F_\lambda$$

with  $H_c$  being the enthalpy of combustion (J g<sup>-1</sup>) and  $F_\lambda$  (—) the fraction of radiation emitted in the band of interest determined mainly by the

combustion temperature,  $T_c$ . As no significant changes in spectral efficiency are observed the burn rate modification must be due to physical effects not affecting either enthalpy of combustion or combustion temperature.

These may be:

- Increased heat feedback from gas phase to condensed combustion zone due to the high emissivity/absorbtivity of graphite.
- Increased thermal conductivity of pyrolant grain due to high thermal conductivity of graphite thus promoting pre-ignition reactions far behind the regular reaction zone.

If this accounts for the actual mechanism then addition of diamond particles should be even more beneficial as they possess the highest thermal conductivity of any material available and are easily converted to highly emissive graphite particles within the condensed combustion zone.

## Acknowledgement

This work has been carried out in 2005. My former co-worker Mr Johann Licha is thanked for carrying out the blending and drying operations with MTV.

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# A Thermokinetic Model for the Combustion of Strobe Composition

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**Abstract:** *A model chemical reaction scheme, in which a substance undergoes a two-stage decay process, is developed. It is shown that this reaction scheme follows the Shimizu hypothesis for pyrotechnic strobe combustion; both decay stages are temperature dependent with only the second generating a significant quantity of heat. The model is derived from the combustion reaction between ammonium perchlorate and fine magnesium powder although reaction of other strobe compositions is expected to proceed in a similar manner. It will be shown that the effects of additives, such as potassium dichromate as a frequency modifier, can be investigated without explicitly including them in the model. The model is therefore a first step towards a useful design tool for developing compositions with specific strobe characteristics.*

**Keywords:** *thermokinetic model, strobe composition, Shimizu hypothesis, bifurcation theory, two-stage decay*

## Introduction

Pyrotechnic compositions are usually designed and expected to burn at an almost constant linear velocity to produce an effect such as light, sound, heat or smoke. The occurrence of irregularities is usually dismissed as due to variability in manufacture or experimental noise. However, in some instances, it is desirable to deliberately produce fluctuations in an effect. Pyrotechnic strobe compositions burn in an oscillatory manner such that there is a marked variation of emitted light intensity as a function of time. According to Jennings-White<sup>1</sup> it is not necessary for the minimum light intensity to extend to zero but the peaks must be separated by a sufficiently long time interval such that each can be individually identified by an observer.

It is probable that the first pulsating flash composition was discovered by chance. Brock's Fireworks Ltd. documented the first recorded oscillatory pyrotechnic combustion system in 1898 under the heading "Orion Flashing Guns".<sup>2,3</sup> The composition:

51% Sulfur

25% Barium nitrate

17% Fine magnesium powder

7% Fine aluminium pyroflake

was pressed into hard pellets and it was observed to burn periodically, after ignition, with white flashes. Since then, several mixtures with oscillatory combustion behaviour have been reported in the literature.<sup>1</sup>

It is of interest to understand the mechanisms that give rise to oscillations in pyrotechnic combustion processes so that the desired effects can be optimised and unfavourable conditions such as thermal runaway can be avoided.

A common interpretation of oscillatory strobe combustion, attributed to Shimizu,<sup>4</sup> is that two different kinds of pyrochemistry are involved; one in the light (flash) phase and one in the dark (smouldering) phase. It was suggested by Shimizu, with earlier contributions from Wasmann<sup>5</sup> and Krone,<sup>6</sup> that during the dark phase of an oscillation, hot spots develop in the smouldering slag layer. These hot spots grow in size and temperature until a critical point is reached when the flash reaction commences. It was thus conjectured that the dark reaction should have a small activation energy with a relatively low (possibly zero) heat

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output whilst the flash reaction should have a large activation energy as well as a large heat output. A later experimental study,<sup>7</sup> using scanning electron microscopy to analyse an extinguished strobe star, showed that generation of hot liquid on the surface of the star was necessary for initiation of the flash process.

Feng *et al.*<sup>3</sup> applied a pool chemical approximation to the Gray–Scott model<sup>8</sup> (a cubic autocatalytic model) to mimic experimental observations. The effect of temperature was represented by the autocatalytic step and no temperature dependence was included via the Arrhenius function. However, the model was not investigated in any detail and no attempt was made to relax the pool chemical approximation in accordance with the finite quantities involved in the experimental system.

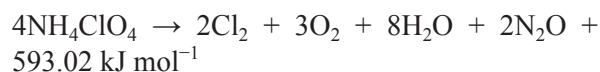
Here a ‘minimal oscillator model’ scheme is proposed, which represents the minimum number of chemical steps required to qualitatively reproduce the experimentally observable behaviour.

## Combustion of a pyrotechnic strobe composition

The ammonium perchlorate–magnesium composition was chosen, for pedagogical reasons, as a suitable example of the strobe effect but it is anticipated that other strobes function through a similar mechanism. When the pressed composition is ignited the low temperature reactions include the decomposition of ammonium perchlorate as described by:



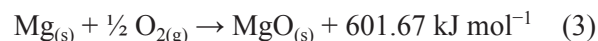
$$150^\circ\text{C} < T < 300^\circ\text{C} \quad (1)$$



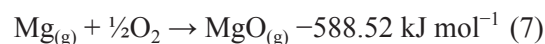
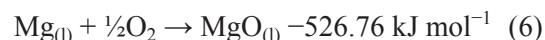
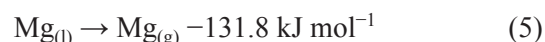
$$T > 300^\circ\text{C} \quad (2)$$

Since reaction (2) is exothermic it increases the temperature and hence enhances the rate of decomposition. When the temperature reaches 450 °C, ammonium perchlorate decomposes fully to generate O<sub>2</sub>. Potassium dichromate is commonly added to this composition to control the frequency of oscillation. It begins decomposition at 390 °C and decomposes fully at 500 °C absorbing a large amount of heat in the process. It thus has the effect of restraining the increasing rate of

reaction. However, potassium dichromate is not included explicitly in the current scheme. The rate-determining step in this smouldering/dark phase is the oxidation of solid magnesium, given by:



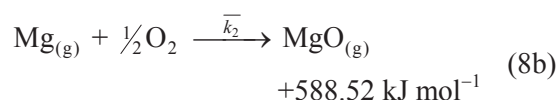
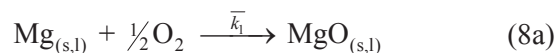
The composition takes on a honeycomb-like structure, comprising solid magnesium covered by magnesium oxide, as the ammonium perchlorate is consumed. This offers a large surface area of magnesium for oxidation. There is a creeping rise in the temperature during the above processes and when 650 °C is reached, the magnesium begins to melt. The magnesium undergoes a second phase change, to the gaseous state, at 1107 °C. The major reactions then become:



The principal reaction is the gas phase oxidation of magnesium, which liberates large amounts of heat. As the magnesium quickly reaches boiling point, the concentration of vapour phase magnesium increases rapidly. Both the reaction rate and temperature increases suddenly and flash combustion occurs. The extremely high temperatures evaporate the MgO and the honeycomb structure disappears; the duration of the flash event is very short. This results in the majority of heat being transferred to the surroundings and not into the un-reacted composition. In addition, the vapour phase concentration of magnesium decreases rapidly and hence the reaction rate decreases abruptly, returning to the smouldering dark phase.

## Problem formulation

From the discussion in the previous section it is clear that oscillatory combustion is caused by the competition between the three phases of magnesium for oxygen.





Where  $\bar{k}_i$ ,  $i = 1, 2$  represents the temperature dependence of the reaction through the Arrhenius function:

$$\bar{k}_i = A_i e^{-E_i/RT} \quad (9)$$

The decomposition of ammonium perchlorate results in a stoichiometric excess of oxygen in the early stages of the smouldering process. Consequently, the concentration of oxygen can be combined with the reaction rate constant. The rate constants for the above reaction steps are:

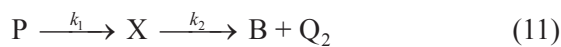
$$\begin{aligned} k_1 &= \bar{k}_1 [\text{O}_2] \\ k_2 &= \bar{k}_2 [\text{O}_2] \end{aligned} \quad (10)$$

From previous arguments, it is clear that the reaction scheme adheres to the Shimizu hypothesis that:

$$\begin{aligned} Q_1 &\approx 0, E_1 > 0 \\ Q_2 &> 0, E_2 > 0 \quad E_1 < E_2 \end{aligned}$$

where  $Q_i$  and  $E_i$  are the heat generated by, and the activation energy of, the  $i$ th reaction step respectively.

Implementing the above conditions, the model reaction scheme takes the form:



Where P is a generalised set of reactants ( $\text{Mg}_{(\text{s,l})}$  in this case), X represents the intermediate chemical species produced ( $\text{Mg}_{(\text{g})}$  in this case) and B the final combustion products ( $\text{MgO}_{(\text{s,l,g})}$  in this case).

This model scheme resembles the simplest example in combustion theory of an oscillatory chemical reaction as studied by Sal'nikov.<sup>9</sup> The Sal'nikov prototype combustion system, developed later by Gray and Roberts<sup>10</sup> and Kay and Scott,<sup>11</sup> only involves the first step of the above scheme but with  $Q_1 > 0$ .

The dynamical system considered here can be written as a set of mass conservation equations, thus:

$$\frac{d\bar{p}}{dt} = -A_1 e^{-E_1/RT} [\text{O}_2] \bar{p} \quad (12)$$

$$\frac{d\bar{a}}{dt} = A_1 e^{-E_1/RT} [\text{O}_2] \bar{p} - A_2 e^{-E_2/RT} [\text{O}_2] \bar{a} \quad (13)$$

$$\begin{aligned} \rho c V \frac{d\bar{T}}{dt} &= V Q_2 A_2 e^{-E_2/RT} [\text{O}_2] \bar{a} \\ &\quad - \chi S (\bar{T} - \bar{T}_a) \end{aligned} \quad (14)$$

subject to the following initial conditions:

$$\begin{aligned} \bar{p}(t=0) &= p_0 \\ \bar{a}(t=0) &= 0 \\ \bar{T}(t=0) &= T_{ig} \end{aligned} \quad (15)$$

See Nomenclature for a complete list of symbol descriptions.

Let:

$$Z_1 = A_1 [\text{O}_2]$$

$$Z_2 = A_2 [\text{O}_2]$$

Defining the following quantities:

$$\begin{aligned} \tau &= \frac{t Z_2}{p_o}, \quad a = \frac{\bar{a} Q R}{\rho c E_2}, \quad T = \frac{\bar{T} R}{E_2}, \quad T_a = \frac{\bar{T}_a R}{E_2}, \\ l &= \frac{\chi S p_o p_o}{V \rho c Z_2}, \quad p = \frac{A_1 \bar{p} Q_2 R}{A_2 \rho c E_2}, \quad \mu = \frac{E_1}{E_2} \end{aligned} \quad (16)$$

the governing equations, (12)–(14) can be re-cast in the following dimensionless form:

$$\frac{dp}{d\tau} = -p e^{-\mu/T} \quad (17)$$

$$\frac{dp}{d\tau} = -p e^{-\mu/T} \quad (18)$$

$$\frac{dT}{dt} = a e^{-1/T} - l(T - T_a) \quad (19)$$

The system contains four parameters:  $\mu$ ,  $l$ ,  $T_a$ ,  $p_o$ . The last three are genuine control parameters in that they can, to a certain extent, be controlled in the laboratory. The first parameter is not, insofar as it is fixed for a given chemistry. This set of equations reduces to the classical Sal'nikov oscillator for

$\mu = 0$ . Nevertheless,  $\mu$  is treated here as a parameter and included in a later analysis to determine the effect of changing the reaction chemistry by, for example, changing the reactants.

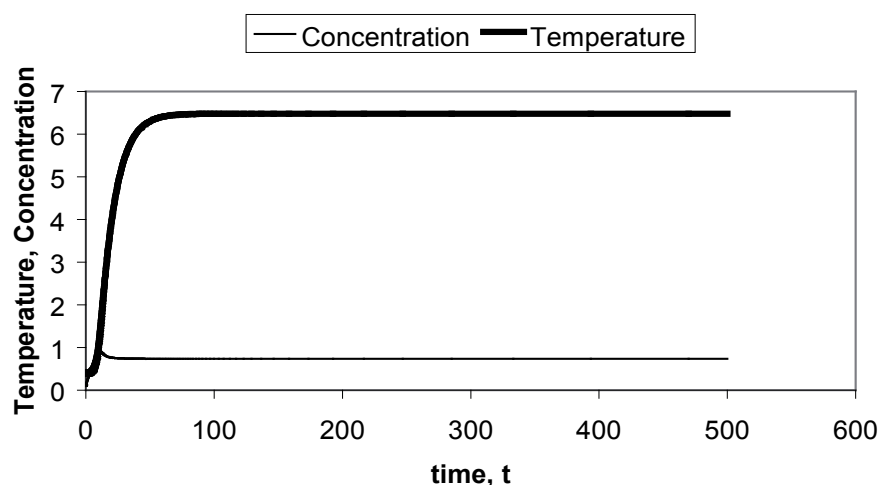
We will proceed initially by assuming the pool chemical approximation for  $p$ :

$$\frac{dp}{dt} = 0, \quad p = p_o \quad (20)$$

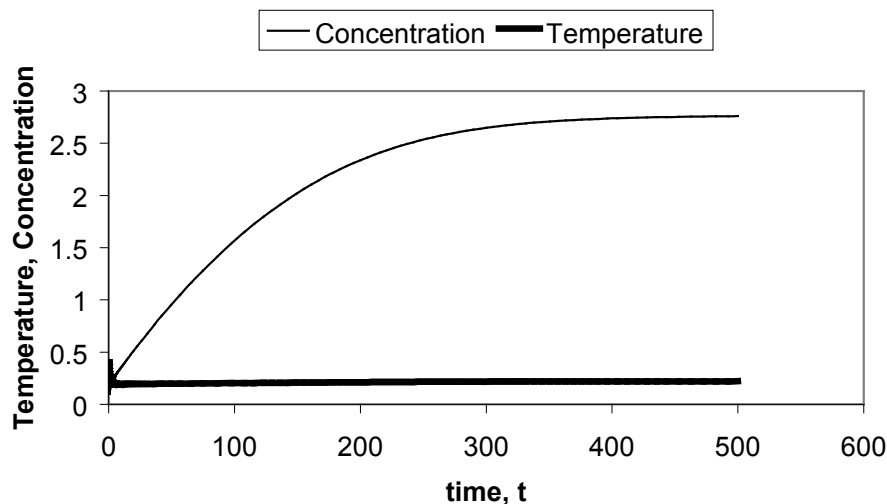
We thus have a two variable system with four parameters.

