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CAUTION

The experimentation with, and the use of, pyrotechnic materials can be dangerous; it is felt to be important for the reader to be duly cautioned. Without the required training and experience, no one should ever experiment with or use pyrotechnic materials. Also, the amount of information presented in this Journal is not a substitute for necessary training and experience.

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

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Hazards Associated with the Storage of Fireworks

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ABSTRACT

Large quantities of a whole range of materials, including fireworks, are moved around the world in steel ISO containers. In recent years in the UK, manufacturers and retailers have used such containers to store fireworks. It has been long recognised that confinement can increase the hazard of energetic materials such as pyrotechnics and propellants. Recent incidents involving fireworks and large-scale fire engulfment trials on ISO containers filled with fireworks have raised concerns about the possible effects of confinement on the hazards presented by the more energetic fireworks. This paper presents information on one such fireworks incident in the UK and the action taken following this incident; together with a summary of the fire trials conducted to date by the UK's Health and Safety Executive (HSE) on packaged fireworks in ISO containers.

Keywords: fireworks storage, fire, explosion, hazard, explosive storage

Introduction

Under the UN Scheme for the Transport of Dangerous Goods,[1] substances and articles are assigned to one of nine classes according to the most predominant hazard they present. Some of these classes are subdivided into hazard divisions. Although fireworks fall into Class 1 (explosives), many of them are assigned to explosives hazard sub-divisions that are considered not to present either a mass fireball or a mass explosion hazard. Internationally a variety of arrangements exists for classifying fireworks. This ranges from self-classification by the importer to a formal application of the UN test scheme.[1]

In 1980[2] the Seattle Fire Department, USA, conducted a bonfire test on 2,540 kg (presumably gross weight) of unspecified confiscated Chinese fireworks held in a 6.1 m long steel ISO container. Just after 2 minutes the container burst violently, expelling the contents 45–60 m in the air, and up to 215 m horizontally, causing fire damage to 20,000 m^2 of land.

Because of the increasing use of ISO containers for the bulk storage of fireworks in the UK, the HSE's Health and Safety Laboratory was commissioned to undertake research into the potential effects of confinement on fireworks held in storage. Specifically, a limited number of fire trials have been carried out on fireworks held in steel ISO containers.[3] This work is against a background of several firework storage incidents such as those at Culemborg (The Netherlands, 2 Feb 1991), Stourbridge (The Midlands, UK, 14 Mar 1996), Uffculme (Devon, UK, 17 Nov 1998), and more recently at Enschede (The Netherlands, 13 May 2000), which raise further questions about the possible effects of confinement on the potential hazards presented by fires involving stored fireworks.

At any one time, large numbers of fireworks types and sizes are available on the market, and new types are continually being introduced. Because of this, some years ago the UK introduced a *default* classification system for fireworks. Also due to concerns about the possible effects of confinement on fireworks in bulk storage, the UK introduced a *hazard type* (HT) rather than hazard division (HD) concept (as used for transport) for the purposes of licensing manufacture and storage. Both the fireworks *default classification* and *hazard type* schemes have been discussed and agreed to by the UK fireworks industry.