## Discussion

To demonstrate the usefulness of this model, we choose to investigate the influence of the heat loss parameter,  $l$ , on the combustion behaviour of this particular strobe model. For subsequent calculations, the following parameter values were fixed  $p_o = 0.7$ ,  $T_a = 0.19$ ,  $\mu = 0.7$ . Intuitively, if the rate of heat loss is low ( $l = 0.1$  say), the temperature of the system will increase rapidly thereby increasing the rate of conversion of the intermediate species to final product. The concentration of the intermediate species therefore



**Figure 1.** Temporal concentration and concentration profiles for a reaction with low heat loss ( $l = 0.1$ ).



**Figure 2.** Temporal concentration and concentration profiles for a reaction with high heat loss ( $l = 1.0$ ).

remains low. This is the “fast burn” (flash) regime (Figure 1). Conversely, a high rate of heat loss ( $l = 1.0$  say) causes the temperature to remain relatively low and conversion of the intermediate species to final product is slow. The intermediate species therefore slowly accumulates in the system. This is the “slow burn” (smoulder) regime (Figure 2).

The question now arises: What happens at intermediate heat loss values? An intensive parametric search could be undertaken by slowly varying the heat loss parameter. However, this is inefficient and instead bifurcation theory is employed.

Bifurcation theory seeks to identify parameter ranges that separate regions of qualitatively different behaviour by defining conditions for the behavioural changes. In this instance, regions of parameter space in which oscillatory combustion phenomena may be observed are identified. The defining conditions for oscillations are:<sup>12</sup>

$$f = g = \text{tr}(J) = 0, \quad \det(J) > 0 \quad (21)$$

where  $f = da/dt$  (18),  $g = dT/dt$  (19), and  $\text{tr}(J)$  and  $\det(J)$  are the trace and determinant of the Jacobian matrix ( $J$ ) given by:

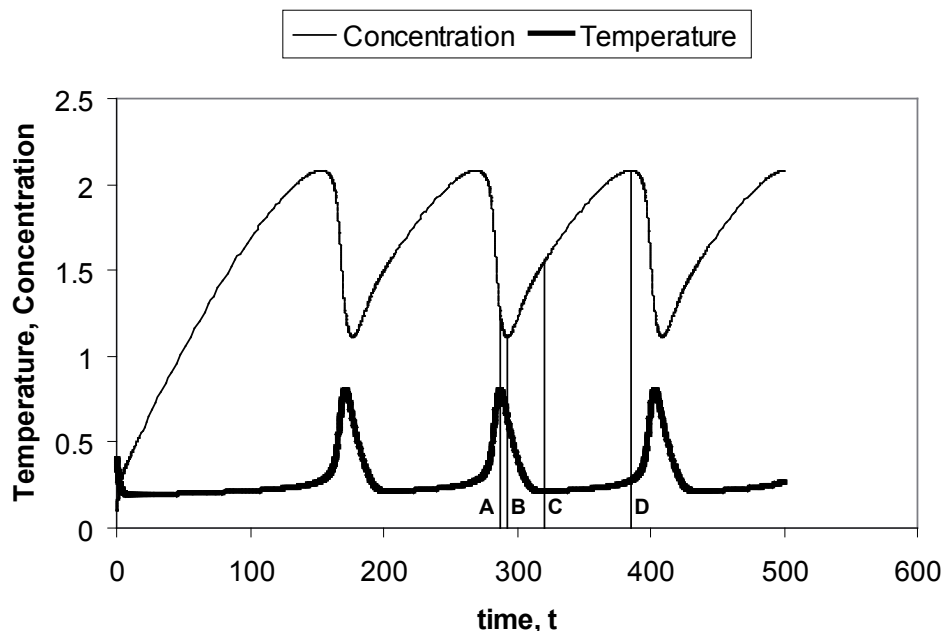
$$J = \begin{bmatrix} \frac{df}{da} & \frac{df}{dT} \\ \frac{dg}{da} & \frac{dg}{dT} \end{bmatrix} \quad (22)$$

$$\text{tr}(J) = \frac{df}{da} + \frac{dg}{dT}$$

$$\det(J) = \frac{df}{da} \frac{dg}{dT} - \frac{df}{dT} \frac{dg}{da}$$

Solving equations (21) defines the oscillatory range to be contained within the limits  $l = 0.5503, 0.6777$ . Choosing  $l = 0.6$ , the concentration of the intermediate species ( $a$ ) and the system temperature ( $T$ ) exhibit temporal oscillations (Figure 3). Figure 4 shows the phase plane plot where the temporal dependence of the variables is removed and the correlation between concentration and temperature is more clearly displayed.

At point A in Figures 3 and 4, the system temperature is high and the cycle is just at the end of a flash phase. The system begins to cool but the temperature is still sufficient to convert the intermediate species to product so the concentration continues to decrease towards point B. At point B, the system is still cooling but the temperature has dropped below the critical level



**Figure 3.** Self-sustained oscillations in concentration and temperature for an intermediate heat loss value ( $l = 0.6$ ) showing temporal dependence.

required to convert the intermediate species into product (reaction step 2), so the concentration of the intermediate species begins to increase towards point C (reaction step 1 dominates). At point C, the concentration of the intermediate species reaches a level which begins to drive reaction step 2. As reaction step 2 progresses, heat is generated and the temperature is thus increased slowly towards point D. This is the smoulder phase. The increasing temperature causes reaction step 2 to accelerate thereby producing more heat and further enhancing the reaction rate. At point D, the concentration of the intermediate species reaches a critical level and reacts very rapidly producing a large quantity of heat which is observed as a jump in temperature back to point A and a consequent decrease in the intermediate species concentration as it is converted to product. This final (flash) stage completes the cycle.

The simplification made early in the development of the model, namely the pool chemical approximation is now addressed. The generalisation is relaxed so that the concentration of the reactant decays with time. Direct integration of equation (17) yields the result:

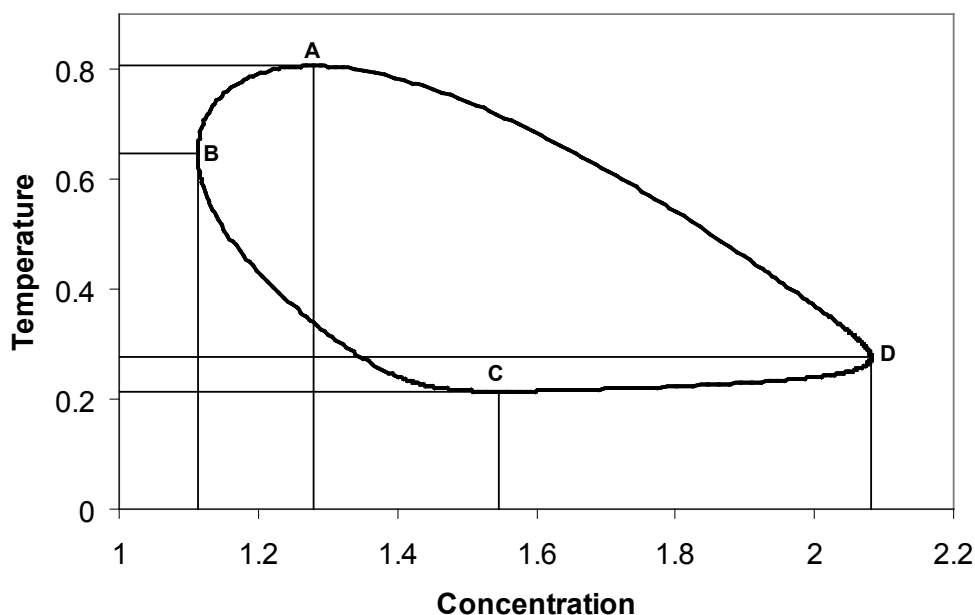
$$p = p_o e^{-\mu/T} \quad (23)$$

Substituting (23) into (18) and solving (18) and (19) numerically yields Figure 5.

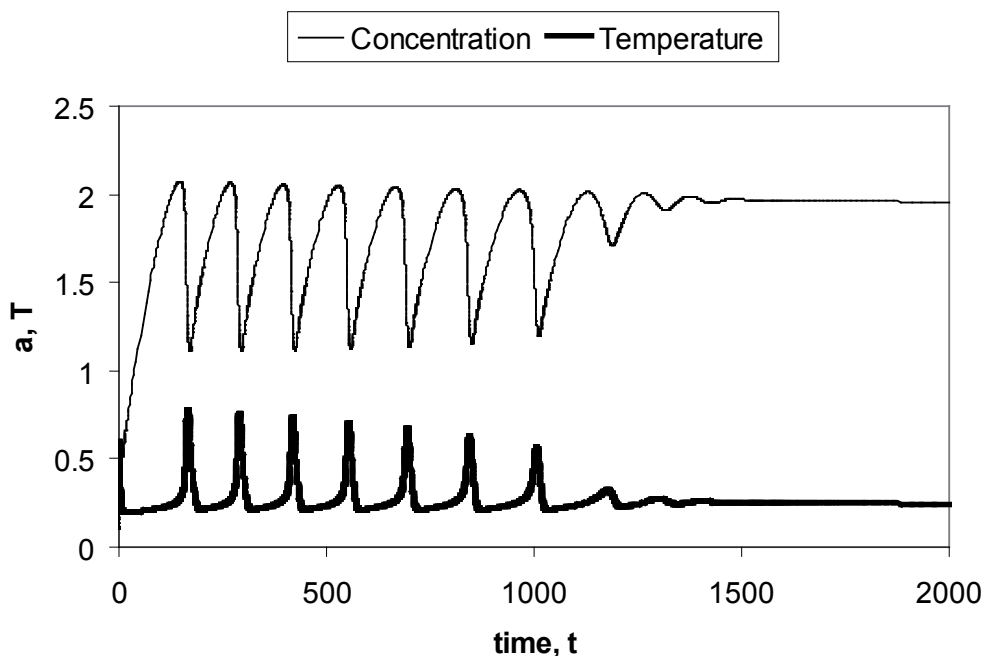
In Figure 5, a decrease in the system temperature is observed initially as reactant is consumed during reaction step 1 when little or no heat is generated. During this time, the intermediate species concentration increases slowly. Eventually, the concentration of reactant decreases to a critical value; the concentration of intermediate is at a sufficiently high level to cause the temperature to increase rapidly in a flash reaction. The sudden temperature increase causes a rapid conversion of the intermediate species to final product. Rapid consumption of the intermediate causes the temperature to drop and the cycle begins again. As the initial reactant is consumed, the amplitude of the oscillations decreases and the period lengthens until eventually the oscillations die out completely and the reactant concentration decays to zero.

## Conclusions and further work

A model has been derived, which follows the



**Figure 4.** Self-sustained oscillations in concentration and temperature for an intermediate heat loss value ( $l = 0.6$ ) showing correlation between concentration and temperature.



**Figure 5.** *Transient oscillations in temperature and concentration as a result of precursor decay.*

Shimizu hypothesis for the combustion of pyrotechnic strobe composition. The mechanism dictates that the combustion process takes place in a two-stage decay process; the rates of both steps are affected by temperature. Bifurcation theory has been employed to identify regions of the heat loss parameter space where self-sustained oscillations exist. The theory can be applied to any other parameter to allow suitable design of strobe compositions.

No elaboration on the behaviour of the oscillations has been given. A description of how to determine the frequency and amplitude of the emerging oscillations is deferred to a later paper. It is likely that multiple stationary states exist in this system and that oscillatory behaviour can coexist with steady (slow or fast) burning. In this case, it becomes critical to ensure that the initial conditions are well established in the basin of attraction in which the system is intended to operate. Given the large manufacturing tolerances associated with fireworks, minor deviations in composition can send the system towards the wrong end state with disastrous consequences. This will be discussed further in subsequent articles on the combustion of pyrotechnic strobe composition.

## Nomenclature

Symbol	Definition
$A$	Pre-exponential factor, $s^{-1}$
$B$	Final combustion products
$E$	Activation energy of reaction
$P$	Generalised set of reactants
$Q$	Heat generated by reaction
$R$	Ideal gas constant
$S$	External surface area of sample
$T$	Dimensionless system temperature
$T_a$	Dimensionless ambient temperature
$V$	Sample volume
$X$	Intermediate chemical species
$Z$	Modified pre-exponential parameter
$a$	Dimensionless concentration of X
$c$	Heat capacity of material
$k$	Reaction rate constant
$l$	Dimensionless heat transfer coefficient
$p$	Dimensionless concentration of P
$p_0$	Initial concentration of P
$t$	time, s
$\chi$	Heat transfer coefficient
$\mu$	Ratio of activation energies
$\rho$	Material density
$\tau$	Dimensionless time



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# Fireplay

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**Abstract:** *“Fireplay” is a generalist overview of pyrotechnics. It is indebted (and acknowledges its debt) to seminal works such as Brock’s “History of Pyrotechnics” (1949), yet develops an aesthetic – even metaphysical – discussion of the key question for our profession: ‘Why do fireworks move people?’*

**Keywords:** *History, aesthetics, gunpowder*

Taciturn, considered, with the rueful grin of a condemned man. He (in literature it is typically ‘he’) is tense across the shoulders, as if lifting every effect with his back. The launching charge is labour, the spreading charge pleasure. When the starshell explodes so does the pyrotechnician’s heart, again and again.

Naturally he enacts the masculine principle. This is true of rigging as much as it is of ignition. According to Chao Hsueh-min’s *Outline of Pyrotechnics* (circa 1753),<sup>1</sup> ‘If the powder is packed by women, the crackers will change into fountains and vice versa.’ More credibly, he observes that ‘rockets are the eyes of fireworks, and are fired before the main display to quieten the audience.’ Unlike a woman, a man must remain invisible; his work not his person must be admired. The rockets direct attention and that attention, in turn, directs the pyrotechnician. ‘The heavens were all on fire, the earth did tremble...’<sup>2</sup> A display marries sulfurous earth with electrified sky: Rangi reaches up for Papa, then pulls her down. She drops upon him with the waterfall shell, her shoulders drooping.

*Aesthetic feeling is not what is being aroused in us. It is more like a sense of wonderment in the presence of what we behold; a sense of being overwhelmed in the presence of a phenomenon that is non-conceptual while at the same time being determinate.*

[Adorno,<sup>3a</sup> 1970]

Before fireworks language is an inert gas; either helium or neon, it will not combust. Yet poetry informs my vocation as a pyrotechnician. It’s possible to plot a whimsical parallel between the silence that underwrites a poem and the space that is articulated by fireworks. I use explosives to ‘write’ on the night so that an audience can say they’ve ‘seen the light’. As a poet I want the same response from my readers; the sense that something wonderful has announced itself, however briefly, and in doing so has removed the cataracts of habit such that they can see anew. There is an optimum order for the parts of speech in a sentence. And there is also one for the not-so-various effects in a pyrotechnics display. If a poem operates within the context of locale and tradition, then a display operates within the constraints of site and client brief. In both professions it is necessary to connect apparently disparate elements in order to make things whole.

But there are differences. Whereas a poem tries to outstay its welcome with lines that resound inside the skull, a fireworks display delights precisely because it is fleeting. Vanuzzio Biringuccio in *Pirotechnia* (1540)<sup>4</sup> regretted that fireworks ‘endure no longer than the kiss of a lover for his lady, if as long.’ Pyrotechnic effects don’t accrete like metaphors into a conceit; instead they disappear into either darkness or the more intense light of their successors in the firing sequence. Poetry can brand the mind for as long as forever is, but fireworks turn into smoke that clears with the crowd. And this is the secret of their

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power: 'Fireworks are the greatest artists, as they withdraw themselves from the spectator's view at the moment of the height of their completion.'<sup>3</sup>

Like all manufactured things, a fireworks display has the optimism of commitment. It is not indifferent like nature. However the purpose of every firework is to confound industry by destroying itself, by valorizing no-thing. And nothing has the indifference of Nature. The narrative of the firing sequence is clear—although delay fuses can result in visual ellipses, where the audience waits in the dark. Whereas a writer can choose to break the laws of grammar, a pyrotechnician must observe the laws of physics and chemistry.

In literature there are direct sources, however the urtext of fireworks will never be discovered. No glowing shell called *Stephen Hero* will shed light over an explosive *Portrait of the Artist as a Young Man*. Always and only *the* original recitation, each pyrotechnic display displaces the familiar in order to bring the viewer home, assuming 'home' denotes the total potential of the individual. But literature and fireworks share a capacity to sear the layers of preconception that prevent people from 'feeling themselves' and more than themselves. As modes of transport, they bring us into being even as they shift us from our default position at the centre of existence. Then the search for origins becomes nostalgia for the future. The word for this is *wonder*.

*The world, an entity out of everything, was created by neither gods nor men, but was, is and will be eternally living fire, regularly becoming ignited and regularly becoming extinguished.*

[Heraclitus,<sup>5</sup> c.535–c.475 BC]

If Man possesses fire when other animals are possessed by it, then the spontaneous forest conflagration and volcanic eruption must have stimulated his inventiveness. Every recorded society has maintained itself through the management of fire to warm shelters, cook the day's prey, and to celebrate the divine with burnt sacrifice or, more gently, altar candle.

How did we move from fire to fireworks, from saltpeter through tinder to gunpowder? Common

knowledge has it that fireworks are nearly antediluvian. Common knowledge (Earth is the centre of the universe, created for man by a loving God) is wrong. The mythology of ancient origins says more about our need for the antique than it does about the progenitors of gunpowder, the propulsive force behind fireworks. The speculative consensus is that a not so ancient Chinese cook, being far from the sea, substituted saltpeter crystals (potassium nitrate) for those of common salt (sodium chloride) and then dropped some on the embers, which grew fiercer. Eventually the dinner guests turned chemists. Taoist alchemists, seeking the elixir of life for their emperor, inadvertently created fire effects that were used in celebrations for centuries before being developed for that most enduring ceremony, war.

By 1044 AD the Chinese had recorded recipes for gunpowder, whereas the earliest European formula dates from the late thirteenth century. There were fiery precursors, most notably that resinous napalm which the Syrian exile Kallinikos invented in Byzantium around 675 AD. It crisped besieging enemies generations before those scions of gunpowder, artillery and the handgun, completed the common soldier's misery.

However pyrotechnics proper post-date the fall of the Roman Empire and the rise of Arab science. In 1280 the Syrian Hasan al-Ramma compiled a treatise detailing 'machines of fire to be used for amusement or useful purposes'.<sup>6a</sup> Hasan's contemporary, the Franciscan friar Roger Bacon, alerted Pope Clement IV to:

*a child's toy of sound and fire made in various parts of the world with powder of saltpeter, sulphur and charcoal of hazelwood... By the flash and combustion of fires and by the horror of the sounds, wonders can be wrought and at any distance that we wish – so that a man can hardly protect himself or endure it...if an instrument were made of solid material, the violence of the explosion would be greater.*

[Kelly,<sup>6b</sup> 2005]

Another four hundred years saw the refinement of modern scientific method, the Reformation's predestined innovations, and the discovery of

the ‘light-bearer’ phosphorus by the latter-day alchemist Hennig Brand (1669) – yet little change to either black powder’s unforgiving nature or the way it was manufactured. Roger Bacon would have recognized the Surrey powder works that John Aubrey visited in 1673. Master *Brief Lives* reported ‘a nursery of earth for the making of saltpeter’.<sup>7</sup> Despite the false messiahs of the market, nuclear fission, cybernetics and carbon credits, today we still mill gunpowder from saltpeter (75%), sulphur (10%) and charcoal (15%). While water sprays over them, this nefarious trinity is crushed under metal rollers, compressed into cakes and then into grains that are sieved, graded, dried like the souls of heretics in a lost painting by Hieronymus Bosch.

Black powder burns at 2138 degrees centigrade, rivaling the inner circles of a medieval Hell. Ben Jonson posited a magician ‘who from the Divil’s-Arse did guns beget’.<sup>8</sup> Perhaps he intended the legendary Berthold Schwartz, a Franciscan from Freiburg, who has the dubious distinction of designing the first gun in the western world. Not peace but pieces on earth. Yet fireworks are Utopian, ‘for triumph as well as for war’.<sup>9</sup> They reach for the sky

*As swift as pellet out of gone  
When fire is in the poudre ronne.*

[Chaucer,<sup>10</sup> 1384]

And we reach with them, believing momentarily in the prospect of a better world. Perhaps. In sixteenth century Sienna and Florence, on the Feasts of St John and the Assumption, theatrical figures of wood and plaster spouted fire from their mouths while fireballs were projected from a pedestal.<sup>4</sup> These days, as the pop star Bono confers with a less than celestial Pope, fireplayers combine the carnival figures that Biringuccio’s contemporaries admired with electronic images that speak to the crowd on an epic scale. We still engage with viewers in intimate acts of trust that transcend the barriers of speech, juggling fire for a smile. We are the descendents of the green men who led a procession to Chester Races, England, on St George’s Day, 1610:

*Two men in green ivy, set with work upon  
their outer habit, with black hair and black  
beards, very ugly to behold, and garlands  
upon their heads, with great clubs in their  
hands, with fireworks to scatter abroad to  
maintain the way for the rest of the show.*

[Brock,<sup>11a</sup> 1949]

As they set off the Catherine Wheels that recall a third-century Christian saint who was tortured on a circular rack, fireplayers learn from religious ritual and secular theatre. We impose symbolic significance on a site by establishing a storyboard that is enacted by costumed performers; a city street becomes a native forest with giant moas, a hotel lobby becomes Chinatown complete with street-stall vendors, a harbour view incorporates a fifty metre long anaconda sweeping along the foreshore. Such wonders were anticipated when Anne Boleyn was escorted from Greenwich to Westminster for her coronation in 1553:

*wafter full of ordnance, in which foyste was  
a great red dragon continually moving and  
casting fiorth wild fire and round about were  
terrible monstrous wild men casting fire and  
making a hideous noise*

[Brock,<sup>11a</sup> 1949]

Ten years earlier, Anne’s gluttonous husband had employed two Dutch pyrotechnicians, Peter Brand and Peter van Cullen, who:

*caused to be made certain mortar pieces  
being at the mouth eleven inches unto  
nineteen inches wide, for the use whereof  
to be made certain hollow shot of cast-iron,  
to be stuffed with fire-work or wild-fire,  
whereof the bigger sort for the same had  
screwes of iron to receive a match to carry  
fire kindled, that the fire-work might be  
set on fire for to break in pieces the same  
hollow shot, whereof the smallest piece  
hitting any man would kill or spoil him.*

[Stow, quoted Brock,<sup>11a</sup> 1949]



The luminous daughter of Henry VIII and Anne Boleyn, Elizabeth I lent her status to the promotion of set displays rather than the improvisatory and anarchistic character of the green man. With an eye to munitions, in 1561 she had commissioned a 'statement of the true and perfect art of making saltpeter grow' from the German Gerrard Honrick. But in August 1572 she was baptized by ceremonial fire while visiting Ambrose Dudley, Earl of Warwick and Master-General of the Ordnance. *The Black Book*,<sup>12</sup> from Warwick Castle's archives, records:

*The wyld fire falling into the river Avon would for a time lye still and then again rise and fly abroad, casting forth many flashes and flames, whereat the Queen's Majesty took great pleasure till by mischance a poor man or two were much troubled, for at the last when it was appointed that the overthrowing of the fort should be, a dragon flying casting out huge flames and squibs, lighted upon the fort and so set fire, but whether by negligence or otherwise it happened that a ball fell on a house at the end of the bridge, wherein Henry Cooper dwelled and set fire to the same house, the man and wife being both in bed and asleep which burned so before they could rescued be, the house and all in it utterly perished with so much ado to save the man and woman and beside that house another house or two adjoining were also fired – and no small marvail was it that so little harm was done for the fire balls and squibs cast up did fly quite over the Castle and into the midst of the town to the great peril and fear of the inhabitants of the Borough.*

In July 1575 Elizabeth I visited Kenilworth and was treated to a display that threatened death only to bring deliverance. Her guest, Mr Laneham, reported:

*After a warning shot or two, was a blaze of burning darts flying to and fro, beams of stars coruscant, streams and hail of fire sparks, lightnings of wildfire on the water; and on the land, flight and shot of thunderbolts, all with such continuance, terror and vehemence, the heavens thundered,*

*the waters surged and the earth shook; and for my part, hardy as I am, it made me vengeably afraid.*

[Nichols,<sup>13</sup> 1575]

Raised from the quasi-fool role of green men to be either military engineers or independent contractors, pyrotechnicians have regularly consummated the Ozymandian glory of the warlord, the emperor, the monarch, the president and, latterly, the chairman of the board:

*They take pleasure to see some pageant or sight go by as at a coronation, wedding or such like solemn niceties to see an ambassador or prince received and entertained with masks, shows and fireworks.*

[Burton,<sup>14</sup> 1621]

During 1613, for a display to celebrate the wedding of King James I's daughter, the Thames was closed to traffic. Doubtless rebellious water rats came and went as if by the divine right they defied. Barges held charges controlled by Thomas Butler, William Fishenden, John Nodes and John Tindale. They were supported from the shore by William Hammond, the Master-Gunner of England, who let fly:

*First, for a welcome to the beholders a peale of Ordnance like unto a terrible thunder rattled in the ayre... Secondly, followed a number more of the same fashion, spredding so strangely with sparkling blazes, that the sky seemed to be filled with fire... After this, in a most curious manner, an artificiall fire-worke with great wonder was seen flying in the ayre, like unto a fiery Dragon, against which another fiery vision appeared flaming like to St George on Horsebacke, brought in by a burning Inchanter, between which was then fought a most strange battell continuing a quarter of an howre or more; the dragon being vanquished, seemed to roar like thunder, and withal burst in pieces, and so vanished; but the champion, with his flaming horse,*



*for a little time made a shew of a triumphant conquest, and so ceased.*

*After this was heard another ratling sound of Cannons, almost covering the ayre with fire and smoke, and forthwith appeared, out of a hill of earth made upon the water, a very strange fire, flaming upright like a blazing starre. After which flew forth a number of rockets so high in the ayre, that we could not chose but approve by all reasons that Arte hath exceeded Nature, so artificially were they performed. And still as the Chambers or Culverines plaide upon the earth, the fire-workes danced in the ayre, to the great delight of his Highnes and the Princes.*

*Out of the same mount or hill of earth flew another strange piece of artificiall fire-workes, which was in the likenes of a hunted Harte, running upon the water so swiftly, as it had been chased by many huntsmen.*

*After the same, issued out of the mount a number of hunting-hounds made of fire burning, pursuing the aforesaid Harte up and downe the waters, making many rebounds and turnes with much strangenes; skipping in the ayre as it had been a usual hunting upon land.*

*These were the noble delights of Princes, and prompt were the wits of men to contrive such princely pleasures. Where Kings commands be, Art is stretcht to the true depth; as the performance of these Engineers have been approved.*

[Brock,<sup>11b</sup> 1949]

If the monarch rules by divine right then an all-seeing God does not always honour the spirit of that contract. King James I thanked the Father for thwarting every pyrotechnician's hapless benefactor, Guy Fawkes, on 5 November 1605. His Royal Decree compelled citizens to celebrate the deliverance of the King. It was not lifted until 1859, which accounts for the former colonies

New Zealand and Australia marking the day with community displays and, incidentally, explains the Anglophile character of this essay. Even if God is Christian rather than Taoist or Confucian it seems He intervenes sporadically and, according to this Jacobean doggerel, never on behalf of Catholics:

*Guy Fawkes, Guy Fawkes, t'was his intent  
To blow up King and Parli'ment.  
Three-score barrels of powder below  
To prove old England's overthrow;  
By God's providence he was catch'd  
With a dark lantern and burning match.  
Holloa boys, holloa boys, let the bells ring.  
Holloa boys, holloa boys, God save the  
King!*

[Anonymous<sup>15</sup>]

When it is 'stretcht to the true depth', art can have consequences that are unforeseen by even God's favourites. In 1613 the King's Players performed Shakespeare's *Henry VIII*. They fired gunpowder to mimic battle and the illusion was made real when sparks caught roof-thatch, reducing the Globe Theatre to ashes. If all the world's a stage then perhaps a capital city is a proscenium arch? On 23 July 1699 the diarist John Evelyn, whose family wealth derived from gunpowder production, records: 'The city of Moscow burnt by the throwing of squibs'.<sup>16</sup>

In 1748 the War of the Austrian Succession ended, although the peace brought more deaths. The treaty signed at Aix-la-Chapelle was marked and marred by a fireworks display in which it is reported that 'there were forty killed and nearly three hundred wounded by a dispute between the French and the Italians, who, quarrelling for precedence in lighting the fires, both lighted at once and blew up the whole'.<sup>11c</sup> National ambition meant the fate of the military was visited upon the civilian with a bang and a whimper.