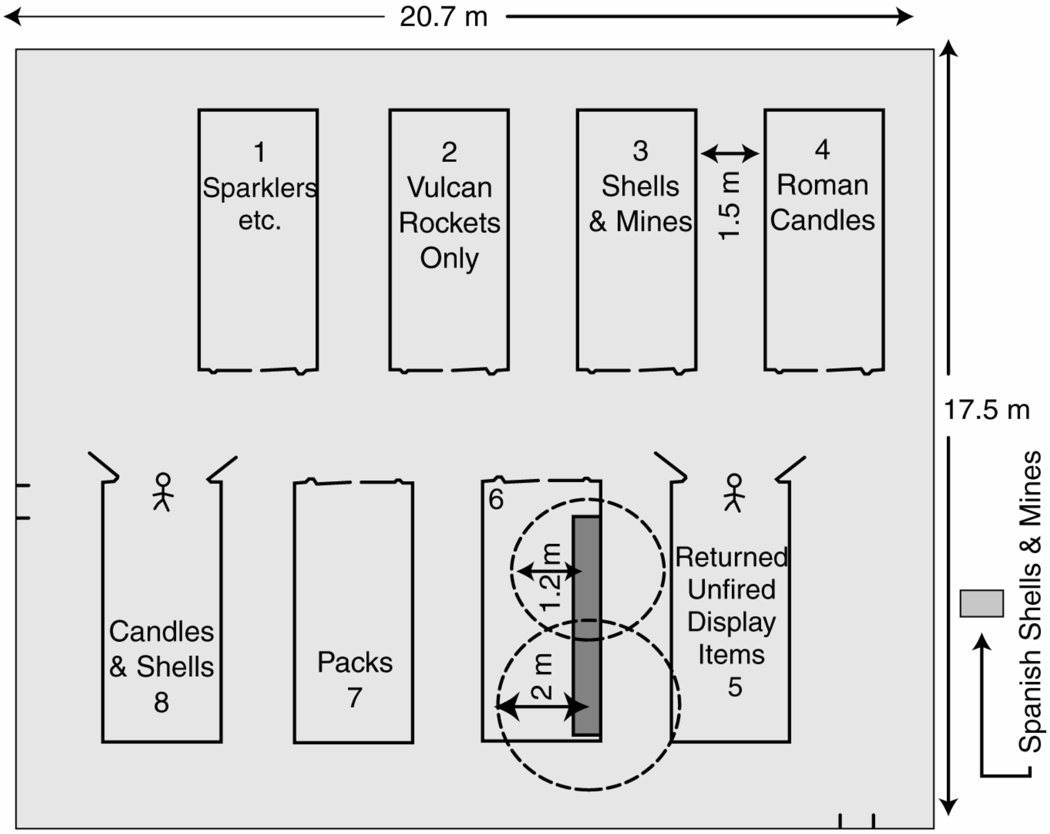

Figure 1. Approximate locations of ISO containers in the storage building before the explosion.

Fireworks Incident at Uffculme, Devon

On 17 November 1998 an explosion occurred at a licensed explosives factory in Uffculme, Devon. The explosion occurred in container number 6 of the eight fireworks-containing steel ISO containers (6.1×2.4×2.4 m), which were co-located inside a metal clad steel-framed building (see Figure 1). The centre of the explosion was marked by two depressions in the floor of the building as indicated. The explosion was preceded by an intense fire inside the building, which had been initiated by a prohibited operation in the entrance to container number 5. The building and containers were completely destroyed by the explosion, and fragments were scattered to a distance in excess of 200 m. Other buildings on and off site were damaged by blast, fragments and/or fires.

All records of the precise contents of each magazine were lost in the fire that followed the explosion. A combination of contact by the company with their fireworks suppliers and recollections by the magazine attendants has enabled a fairly reliable estimate to be made of the magazine contents (see Table 1 and Figure 2). The facility licence required that the fireworks be held in the packages as received from the supplier.

The explosion(s) resulted in the destruction of the building and destruction or movement of the other ISO containers (Figure 3). The centre of the explosion was marked by two depressions in the 163 mm thick concrete base of the building. The largest depression in the concrete floor was approximately 113 mm deep by 4 m in diameter. The second depression, centred some 3 m away, was approximately 50 mm deep by 3 m in diameter. A summary of the damage to other buildings in the immediate vicinity of the blast (see Figure 4) is presented in Table 2. Metal cladding from the steel portal building which housed the ISO containers, together with fragments from the ISO containers (primarily containers 5 and 6), were dispersed around the sur-

Table 1. Uffculme Incident: Contents of Container Number 6.