The same inglorious treaty also favoured Georg Handel with a commission from George II of the United Kingdom. His wonderfully bumptious *Music for the Royal Fireworks* honoured 14500 pounds sterling of pyrotechnic errors at Green Park on 27 April 1749. The English and Italian supervisors argued over the effectiveness and safety of gunpowder trains, which the Italian experts

Ruggieri and Sarti preferred as an alternative to quickmatch for igniting effects. When the north pavilion erupted into flames, the English pressed their point. An outraged Cavaliere Servandoni, designer of the 'machine' (the stage and set), tried to press his; he drew his sword upon the English Comptroller Charles Frederick. On 3 May Horace Walpole reported to Horace Mann:<sup>17</sup>

*The fireworks by no means answered the expense, the length of preparation, and the expectation that had been raised... The machine itself was very beautiful and was all that was worth seeing. The rockets and whatever was thrown into the air succeeded mighty well, but the wheels and all that was to compose the principal part, were pitiful and ill conducted with no change of coloured fires and shapes...and lighted so slowly that scarce anybody had patience to wait for the finishing.*

Fireplayers are paid to keep the audience's patience. Fireworks are popular because they are anticipated, celebratory, a memorial to the unpredictable. In 1814 a display was staged in the London Parks to honour the Centenary of the House of Brunswick on the British Throne, the General Peace, and the sixteenth anniversary of the Battle of the Nile. It might as well have marked the passing of Everyman's indigestion. On 9 August 1814, in a letter to William Wordsworth, Charles Lamb admitted:

*After all the fireworks were splendent – the Rockets in clusters, in trees and in all shapes, spreading about like young stars in the making, floundering about in Space (like unbroken horses) till some of Newton's calculations should fix them, but then they went out. Anyone who could see 'em and the still finer showers of gloomy rain fire that fell sulkily and angrily from 'em, and could go to bed without dreaming of the Last Day, must be as hardened an Atheist as...*

[Talfourd,<sup>18</sup> 1837]

Whilst professing Mormonism in later life, perhaps the Maori King Tawhiao I was a hardened atheist when he visited England in 1884? Understandably

unimpressed by Queen Victoria's reluctance to meet him (she fobbed him off with Lord Derby, Secretary of State for the Colonies), Tawhiao's mood darkened further when a fireworks display in his honour was staged at Sydenham. With black sparks an impossibility, the despairing pyrotechnician rendered his subject's *moko* in glowing white:

*...dissatisfaction was due to the colour in which the lines of his intricate facial tattoo-marks were rendered. In addition, he was perhaps not in the best possible frame of mind to appreciate fireworks. Decked out in unaccustomed frock-coat and top-hat, and with a pair of patent leather boots on his feet, he had been taken for an exhaustive tour of the building, when at last he decided he had had enough of it. Plumping himself down on a convenient bench, he had ripped off the torturing footwear, and, casting them from him, announced his intention of calling it a day. Deaf to all arguments, there he remained until a gouty member of the staff who was in the habit of wearing felt slippers in his office fetched them. Under their soothing influence the king allowed himself to be persuaded to continue his itinerary.*

*A pathetic note was struck by his remark, no doubt with the thought of the dwindling number of his subjects in mind, as he looked down from the royal box on the assembled crowd lit up by the fireworks: "I did not know that there were so many people in the world." His comment on the display, repeated again and again, was, "I don't believe it! Such things cannot be!"*

[Brock,<sup>11d</sup> 1949]

But such things can and must be. If this is the best of all possible worlds, then pyrotechnicians try for an impossible world where dragons are more common than cars. They are 'profound necromancers, who by their art caused things to appear whilk are not, as follows: fowls flying in the air spouting fire on others...' <sup>19</sup>

Everybody dreams of beautiful things they have never seen and never expect to see: it is the task of

fireplayers to show people those things. After all, the Latin root of explosion means ‘to drive out by clapping’.

To recap: for a drum-roll of centuries black powder was our only explosive. While essential to ceremonies, it was also put to military use during the Sung Dynasty. From 960 AD the Chinese emperors understood that magic and mortality are partners. During the late eighteenth century other propellants were synthesized for war and industry, however the devil’s distillate retains its primacy for pyrotechnics. Such longevity is unusual because the production of industrial and cultural commodities is inherently innovative in character, with the expectation that every product should (claim to) be better than its predecessors, even unique. That such claims are usually specious only adds to their regularity. But gunpowder does have a unique status, one that bridges the military and the pacific, the commercial and the spiritual. It inaugurates presidencies and it ends battle campaigns; it blesses royal babies and it marks the passing of kings.

States, multinational companies, and patrons of the arts all commission pyrotechnicians. Our ancient craft no longer exclusively serves the warlord; rather it serves the tyranny of the new: the new team, the new sponsor, the new competition. When families attend the fireworks display at Everyman Stadium they hear, punctuated by titanium salutes, the good news of the marketer rather than the evangelist. If anniversary extravaganzas have the majesty of religious ritual, then they are not so much the opiate as the chlorate of the masses:

*To set the rabble on a flame,  
And keep their governors from blame,  
Disperse the news the pulpit tells,  
Confirmed with fireworks and with bells.*

[Butler,<sup>20</sup> 1678]

But few human activities are circumscribed by intention. While an economic trajectory is clear and measurable, the arc of our hearts is arguably more mysterious than God’s movements. Patronized for their ability to glorify and so maintain the status quo, fireworks also shift the known; the pursuit of happiness ends unexpectedly in discovery. Let there be light.

*“What are fireworks like?” she had asked the Prince, one morning, as she was walking on the terrace.*

*“They are like the Aurora Borealis,” said the King, “...only much more natural.”*

[Wilde,<sup>21</sup> 1888]

A fifteen-minute display traverses centuries; it contains the journey of each viewer’s ancestors. Those ancestors twist and turn within every viewer as he flinches with delight when the shock of the launching charge hits the perimeter of the pyrotechnic exclusion zone.

Up close and personal, fireplayers try to return to physical capability, to the eroticism of sweat, as the defining element of spectacle. He swings a flaming staff, outlining a globe that is itself yet a symbol. With fire-pois she knits a filigree bodice for her breasts, which glisten in the red light shed by exploding peonies. What unites pyrotechnician, fireplayer and viewer is not the false promise of technical innovation but the opportunity to experience the theatre of the senses afresh, to make things (and no-thing) cohere – although pyrotechnics posit unity without a fixed centre; they are the artistic corollary of a community without the State.

*Something goes its own path, follows its own law. But I don’t want that, I think, and once again want to jump up, but then remain seated and want to replace the thought that there might be something going along inexorably, and rolling over me, with a different thought, one more appropriate.*

[Hofmann,<sup>22</sup> 1979]

Do fireworks promote in people an expansive, even pantheistic, openness that momentarily banishes the ego’s demands? Fireworks try to burn through the ties that hold definitions of self in place (and place in self) until the viewer glimpses, through the sheet of aerial effects, the sleeping self-to-be. A barrage of chrysanthemum shells is a wake-up call that rolls over the ego. Yet it also reassures the audience: ‘You need never squint through a keyhole until your neck hurts; no more staring out

windows in the hope that your lover will come; for one evening everything will be complete. You need never desire again.' Priceless?

*"What do you think of a brilliant display of fireworks?" said Mr Crummles.*

*"That it would be rather expensive," replied Nicholas drily.*

*"Eighteenpence would do it," said Mr Crummles. "You on the top of a pair of steps... Farewell as a transparency behind; and nine people in the wings with a squib in each hand – all the dozen and a half going off at once – it would be very grand – awful from the front, quite awful."*

[Dickens,<sup>23</sup> 1839]

Fireplayers admire, even aspire to, the useless. Yet our ability to deliver quality displays cost-effectively comes from analysis of the assumptions guiding the site architect, the set designer, the celebrity speaker, the star fullback, the fire safety officer, the insurer, the client and the client's client. We appreciate that sports, the arts and commerce have a common interest in audience response and the technical means of achieving it. But we also know that fire can hold everything and everyone to account.

*We represent also ordinance and new mixtures of gun-powder, wild fires burning in the water and unquenchable, and also fire-workes of all variety*

[Bacon,<sup>24</sup> 1627]

Whereas aesthetic contemplation involves 'pure' observation of an event, commerce uses contemplation of an event to direct audience response towards brand awareness and product consumption. Often fireworks focus attention on specific areas of the site; they act as preludes to prize-giving ceremonies or concerts, and as codas that allow the safe exit of dignitaries by taking the audience's attention. However 'the event is what it is by reason of the unification within itself of a multiplicity of relationships'.<sup>25</sup>

These relationships may be economic in origin but their nature is greater than the purview of commerce, otherwise fireworks would not survive the next marketing fad. At its best pyrotechnics is revelatory and lights what Walter Benjamin dramatically termed, in *World and Time* [circa 1919], 'the theatre of history'.<sup>26</sup> The fact of the act is that fireplayers describe a tension between the known past (what the audience remembers about a familiar site) and the unknown future (what the audience comes to experience through our work on the site). We do this by generating a spectacle that returns the audience to a world where transfiguration and wonder are the twin poles.

*How she cried O, O, O, as the rocket soared into the air, and showered them in azure, and emerald, and vermilion! As these wonders blazed and disappeared before her, the little girl thrilled and trembled with delight...*

[Thackeray,<sup>27</sup> 1848]

We attempt nothing less than to bring up the archetypal child inside everyone, a child who embraces the world in all its variety. The desire to resurrect, to perfect, is behind every explosion. And every fizzer.

*At the centre of contemporary antinomies is that art must be and wants to be utopia, and the more utopia is blocked by the real functioning order, the more this is true; yet at the same time art may not be utopia in order not to betray it by providing semblance and consolation.*

[Adorno,<sup>3b</sup> 1970]

By reducing expensive products to smoke pyrotechnicians turn Adam Smith on his head and mimic the second law of thermodynamics, which insists that systems move over time from order to disorder. Yet displays are held to celebrate a material ideal. The culture industries and the spendthrift audience are one in their hunger for the new, the inclusive 'exclusive' experience that is beauty.

Is it all smoke and mirrors? Beneath coloured



smoke the primary – perhaps the only – mirroring is of the human spirit. To do their job properly pyrotechnicians have to value intensity, which is often (questionably) viewed as an indicator of authenticity. But what can be more authentic than to provoke recognition of the inexorable? Jorge Luis Borges asserted, ‘The Inferno of God is not in need of the splendour of fire.’<sup>28</sup> However the Inferno of Earth is. Jeffery Baker, who makes flamethrowers and fireballs, recalls:<sup>29</sup>

*I grew up in Texas, which is the most boring place ever. To cure my boredom my friends and I would amuse ourselves building small bombs, making our own napalm and burning whatever we could find that would burn. We made our own flash powder, using potassium nitrate, sulfur and charcoal. Somehow I made it through that era with all my fingers intact.*

*In 1999 my wife talked me into attending the Burning Man Festival. At first I was more interested in the naked women. After three hours that passed. I saw the most spectacular fire effects. While these huge explosions and fireballs lacked the ‘sophistication’ of your average fireworks display, there was a primal affection to the experience. The next morning, after I had sobered up, it became clear that my childhood adventures with fire were totally natural as a human. Watching the huge fires was not only ecstatic but deeply comforting. It was a religious experience.*

With fire seeing is believing. No one can make meaning without context. If site provides context then fireworks don’t so much map as transcend it because they take the viewer into an apprehension of the eternal through the momentary. The report of a launching charge is more than a deafening report on experience.

Exposed by the exploding shell, perhaps site is akin to the light-sensitive paper that photographs are printed on – but a paper that has not been treated with fixative. When the spreading charge transforms common chemicals into uncommon effects, then the audience participates more than the pyrotechnician. No exposure matches that of

the spirit – it cannot be captured.

After all, is this so different from what happens with language? Words turn around the world, searching the pockets of discarded jackets for secrets. See, here is a piece of crumpled paper. It is the charred casing of a star shell.

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# Sound Level Analysis of Firecrackers

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**Abstract:** The noise levels from sound-producing firecrackers, both commercial and newly formulated, were measured. Commercial sound-producing firecrackers produce noise in the range of 130.7 dB(A)/150.4 dB(C) peak to 142.8 dB(A)/162.6 dB(C) peak at a distance of 4 m. A set of pyrotechnic compositions of potassium nitrate ( $\text{KNO}_3$ ), sulphur (S), aluminium (Al) and boric acid ( $\text{H}_3\text{BO}_3$ ) was used to produce different varieties of sound-producing firecrackers for analysis. A bulk density of  $0.44\text{--}0.50\text{ g cm}^{-3}$  was maintained for homogeneity of the mixture. The factors influencing the sound from firecrackers, such as amount of mixture, weight percentage of oxidizer and fuel, particle size of the ingredients, bursting strength of the paper used for the inner paper case of the firecracker unit and variation in percentage composition, were studied. The noise level produced from different sizes of firecracker units shows a linear relationship with the weight of the mixture used and the bursting strength of the paper. It was found that the pyrotechnic mixture of composition 57.5/20/22/0.5%  $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$  in a firecracker unit made from 240 gsm kraft paper and bursting strength  $2.2\text{ kg cm}^{-2}$  produced allowed sound levels of  $<125\text{ dB(A)}/145\text{ dB(C)}$  peak at 4 m distance. The efficiency of the pyrotechnic mixture for making fireworks is explained by measuring the safety characteristic data of thermal and mechanical sensitivity. Furthermore, a comparison between a mixture containing potassium chlorate, i.e.  $\text{KClO}_4/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$ , and  $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$  was made on the basis of sensitivity measurements. The limiting impact energy (LIE) of pyrotechnic flash compositions of  $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$  falls in the range of 5.3 J making the mixtures class III explosives. The ignition temperature was found using differential scanning calorimetric (DSC) analysis to be in the region of  $437.9\text{--}498\text{ }^\circ\text{C}$ . Self-propagating decomposition occurred only at high temperatures for  $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$  making the mixture thermally stable.

**Keywords:** Sound level, noise level, pyrotechnic mixture, impact sensitivity, friction sensitivity, flash composition, firecrackers.

## Introduction

Fireworks are made from pyrotechnic mixtures of an oxidizer and a fuel and, optionally, a colour enhancing chemical and a binder. The chemicals employed and their compositions vary depending on the type of firework being produced. Fireworks are of two types, light-producing and sound-producing. Magnesium powder is frequently employed as a fuel for high light output and magnesium fuel is replaced by another metallic fuel in combination with sulphur

for high sound output.<sup>1</sup> Pyrotechnic mixtures are energetic compounds susceptible to explosive degradation on ignition, impact and friction and are obtained by mixing finely divided (reducing) metal powders with inorganic oxidizing agents that are capable of undergoing self-sustaining combustion.<sup>2</sup> The compositions have a wide range of applications utilizing the production of light, heat, sound or smoke.<sup>3</sup> Pyrotechnic compositions used for firecrackers differ from explosives and propellants in that they do not necessarily give rise to a violent expansion of gas

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and their rate of reaction is normally considerably less than that of either explosives or of recognized propellants. During the firework manufacturing process, chemicals are initially mixed to produce a reasonably homogeneous mixture. During these operations impact, friction, spark and heat stimuli may occur and under certain conditions one or more stimuli may be enough to cause ignition of the compositions. The results from burning a particular pyrotechnic composition depend on various factors. Chemicals used as additives even in small quantities to improve the mechanical properties can alter the combustion process and lower the ignition temperature. The effectiveness of firecrackers depends not only on the composition of the mixture, but also on factors such as particle size and shape, choice of fuel and oxidizer, fuel to oxidizer ratio, degree of mixing, moisture content, physical form, packing density, presence of additives, local pressure, degree of confinement, degree of consolidation, crystal effects and purity of the chemicals.<sup>4</sup>

As per the Indian Explosives Act, 1884, using a mixture of chlorate and sulphur is prohibited due to its ease of ignition and sensitiveness to undergo explosive decomposition.<sup>5</sup> Alternative mixtures have been widely used in the fireworks industry and accidents still occur. The main reason is poor understanding of the explosive nature and lack of mechanical and thermal sensitivity data for mixtures used in the firework industry. In the past, researchers have studied the thermal and mechanical sensitivity of sulphur and chlorate mixtures.<sup>6,7</sup> Very little work on the impact sensitivity of mixtures containing  $\text{KNO}_3/\text{S}/\text{Al}$  has been reported.<sup>8,9</sup> However, the analysis of sound levels produced from firecrackers and ways to control sound levels have not yet been reported. As per the Government of India notification 'Sound emitting fire crackers with sound level exceeding 125 dB(A) or 145 dB(C) peak at 4 m distance from the point of bursting are prohibited.'<sup>10</sup> The present work focuses on analysing the noise levels produced from commercially available firecrackers at 4 m distance and on controlling the sound levels within the allowed limits by varying parameters such as amount of mixture used, weight percentage of oxidizer and fuel, particle size of the ingredients, bursting strength of paper used for making the shell, and composition. The study also assesses

the impact and friction sensitivity of the optimized pyrotechnic mixture for safety considerations and to classify the pyrotechnic mixture according to the Andreiev-Beliaev classification.<sup>11</sup> The study helps to choose an ideal composition so that environmental pollution due to excessive usage of chemicals and noise pollution can be minimized.

## Experimental

### Chemicals and materials

The chemicals used for the preparations of the firecrackers were obtained from a firework manufacturing company situated in the southern state of Tamilnadu, India. The purity and assay of the chemicals were  $\text{KNO}_3$  97.6%, S 99.9%, Al 99.8% and  $\text{H}_3\text{BO}_3$  99%. Aluminium powders of grade 999 (200 mesh, 75 micron), potassium nitrate of 120 mesh (125 micron), sulphur of 100 mesh (150 micron) and boric acid of 100 mesh (150 micron) sizes were used for making fireworks. All these chemicals were sieved through a 100 mesh brass sieve. The samples were stored away from light and moisture until they were packed inside the paper case of the fire cracker unit (Figure 1). Two types of papers, kraft paper (brown) and duplex board (white) with different thicknesses which were measured by a GSM meter (gram per square metre) were used for making the inner shells of the firecrackers. Jute string with gum of length 130–260 cm and thin foil paper (cello paper) were used for making the firecrackers. Three types of paper cases, small ( $15 \times 15 \times 15$  mm;  $3.375 \text{ cm}^3$ ), large ( $28 \times 15 \times 15$  mm;  $6.3 \text{ cm}^3$ ) and  $28 \times 28 \times 15$  mm ( $11.76 \text{ cm}^3$ ) (Figure 1) were used to prepare cake-bomb, hydrogen-bomb and thunder-bomb firecrackers respectively similar to commercially available firecrackers.

### Firecrackers

Three types of firecrackers like the cake-bomb, hydrogen-bomb and thunder-bomb were manufactured manually by experienced technicians from a firework manufacturing company situated in the southern state of Tamilnadu, India, for analysis. The chemical mixture of potassium nitrate, sulphur, aluminium, and boric acid in the ratio 57.5 : 20 : 22 : 0.5% and the chemicals were sieved separately and mixed thoroughly on non-conducting surfaces like newspaper, rubber mat etc., by sieving through a No. 40 mesh (425 micron),



*Inner paper case (large)*



*Fire cracker (hydrogen bomb)*

**Figure 1.** Firecracker used for analysis.

4 to 5 times to get a homogeneous mixture. This chemical mixture was used to fill the paper case of the firecracker unit. Thin foil papers (cello paper) were used to cover the paper case and it was sealed with gum and dried in atmospheric air. Jute string with gum of length 130–260 cm was wound round the paper case tightly; 3 windings were done and it was dried in sunlight for 2 to 3 hours. The fuse wire (100 mm, quick match) was inserted with the help of a brass needle and kept in place with charcoal powder. Coloured fancy papers were used to cover the case for appearance and it was dried for about 24 hours in sunlight to make the firecrackers ready for testing. The compositions used to make firecrackers for analysis are given in Table 1.

## Instruments

### Sound level tester

Sound level tests were carried out as per the rules of notification of PESO (Petroleum and Explosives Safety Organisation), formerly known as ‘Dept. of Explosives’, Govt. of India.<sup>9</sup> The noise level was measured with four sound level monitors using Model No. 824L obtained from Larson & Davis,

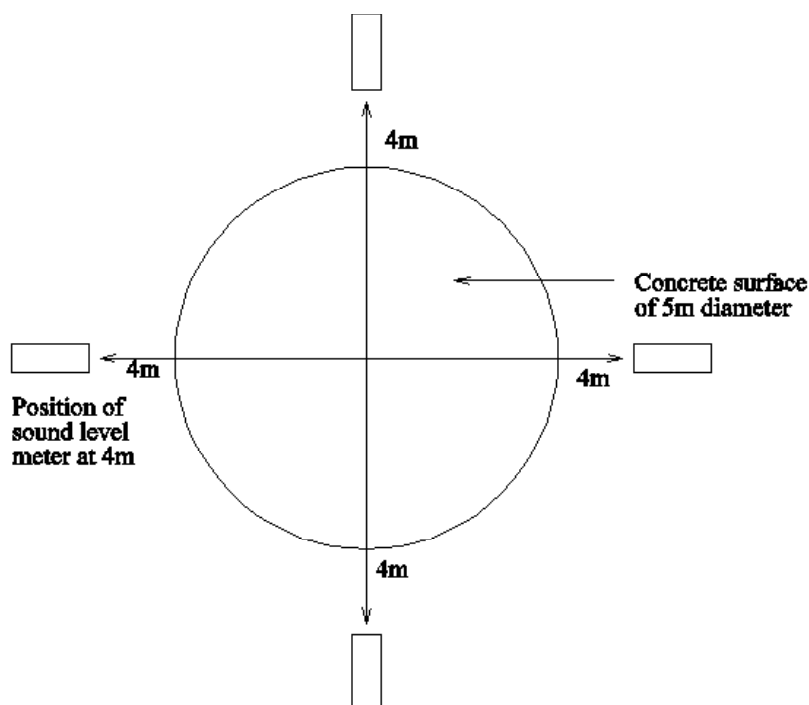
USA and the average values of the four readings were taken as sound level data. Sound is usually measured in decibels (dB), a logarithmic unit used to describe a ratio of sound pressure [ $\log (P_2/P_1)$  dB], or voltage or intensity. While it is used to give the sound level for a single sound rather than a ratio, a reference level is required. The most widely used sound level filter is the A scale, which roughly corresponds to the inverse of the 40 dB (at 1 kHz) equal-loudness curve. Using this filter, the sound level meter is thus less sensitive to very high and very low frequencies. Measurements made on this scale are expressed as dB(A). The C scale is practically linear over several octaves and is thus suitable for subjective measurements only for very high sound levels. Measurements made on this scale are expressed as dB(C). The sound level meters are capable of measuring the noise level in A/C, by flat weightings with slow/fast impulse detectors. The sound level measurements were made with four approved sound level meters simultaneously, equally spaced apart 90° at 4 m distance from the bursting place in a circle, at a height of 1.2 m (Figure 2). A 5 m diameter hard concrete surface was considered as free-field

**Table 1** composition of chemicals used in firecrackers.

Component	% Range
KNO <sub>3</sub>	65–50
S	24–5
Al	44.5–14.5

**Table 2** Impact sensitivity of standards to calibrate the impact sensitivity apparatus

Substance Reported	Impact energy/J Calculated	Impact energy/J	Error (%)
Tetryl (dry)	4	4.05	2
Lead azide (dry)	2.5	2.6	2.5



**Figure 2.** Sound level analysis on site-free field conditions.

**Table 3** Sound level analysis of commercial firecrackers

Sr. No	Source	Trade name of firecrackers	Outer dimensions (mm)	Sound level/ db(A)	Sound level/ dB(C) peak
1	Fireworks Factory I, Sivakasi	Cake-bomb	30 × 20 × 20	137.6	149.2
		Hydrogen-bomb	38 × 20 × 20	134.9	151.6
2	Fireworks Factory II, Sivakasi	Hydrogen-bomb	35 × 20 × 20	136.0	153.3
		Atom-bomb	35 × 20 × 20	134.9	151.6
		Classic-bomb	40 × 35 × 20	134.9	151.6
3	Fireworks Factory III, Sivakasi	Atom-bomb green	40 × 20 × 20	136.0	153.3
		Atom-bomb	25 × 30 × 20	133.9	151.5
		Hydrogen King green bomb	40 × 30 × 20	140	152.2
4	Fireworks Factory IV, Sivakasi	Atom-bomb small	25 × 20 × 20	130.7	150.4
		Atom-bomb big	32 × 25 × 20	133.1	153.4
		Hydrogen-bomb	40 × 28 × 20	135.3	155.0
		Kingkong bomb	35 × 35 × 20	136.1	157.3
5	Fireworks Factory V, Sivakasi	Rectangular bomb	20 × 20 × 20	129.9	149.4
		Minibullet	25 × 19 × 20	126.4	146.2
		Neutron-bomb	31 × 18 × 20	132.8	153.8



**Table 4.** *Effect of amount of pyrotechnic mixture on sound level.*

Types of atom-bomb	Wt of chemicals/g	Sound level/dB(A)	Sound level/dB(C) peak
Cake-bomb <sup>a</sup>	0.5	107.6	131.0
	0.75	113.2	136.3
	<b>1.00</b>	<b>123.8</b>	<b>144.1</b>
	1.25	128.1	151.8
	1.50	133.8	156.2
Hydrogen-bomb <sup>b</sup>	0.75	109.6	135.1
	1.00	113.5	137.8
	1.25	119.8	143.1
	<b>1.50</b>	<b>124.0</b>	<b>144.1</b>
	1.75	128.1	149.8
	2.00	133.5	155.9
Thunder-bomb <sup>c</sup>	1.00	109.6	135.1
	1.50	113.5	137.8
	<b>2.00</b>	<b>122.3</b>	<b>143.1</b>
	2.50	132.4	155.0
	3.00	135.4	158.3
	3.50	135.5	158.6
	4.00	138.6	160.8

<sup>a</sup> Inner box dimension:  $15 \times 15 \times 15 \text{ mm}^3$  ( $3.375 \text{ cm}^3$ ); jute length 130 cm, winding: 3 ply, GSM 240  $\text{g m}^{-2}$ , bursting strength  $2.2 \text{ kg cm}^{-2}$ . <sup>b</sup> Inner box dimension:  $28 \times 15 \times 15 \text{ mm}^3$  ( $6.3 \text{ cm}^3$ ); jute length: 195 cm, winding: 3 ply, GSM 240  $\text{g m}^{-2}$ , bursting strength  $2.2 \text{ kg cm}^{-2}$ . <sup>c</sup> Inner box dimension:  $28 \times 15 \times 28 \text{ mm}^3$  ( $11.76 \text{ cm}^3$ ); jute length: 260 cm, winding: 3 ply, GSM 240  $\text{g m}^{-2}$ , bursting strength  $2.2 \text{ kg cm}^{-2}$ .

conditions for carrying out the sound level test. A microphone converted sound into electrical power and a decibel meter read out the sound power in watts or dB.

#### Impact sensitivity tester

Impact sensitivity of the pyrotechnic mixture was tested using the BAM method<sup>12,13</sup> with an Impact sensitivity tester, supplied by Electro Ceramic Private Limited, Pune, India. The design and principles of the equipment are similar to those of the BAM standard drop fall hammer equipment. The procedure followed in this study was based on a previously reported method.<sup>9</sup> LIE of the sample was calculated using the formula,

$$\text{LIE} = mgh$$

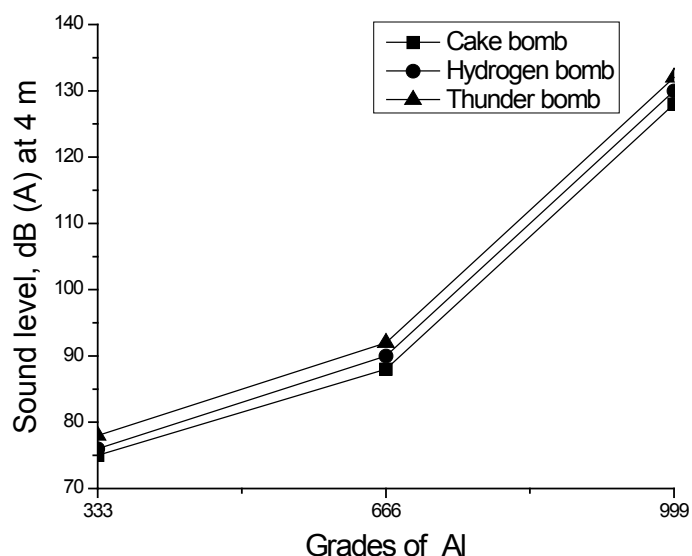
where  $m$  = mean of the drop weight (kg),  $g$  =

acceleration due to gravity ( $9.81 \text{ m s}^{-2}$ ),  $h$  = height (m).

The validity of the results was tested by calibrating the machine with the LIE of standard substances and the results are given in Table 2. The impact energy measured was within acceptable limits of error (1–2%). Several runs were undertaken to check the reproducibility.