Supplier	Type	Size (mm)	Quantity (each)	NEC[(a)] per firework item (kg)	Total NEC (kg)
Arnal	Mine	50	240	0.09	21.6
Arnal	Mine	75	318	0.15	47.7
Arnal	Mine	100	222	0.3	66.6
Arnal	Star Shell	75	84	0.15	12.6
Arnal	Star Shell	100	80	0.3	24
Arnal	Star Shell	125	80	0.5	40
Arnal	Star Shell	150	41	0.75	30.75
Cabeller	Star Shell	75	55	0.15	8.25
Brunchu	Salute Shell	75	25	0.15	3.75
Brunchu	Star Shell	75	235	0.15	35.25
Brunchu	Star Shell	100	80	0.3	24
Brunchu	Star Shell	125	79	0.5	39.5
Brunchu	Star Shell	150	32	0.75	24
Vulcan	Roman Candle	30	50	0.3	15
Vulcan	Roman Candle	25	36	0.17	6.12
Cabeller	Mine	60	40	1.2	48
Pirofantasia	Roman Candle	30	720	0.26	187.2
Pirofantasia	Roman Candle	45	50	0.74	37
Brunchu	Wheel	Aerial	36	0.04	1.58
Arnal	Rocket	14	1,234	0.05	61.7
				NEC in Container	734.6

(a) NEC is the Net Explosives Content.

Note: some information regarding shells from certain manufacturers do not include the weight of any stars in the explosives NEC. The figures given above are taken from the manufacturers' literature.

rounding area (see Figure 5). Not all of the fragments are included in the top left hand quadrant of the plan since some of these had been removed from the yard of the factory premises before the fragment survey was conducted. Even so, one particular fragment, a steel corner of an ISO container weighing approximately 10 kg, fell through the roof of an extension some 140 m away, on the main street of the village.