#### Friction sensitivity tester

The friction sensitivity was determined using a Friction Tester by the general test methods of BAM<sup>12</sup> and corresponds to the UN Recommendations on the Transport of Dangerous Goods.<sup>13</sup> The friction test determines whether a pyrotechnic mixture possesses a danger of explosion or reaction when subjected to the effects of friction. When starting a test, a weight of materials was chosen

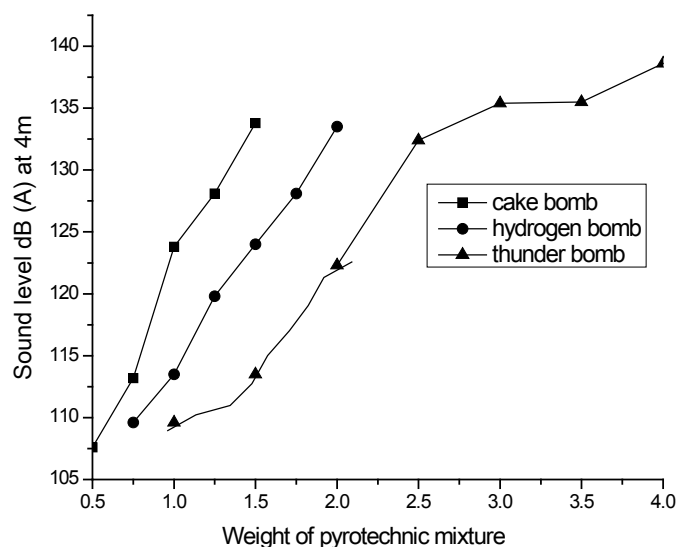


**Figure 3.** *Effect of particle size.*

approximately in the middle of the loading range. If two reactions were detected, then the load would be decreased. If no reaction occurred, then the load would be increased. Friction sensitivity is a relative measurement reported in newtons (N), when inflammation or explosion occurs only once in six repetitions.

### Thermal analyser

Thermal analysis (TA), thermogravimetric (TG) and differential thermal analysis (DTA) was carried out using a Perkin-Elmer Pyris diamond model thermal analyser with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ ,  $30\text{ }^{\circ}\text{C min}^{-1}$  and  $50\text{ }^{\circ}\text{C min}^{-1}$  and a temperature range of the standard system from room temperature to  $1100\text{ }^{\circ}\text{C}$ .



**Figure 4.** *Effect of the amount of pyrotechnic mixture on sound level.*

**Table 5.** *Effect of the quality of paper of the inner shell on sound level.*

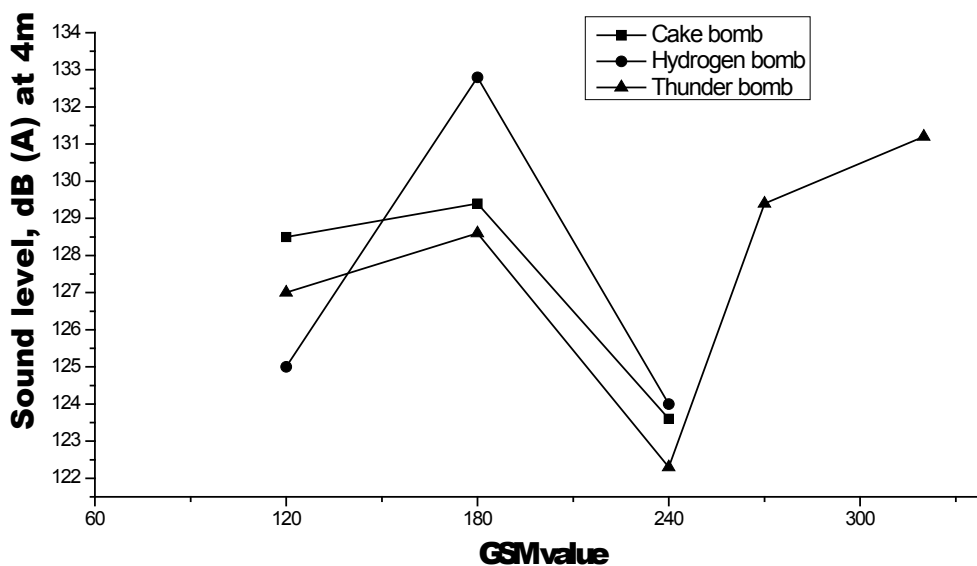
Dimension of the shell	Weight of pyrotechnic mixture/g	Paper weight (GSM)/g m <sup>-2</sup>	Bursting strength/kg cm <sup>-2</sup>	Sound level/ dB(A )	Sound level/ dB(C) peak
Cake-bomb	1.0	120 <sup>a</sup>	2.4	128.5	143.1
		180 <sup>a</sup>	3.2	129.4	148.0
		240 <sup>a</sup>	2.2	123.6	142.1
Hydrogen-bomb	1.5	120 <sup>a</sup>	2.4	125.0	146.5
		180 <sup>a</sup>	3.2	132.8	155.5
		240 <sup>a</sup>	2.2	124.0	144.1
Thunder-bomb	2.0	120 <sup>a</sup>	2.4	127.0	148.5
		180 <sup>a</sup>	3.2	128.6	149.7
		240 <sup>a</sup>	2.2	122.3	145.3
		270 <sup>b</sup>	4.1	129.4	150.2
		320 <sup>b</sup>	5.4	131.2	153.0

<sup>a</sup>Kraft paper (brown). <sup>b</sup>Duplex board (white)

### Differential scanning calorimetry

A Differential Scanning Calorimetry (DSC) module 821 from Mettler Toledo TA instruments was used for thermal stability measurements under ignition conditions. The studies were conducted by using 2 mg sample in an aluminium sample holder under pure nitrogen gas as purge gas and

an air flow rate of 50 ml min<sup>-1</sup> with a temperature range of -65 °C to 450 °C and a heating rate of 10 °C min<sup>-1</sup> and the air flow rate was maintained as 50 ml min<sup>-1</sup>.

**Figure 5.** *Effect of GSM value on the bursting strength of paper.*

**Table 6** Sound level analysis of firecrackers made by different chemical composition

Sample No.	Compositions (wt%)			Onset temp./°C	Peak temp./°C	$\Delta H/J\ g^{-1}$	Sound level	
	KNO <sub>3</sub>	S	Al				dB(A)	db(C) peak
1	50	5	44.5	461.2	491.08	48.45	105.8	125.4
2	50	9.5	40.0	442.04	493.67	106.89	119.8	139.5
3	50	20	29.5	432.14	492.51	120.14	134.8	154.4
4	50	22	27.5	431.56	491.68	118.56	127.2	147.1
5	52.5	20	27.0	434.17	494.16	126.56	132.8	152.6
6	55	20	24.5	435.48	496.34	132.78	130.7	150.4
7	56	20	23.5	436.86	496.88	139.67	129.4	149.0
8	57.5	20	22.0	437.99	498.77	144.62	125.0	144.6
9	57.5	8	34.0	452.17	492.84	96.12	116.0	136.3
10	57.5	16	26.0	434.65	496.71	146.78	128.1	148.4
11	57.5	24	18.0	442.43	492.83	142.67	121.8	141.6
12	58	20	21.5	437.11	497.74	141.52	126.6	148.3
13	60	20	19.5	436.23	498.01	146.87	127.4	147.2
14	62.5	20	17.0	435.82	495.74	138.85	128.8	148.3
15	65	20	14.5	435.67	493.48	134.89	130.3	150.1

1.5 g of firecracker mixture with 0.5% H<sub>3</sub>BO<sub>3</sub> in a paper case of inner box dimension of 28 × 15 × 15 mm<sup>3</sup> (6.3 cm<sup>3</sup>); paper case: GSM 240 g m<sup>-2</sup> and bursting strength 2.2 kg cm<sup>-2</sup>. Jute length: 195 cm, winding: 3 ply.

### Paper quality analysis

The bursting strength of the paper used for making the inner case of the firecrackers was measured using a bursting strength tester (Analog model) and the thickness of the paper was measured using a GSM meter (Analog model).

## Results and discussion

### Sound level analysis of commercial firecrackers

Commercial sound producing firecrackers were obtained from five different well known companies situated in Sivakasi, India. Sound level analysis was carried out and the data are given in Table 3. Commercial sound producing firecrackers produce sound levels in the range 130.7 dB(A<sub>1</sub>)/150.4 dB(C) peak to 142.8 dB(A<sub>1</sub>)/162.6 dB(C) peak at 4 m distance which is much higher than the allowed sound level of 125 dB/140 dB(C) peak. The sound level was measured on varying the following factors.

### Effect of particle size

The effect of sound level from different types of firecracker with different grades of Al based on the particle size was studied (Figure 3). It is clear that as the particle size decreases, the pyrotechnic mixture is effective in producing sound.<sup>14</sup> Al of grades 333 (60 mesh/250 micron size) and 666 (100 mesh/150 micron size) could produce flash instead of producing sound while Al of 999 grade (200 mesh/63 micron size) alone produces sound effectively. Sound level tests were conducted on varying the particle size of KNO<sub>3</sub> in the range 63–250 micron. It was found that increasing the particle size of KNO<sub>3</sub> decreased the sound level but the effect is much smaller than that of the variation of aluminium particle size. This trend was due to the fact that the sound produced depends not only on the composition and the particle size but also on the particle shape, density and compactness of the chemicals. In order to maintain homogeneity of the mixture, the bulk packing density was maintained at 0.44–0.50 g cm<sup>-3</sup>.

**Table 7.** Correlation of sound level and thermal decomposition temperature.

Variables	Correlation coefficient	Significance
Sound level vs. onset temperature	-0.9445	A strong negative correlation
Sound level vs. peak temperature	-0.9025	A strong negative correlation
Sound level vs. heat of reaction	-0.9555	A strong negative correlation

#### Effect of size and quality of paper case

Sound levels produced from firecrackers with inner paper cases (paper box) of different dimensions are given (Table 4). Three different sizes of case were used and the amount of the firecracker mixture required to produce the sound level increases with increasing dimensions of the box (Figure 4). The amount of firecracker mixture required to produce the allowed sound level was optimised as 1.0/1.5/2.0 g for small firecrackers (cake-bomb) and large firecrackers (hydrogen-bomb and thunder-bomb) respectively. If excess mixture is kept in the paper case of the firecrackers, the sound level produced would be higher than the allowed level.

The sound level produced from firecrackers made with different thicknesses of paper for the inner paper case was measured (Table 5). As the GSM value increases, the quality of the paper changes from paper to board. No linear relationship exists between the GSM value and the bursting strength of the paper in the case of kraft paper (brown) while the bursting strength of the paper increases with GSM value of the duplex board paper (Figure 5). kraft paper with a GSM value of 240 and bursting

strength of  $2.2 \text{ kg cm}^{-2}$  was found to produce the optimum sound level. The noise level produced from the firecrackers increases as the bursting strength of the paper increases (Figure 6).

It is possible to produce commercially available firecrackers, using 999 grade aluminium (63 micron size), an optimum quantity of pyrotechnic mixture in an inner box of specified dimensions made up with kraft paper of GSM 240, bursting strength  $2.2 \text{ kg cm}^{-2}$ , which can produce a sound level of <125 dB(A)/145 dB(C) peak at 4 m distance, within the allowed limits as prescribed by the Govt. of India notification.<sup>10</sup>

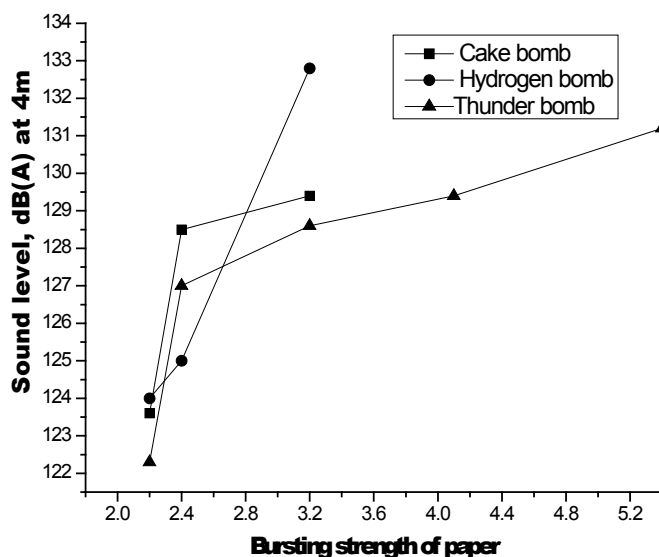
#### Effect of composition on sound level

The composition of the pyrotechnic mixture plays an important role. If the total content of  $\text{KNO}_3/\text{S}$  is high or without using metallic fuel, Al, then the pyrotechnic mixture is not useful for making sound-producing firecrackers; instead it produces dark fumes.<sup>15</sup> Good thermal conductivity is essential for smooth propagation of burning. Metals are the best thermal conductors for the transfer of heat for the  $\text{KNO}_3/\text{S}$  mixture. The results of sound level tests for the different compositions are given in Table 6. It was observed that the sound level varied when the concentration of any one of the components was changed. The plot between the heat of reaction and sulphur concentration (Figure 7) showed that with increasing sulphur concentration, the decomposition energy release increased. It reached a maximum value at 16 wt% of sulphur when the concentration of  $\text{KNO}_3$  is 50 wt% and at 20 wt% of sulphur when the concentration of  $\text{KNO}_3$  is 57.5 wt% and then started decreasing. The concentration of sulphur appeared critical. In Table 6, it is clear that the optimum level of sound is produced in the mixture of composition  $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$  57.5/20/22/0.5%.

**Table 8** Sensitivity measurements of pyrotechnic mixtures.

Pyrotechnic composition Mass fractions (%)	Ignition temperature/ $^{\circ}\text{C}$	Friction sensitivity/N	Impact sensitivity/J
$\text{KNO}_3/\text{Al}/\text{S}/\text{H}_3\text{BO}_3$ 57.5/20/22/0.5	440	324	5.3
$\text{KClO}_4/\text{Al}/\text{S}/\text{H}_3\text{BO}_3$ 57.5/20/22/0.5		168	1.96



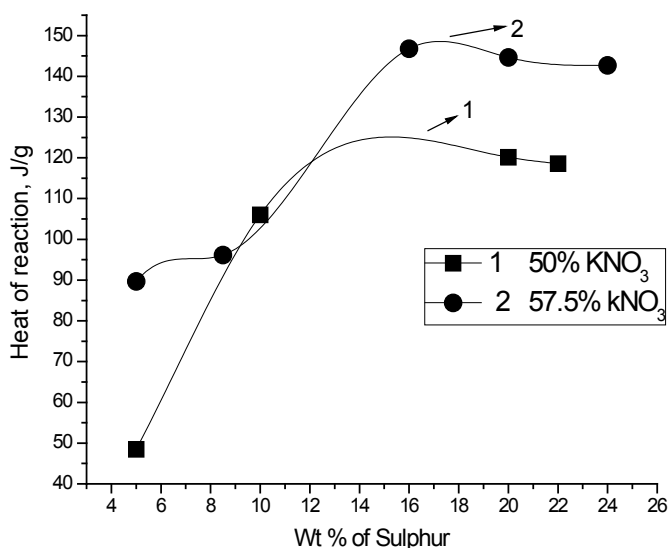


**Figure 6.** Effect of bursting strength of paper on sound level.

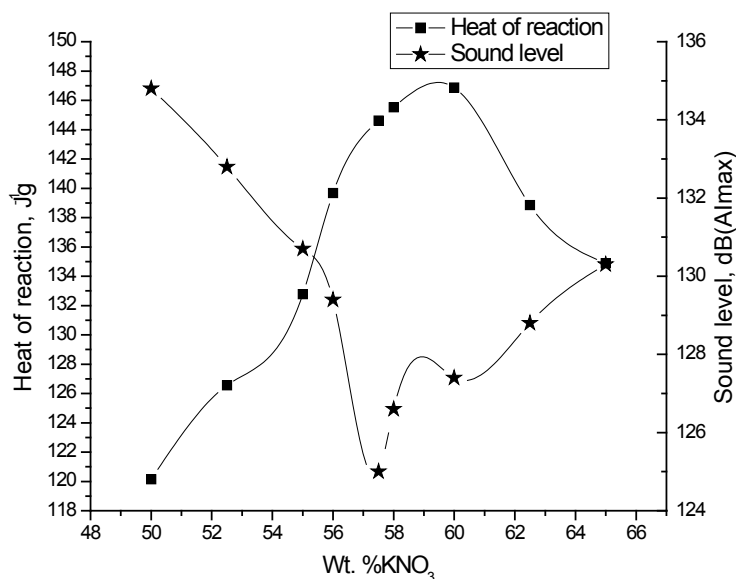
#### Interrelation between sound level and thermal decomposition parameters

The thermal decomposition data were subjected to Karl Pearson's correlation analysis to understand the interrelation between sound level and thermal decomposition parameters and the results are given in Table 7 and in Figures 8 and 9. Correlation analysis refers to the techniques used in measuring

the closeness of the relationship between the variables. If two variables vary such that change in one variable affects the change in the other variable, the variables are correlated. The degree of correlation is measured by correlation analysis and expressed in terms of correlation coefficient or correlation index. Karl Pearson's coefficient of correlation ( $r$ ) is simple and highly reliable and  $r$



**Figure 7.** Effect of concentration of sulphur on the heat of decomposition.



**Figure 8.** Interrelation between heat of reaction and sound level at fixed  $S = 20$  wt%.

between any two variables,  $X$  and  $Y$ , is given as follows (equation 1):

$$r = \frac{n \sum XY - \sum X \sum Y}{\left[ n \sum X^2 - \left( \sum X \right)^2 \right] \left[ n \sum Y^2 - \left( \sum Y \right)^2 \right]}$$

where  $n$  = number of observations and  $\Sigma$  = summation.

The value of the correlation coefficient  $r$  always lies between +1 and -1. If the value of  $r = 0$ , then the variables  $X$  and  $Y$  indicate no correlation. If the value of  $r$  is near +1, then the variables  $X$  and  $Y$  are said to be positively correlated and if the value of  $r$  is near -1, then the variables  $X$  and  $Y$  are said to be negatively correlated.

#### Interrelation between the weight % of oxidiser and sound level

The results of the experiments conducted using DSC for the different compositions of firecrackers are given in Table 6. The heat of reaction,  $\Delta H$ , increases with increasing concentration of  $\text{KNO}_3$  to a maximum between 56 and 60% and  $\Delta H$  decreases above 62 wt% of  $\text{KNO}_3$ . The region 56–60 wt% of  $\text{KNO}_3$  is considered as critical to the sound level produced. A strong negative correlation

coefficient  $r = -0.9555$  (Table 7) reveals an inverse relationship between noise levels and  $\Delta H$  which was determined by DSC analysis (Figure 8).

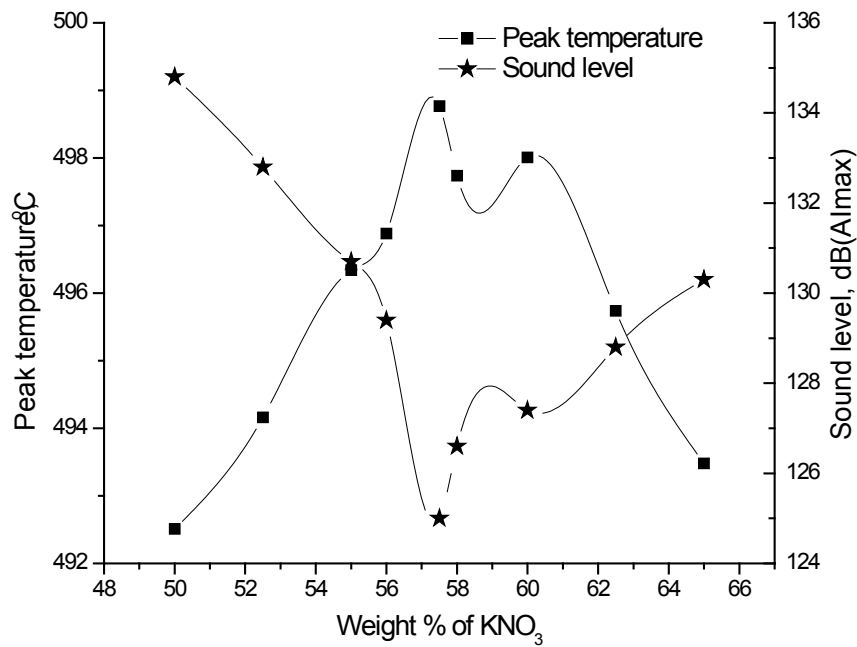
#### Interrelation between peak temperature and sound level

The interrelation between peak temperature (Table 6) which was determined by DSC analysis and sound level at a fixed sulphur concentration ( $S = 20$  wt%) is given graphically in Figure 9. High peak temperature leads to the production of low sound levels in the firecrackers in the region of 56 and 60%  $\text{KNO}_3$ , very similar to the plot of  $\Delta H$  vs. sound level (Figure 8). A strong negative correlation coefficient,  $r = -0.9025$  (Table 7) reveals the inverse relationship between sound level and peak temperature.

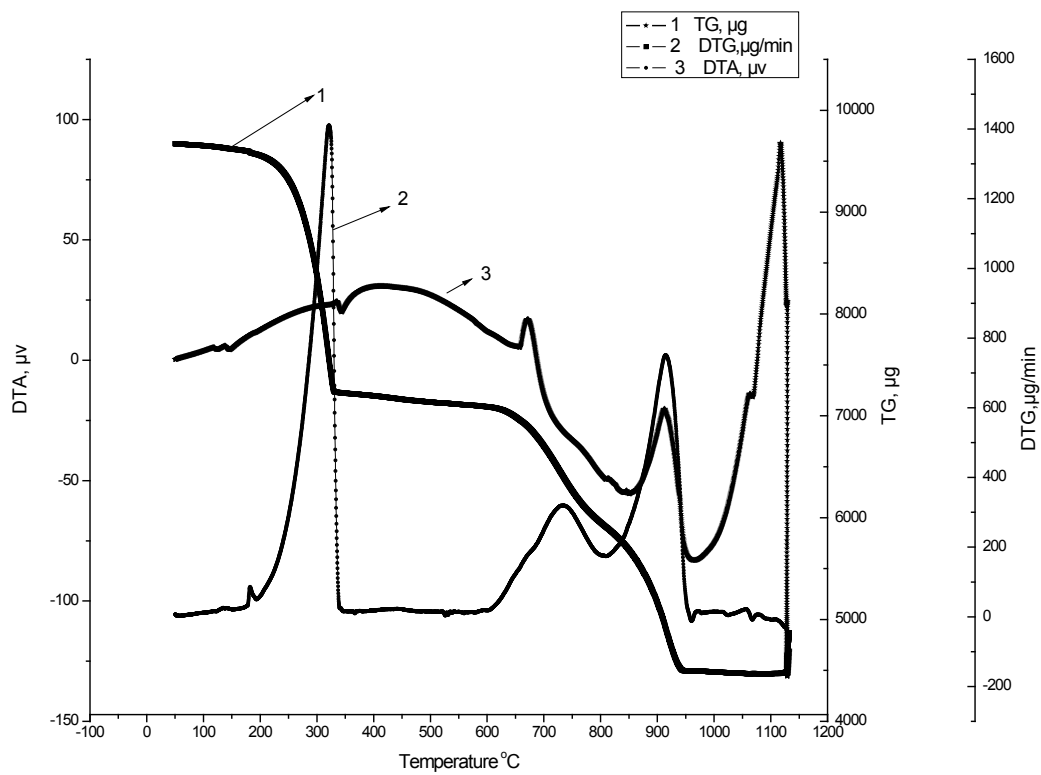
### Mechanical sensitivity measurements

#### Friction sensitivity

A study of the sensitivity of the pyrotechnic mixture  $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$  57.5/20/22/0.5% was carried out (Table 8) to indicate the explosivity nature of the pyrotechnic mixture. The sensitivity to mechanical stress like friction and impact sensitivity of the pyrotechnic mixture was measured.<sup>16</sup> The friction sensitivity is found to be 324 N. High measurements indicate low friction



**Figure 9.** Interrelation between peak temperature and sound level at fixed  $S = 20$  wt%.



**Figure 10.** Thermogram of pyrotechnic mixture (at a heating rate of  $30\text{ }^{\circ}\text{C min}^{-1}$ ).

sensitivity and the pyrotechnic mixture is safe from accidental risk of mechanical stress.<sup>17</sup> Any material with a limiting load less than 80 N is considered too sensitive for transport of military pyrotechnics. In the case of firecrackers, any material that produces a ‘Threshold of Initiation’ (TIL) greater than 184 N is deemed to be fit for transport.<sup>17</sup> In order to compare the sensitivity of pyrotechnic mixtures, a highly sensitive pyrotechnic mixture of  $\text{KClO}_4/\text{S}/\text{Al}(\text{H}_3\text{BO}_3)$  in the same proportions was tested for sensitivity and it was found to be 168 N which is <184 N making it too sensitive for transport.

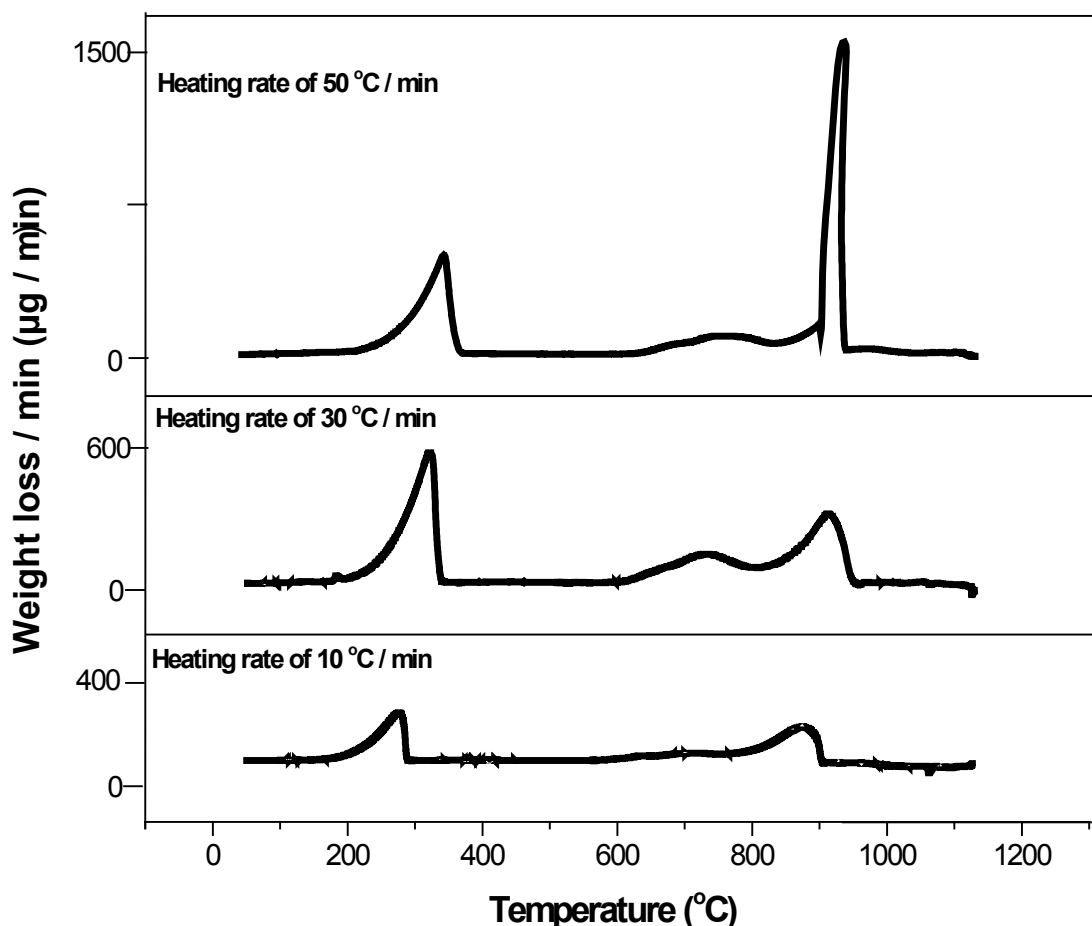
### Impact sensitivity

The impact sensitiveness of the pyrotechnic mixture was measured in terms of the LIE (Table 8). The limiting impact energy was 5.3 J for the firecracker compositions  $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$  (LIE for  $\text{KClO}_4/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$  is 1.9), so they could

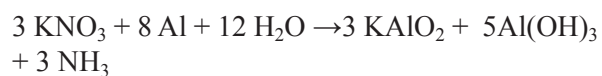
be treated as category III explosives according to the classification of Andreiev-Beliaev<sup>11</sup> indicating that this composition was sensitive to impact. This impact sensitivity indicated that the mixture was prone to hazards from impact and at the same time it could be used to produce good firecrackers.