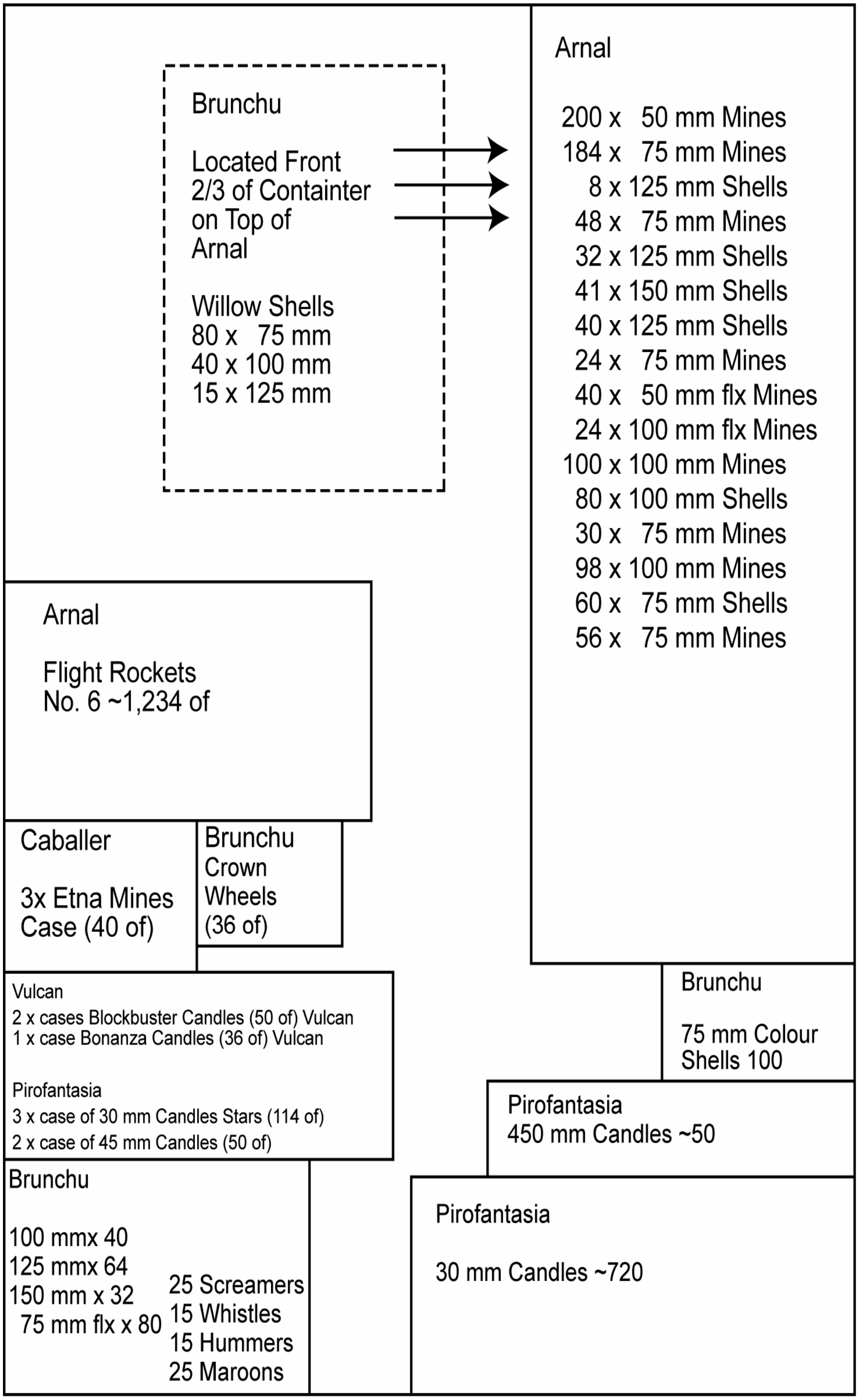

Figure 2. Contents and layout of magazine (container) number 6 before the explosion.

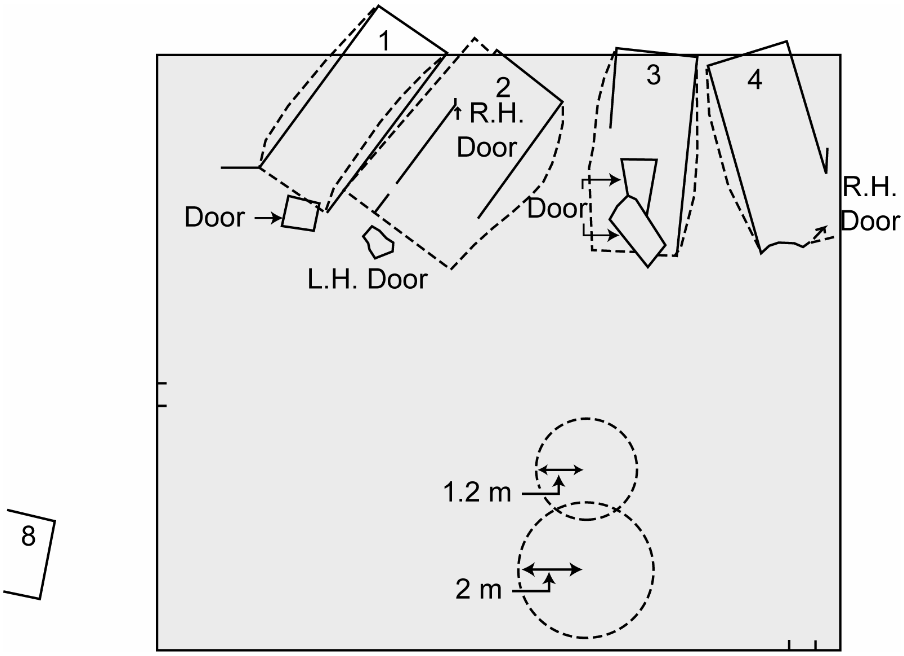

Figure 3. Location of ISO containers inside building after the explosion.

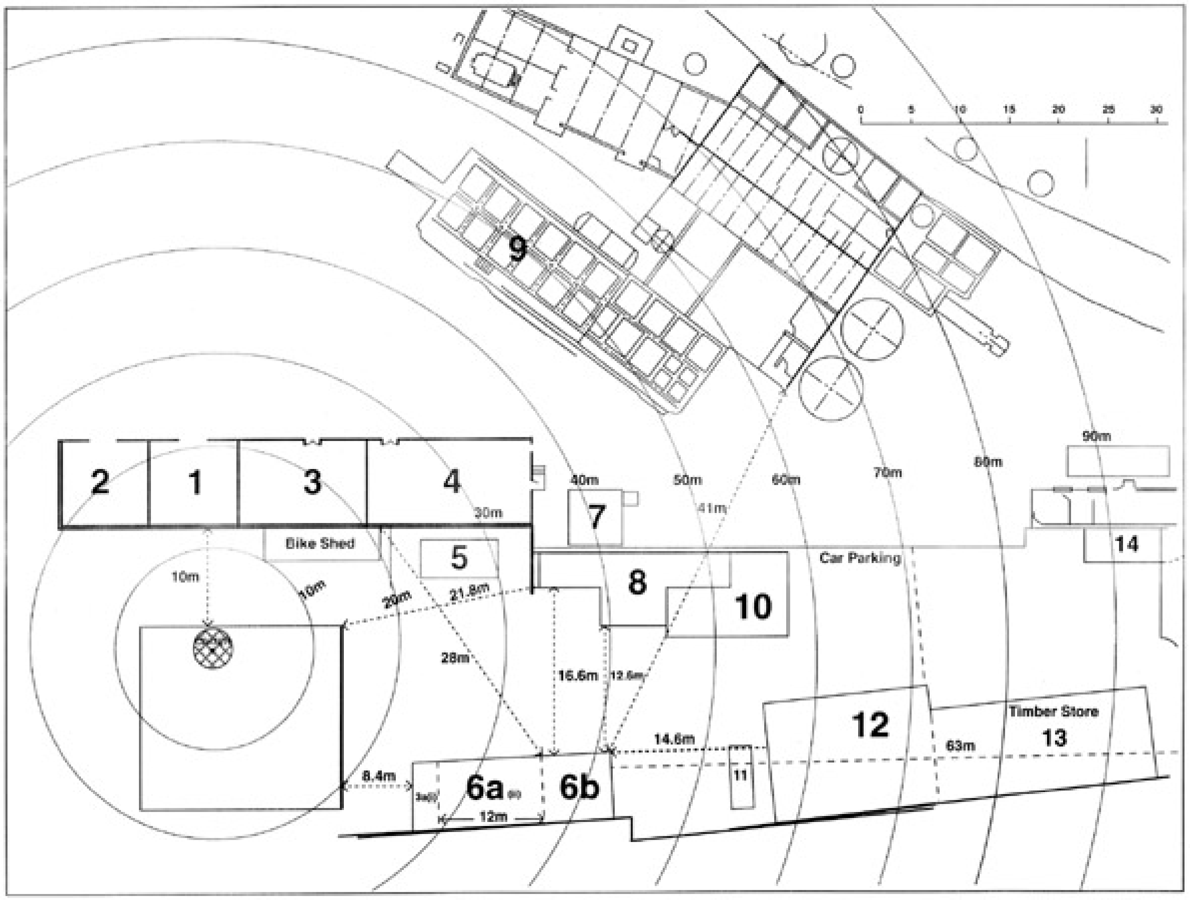

Figure 4. Buildings in immediate vicinity of fireworks explosion.

Table 2. Uffculme Incident: Damage to Adjacent Buildings.

Building number	Distance from blast centre (m)	Description of damage
1	13–22	Single story, solid double concrete block walled room. Wooden trussed roof with asbestos sheeting. Front wall demolished. All of asbestos roofing destroyed and half of the wooden trusses missing.
2	14–26	Construction as above. Front wall and top of gable end blown down. All of roof including wooden trusses missing. Rear wall leaning outwards at angle of 30 degrees to the vertical.
3	13–27	Front wall deflected inwards at centre by approx. 120 mm at top edge. Asbestos roof on front half of room missing. Wooden roof trusses intact.
4	20–38	Approx. 15% of asbestos roof (closest to blast source) missing.
5	22–31	Mobile home destroyed.
6	23–37	Wooden-framed single story building; corrugated iron clad, destroyed.
7	37–44	Single story brick building; flat roof. Little damage.
8	34–53	Steel-framed building, mobile home type construction, destroyed by fire.
9	47–60	Tall metal-framed mill building. Part clad in metal sheeting and part in asbestos sheeting. Asbestos cladding/sheeting facing the blast damaged out to approximately 50 m from the blast source.
10	46–58	Steel-framed building, mobile home type construction, destroyed by fire.
11	53–56	Portacabin destroyed.
12	56–74	Steel-framed building. Asbestos roof (undamaged) and corrugated iron clad. Some minor buckling of the steel cladding.
13	73–95	Minor missile damage to the corrugated asbestos roof.
14	88–100	Single story brick building. Windows broken.