### Thermal analysis

In order to understand the sensitivity of the material to heat and to determine the relative onset decomposition temperature, thermal analysis of the composition  $\text{KNO}_3/\text{S}/\text{Al}/\text{H}_3\text{BO}_3$  as 57.5/20/22/0.5% was carried out (Figure 10) at the three different heating rates of 10, 30 and 50 °C per minute. The decomposition occurred as a two stage process. At 900 °C, complete decomposition occurred leaving 41–46% of a final residue indicating that the final product<sup>18</sup> is  $\text{Al}_2\text{O}_3$  along with other oxides. If moisture is present, the reaction proceeds as follows:<sup>19</sup>



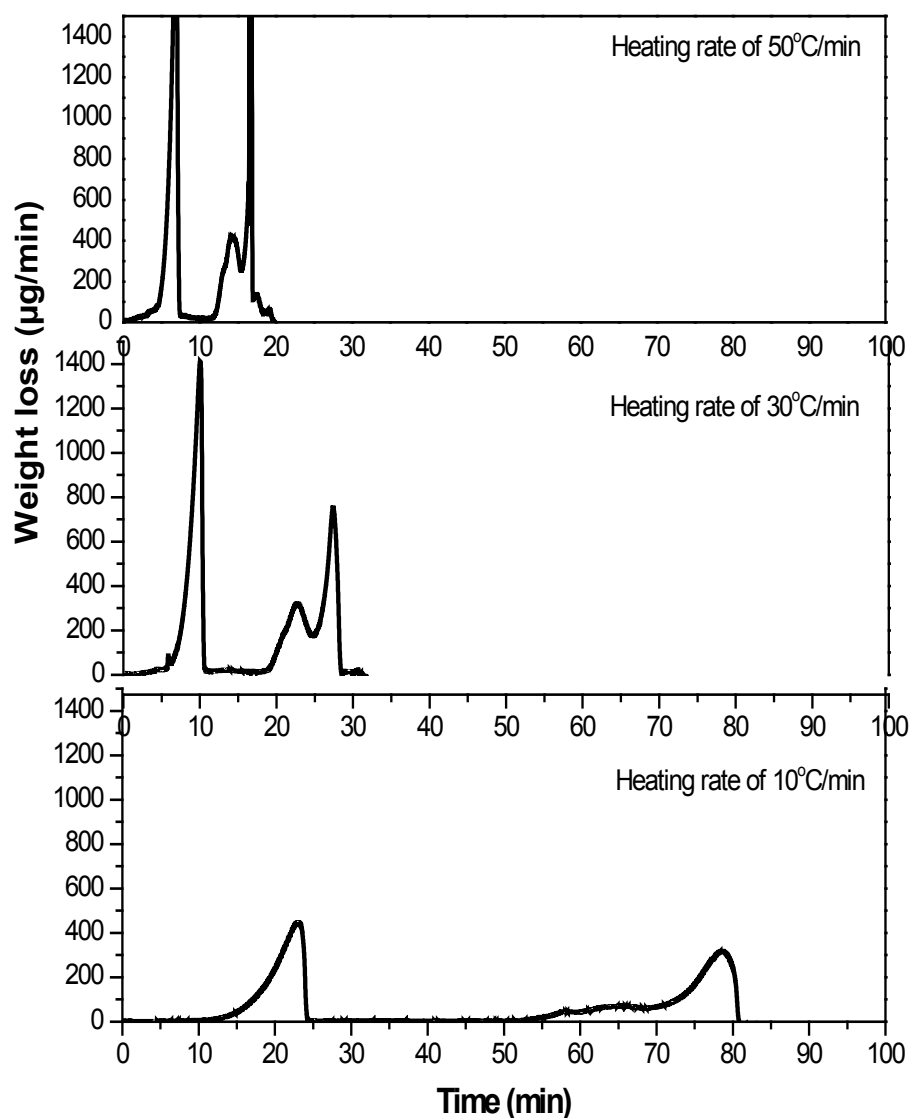
**Figure 11.** Variation of DTG curve with respect to temperature at different heating rates.



The above reaction might occur evolving heat and  $\text{NH}_3$  gas. This reaction is accelerated by the alkaline medium and auto ignition is possible leading to fire accident in the manufacturing unit. A small quantity of a weak acid such as boric acid ( $\text{H}_3\text{BO}_3$ ) can effectively retard the decomposition by neutralizing the alkaline products and maintaining a weakly acidic environment. At the relatively slow heating rate of the thermal analysis instrument ( $10^\circ\text{C min}^{-1}$ ), the result indicates approximately a  $250^\circ\text{C}$  disparity between the onset decomposition temperature of the pyrotechnic mixtures and oxidizer while the value of the

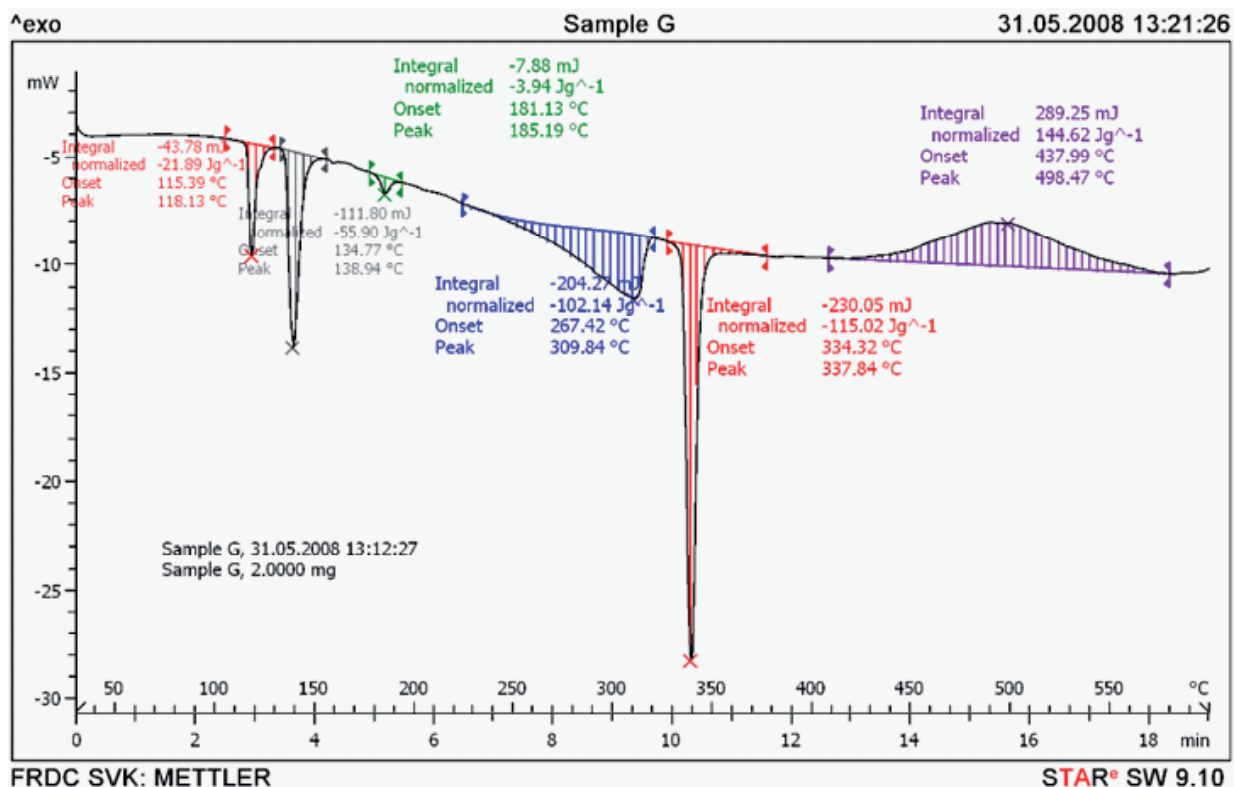
decomposition temperature of both when slowly heated and when heated at the greater rate showed that the ingredients will decompose at precisely the same temperature (Figure 11). The position of the DTG peak with respect to time varies (Figure 12). Within the firecracker unit, the pressure level varies greatly with time, the fuel would continue to decompose in a low pressure and low temperature environment while the oxidizer component would not fully decompose until the incoming pressure pulse had sufficiently raised the temperature of the reaction front.<sup>19</sup>

DSC analysis is used to determine the ignition temperature precisely (Figure 13). There is no overlap of the endothermic peaks and exothermic



**Figure 12.** Variation of DTG curve with respect to time at different heating rates.





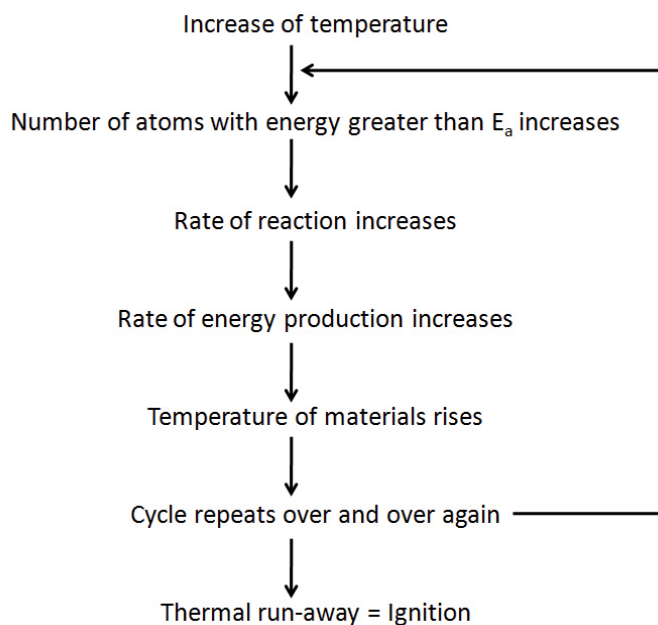
**Figure 13.** DSC analysis of pyrotechnic mixtures.

peaks. Below 437  $^{\circ}\text{C}$ , there is no exothermic peak and only four endothermic peaks were observed. Among the four endothermic peaks, two sharp peaks correspond to the melting points of sulphur and  $\text{KNO}_3$  respectively at 138  $^{\circ}\text{C}$  and at 339  $^{\circ}\text{C}$ . The peaks at 118  $^{\circ}\text{C}$  and 280.5  $^{\circ}\text{C}$  correspond to the phase transitions of sulphur and  $\text{KNO}_3$  respectively. DSC analysis (Figure 12) indicates clearly that auto ignition of the mixture, exothermic reaction occurs only above 437.9–498.47  $^{\circ}\text{C}$  indicating the thermal stability of the mixture.

There was wide variation in the composition used among the Indian firework companies though they had to exhibit a specific level of explosivity. Some manufacturers are using unwanted quantities of chemicals. During hazardous situations, the use of excessive quantities of chemicals will lead to excessive damage to the ecosystem. The composition consisting of 57.5%  $\text{KNO}_3$ , 20% S, 22% Al and 0.5%  $\text{H}_3\text{BO}_3$  appears to be an ideal composition in all respects with reduced impact sensitivity, required explosivity and allowed sound pressure levels.

### Chemistry and mechanism of reaction in firecrackers

The flash composition used in firecrackers consists of an oxidizer, potassium chlorate or barium nitrate with aluminium and sulphur. Sulphur acts as a fuel. When a flash composition is ignited by its fuse, initially, the sulphur melts and the interaction between atoms increases. This results in more atoms with energies exceeding the activation energy that will be in contact and the reaction rate increases with the increasing rate of energy release which leads to thermal runaway at a lower temperature and explosion occurs at a lower temperature. A sharp rise in reaction rate occurs, liberating more heat, raising the temperature further, accelerating the reaction until an explosion occurs or the reactants are consumed. The minimum quantity of the material needed to produce an explosion, under a specified set of conditions, is referred to as the 'critical mass.' In a confined system, the hot gases that are produced can build up substantial pressure driving the gases into the high energy mixtures and causing a violent reaction.<sup>12</sup> High explosive reactions produce high sound. The 'critical mass'



**Figure 14.** Flow chart for the mechanism of firecrackers.<sup>20</sup>

should be considered to produce a limited level of sound.

In firecrackers, a different mechanism<sup>14</sup> takes place as shown in the flowchart (Figure 14). The  $\text{KNO}_3/\text{S}/\text{Al}(\text{H}_3\text{BO}_3)$  pyrotechnic mixture can be considered as environmentally friendly for making sound-producing crackers compared to the high sensitivity  $\text{KClO}_4/\text{S}/\text{Al}(\text{H}_3\text{BO}_3)$  pyrotechnic mixture but the total content of the composition used in the commercial atom-bomb and thunder-bomb can be reduced to produce sound within the allowed limits.

## Conclusion

Fireworks are part of social festivals all over the world. It is imperative that use of fireworks does not pollute the atmosphere. Several agencies at national and international levels have imposed restrictions on the safe use of fireworks. In sound-producing firecrackers, the pyrotechnic mixture  $\text{KClO}_4/\text{S}/\text{Al}(\text{H}_3\text{BO}_3)$  is not safe for transport due to its high friction and impact sensitiveness. An alternative pyrotechnic mixture,  $\text{KNO}_3/\text{S}/\text{Al}(\text{H}_3\text{BO}_3)$ , whose inversion temperature is above  $400^\circ\text{C}$  and which is less sensitive to mechanical stress is safe for transport. Impact sensitivity analysis indicates that the pyrotechnic compositions studied can be categorized as class III explosives that are sensitive to impact. The composition consisting of 57.5%

$\text{KNO}_3$ , 20% S, 22% Al and 0.5%  $\text{H}_3\text{BO}_3$  appears to be an ideal composition in all respects with reduced impact sensitivity, required explosivity and allowed sound pressure levels.

## Acknowledgements

The authors are very grateful to The Standard Fire Works Pvt. Ltd., Sivakasi for providing firecrackers with suitable proportions of pyrotechnic mixtures and MEPCO Engineering College, Sivakasi for the help provided.

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## Events Calendar

### Explosives, Pyrotechnics and Fireworks

#### **36th International Pyrotechnics Seminar**

August 22-28 2009, Rotterdam, The Netherlands

**web:** <http://www.intlpyro.org/index.htm>

#### **Pyrotechnics Guild Int'l Convention**

August 8 - 14, 2009, Mason City, Iowa

**Contact:** Robin Cleveland, Membership Manager

Phone: +1 920-558-4681

email: [membership@pgi.org](mailto:membership@pgi.org)

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#### **Listing of Fireworks Events - Worldwide**

web: <http://fireworksguide.com>

#### **Pyrotechnic Chemistry Lecture Course**

14/15/16 April 2009

(NOTE change of date)

Huntingdon, Cambs. UK

For more information please see

web: <http://www.pyrochemistry.net>

#### **5th EFEE World Conference**

April 26-28 2009, Budapest

Contact Roger Holmberg

email: [info@efee.eu](mailto:info@efee.eu)

web: [www.efee.eu](http://www.efee.eu)

### High Power Rocketry

#### **LDRS 2009**

New York - July 2-6 2009

**Contact:** see web site

web: <http://www.rocketryplanet.com/content/view/2575/28/>

### Model Rocketry

#### **NARAM 2009**

August 8-14 2009, Johnstown, PA

**Contact:**

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For other launch information visit the NAR Web

site: <http://www.nar.org>

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