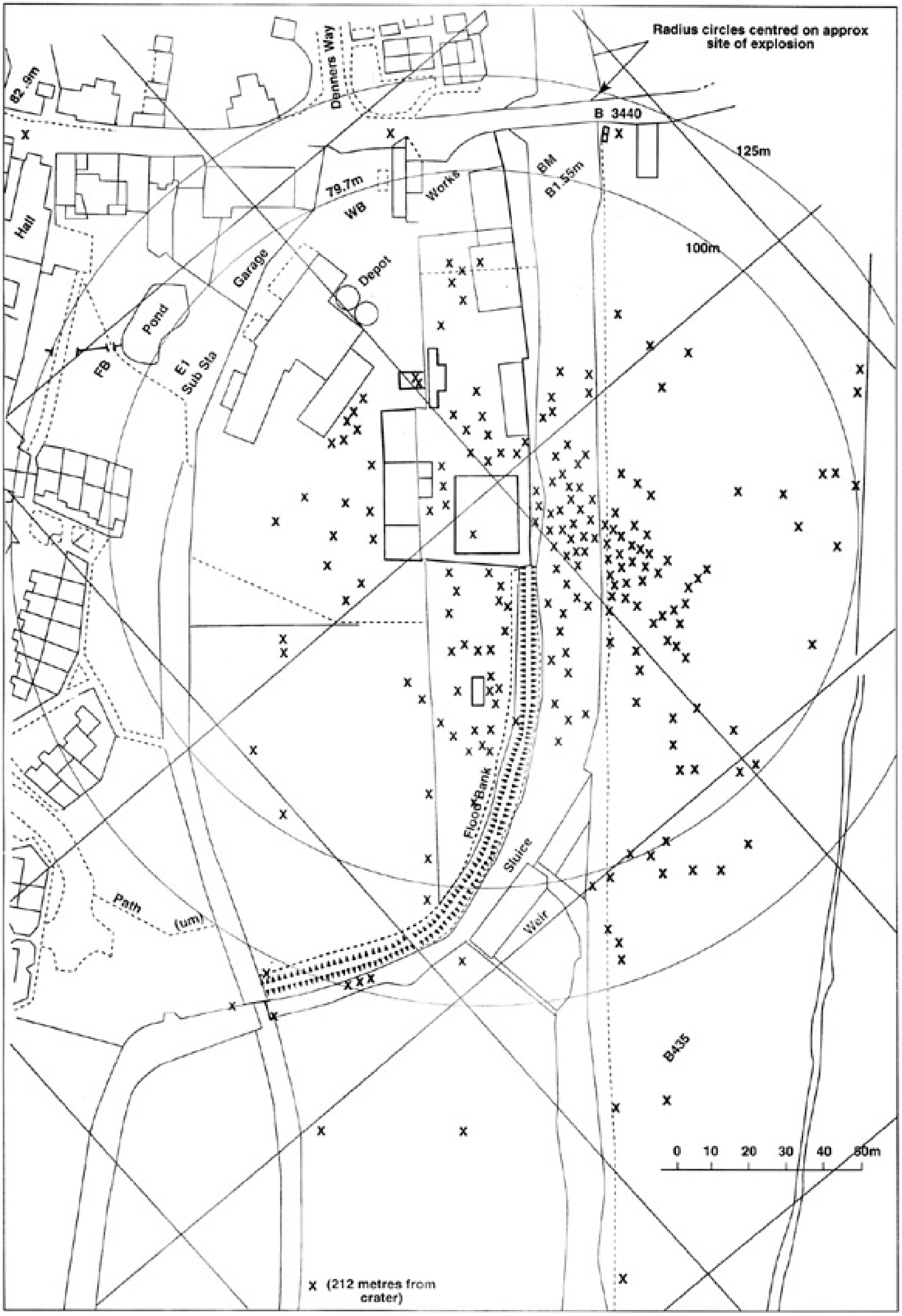

Figure 5. Debris plot.

Estimated TNT-Equivalence from Damage Survey

Crude estimates of the TNT-equivalence of the explosion were made from a simple examination[4] of some of the available damage and other diagnostic markers as follows:

- The double thickness concrete-blockwork buildings in the immediate vicinity of the explosion (numbers 1 and 2 in Figure 4; some 13–20 m away), suffered category B damage,[4] which equates to 50–70% of the walls being destroyed.
- The concrete floor of the building was cleared to a distance of approximately 9.5 m. In the Peterborough Explosion[5] the yard in which the 800 kg of blasting explosive exploded was cleared of all machinery, vehicles, etc. out to a distance (in metres) of 1.5×W0.333; where W is mass of TNT in kg.
- The two furthest missiles were thrown approximately 210 m.
- There was damage to asbestos roofs to 50 m and to metal cladding to 53 m.
- The furthest instance of ceiling damage was at 255 m.
- There was extensive glazing (window) damage: numerous examples were recorded, which are not easily summarised in this paper.

The estimates of TNT-equivalence from these markers surprisingly all fell in a narrow range between 200 and 250 kg. It is worth pointing out that although this explosion produced measurable and damaging blast effects, the greatest potential hazard was produced by fragments. In the future, any quantity-safety distance (QD) arrangement will need to be mindful of this since existing QD arrangements for HD1.1/HT1, HD1.2/HT2, or HD1.3/HT3 might not be appropriate for fireworks in ISO containers that can explode violently (not detonate).

Theoretical TNT-Equivalence of Event

Fireworks in general contain a large range of pyrotechnic compositions. Some shells, for instance, typically contain both gunpowder lifting charges and flash composition bursting charges. It is generally well recognised that for the more energetic pyrotechnics, their TNT-equivalence will depend upon a number of factors including mass, configuration, and distance from the charge. The latter is reflected in the following TNT-equivalences:

- The TNT-equivalence of 127 mm report shells[6] (as tested by subjecting a small number of unconfined, loosely-bound shells to a bonfire) based on pressure, varies from about 0.19 to 0.59 over the scaled distance range from 1 to 7.5 m/kg0.33. The 127 mm star shells are "30% less energetic" than the same size report shells (suggesting TNT-equivalence of 0.13 to 0.41 over the same range).
- The pressure TNT-equivalence of Black Powder (from trials[7] on weights from 227 to 2041 kg) increases from approx. 0.27 at a scaled distance of 0.71 m/kg0.33, to 0.42 at 3.17 m/kg0.33, thereafter decreasing to approx. 0.17 at 15.9 m/kg0.33. The maximum impulse TNT-equivalence was 0.46.

UK *Default* System for the Classification of Fireworks

The Classification and Labelling of Explosives Regulations 1983 (CLER)[8,9] in the UK require that an explosive be classified by the UK Competent Authority (CA) before it may be kept, supplied or conveyed. The CA for commercial explosives is the HSE, and for military explosives is the Ministry of Defence. The purpose of classification is to identify the hazard posed by explosive substances and articles as packaged for transport. Classification under CLER involves the assessment of an explosive to determine whether it is assigned to, or excluded from, Class 1 of the UN classification scheme[10] for the transport of dangerous goods. An explosive assigned to Class 1 is accorded an appropriate United Nations (UN) Serial Number, hazard code and compatibility group, having regard to its composition, type, and hazard.

A number of routes are recognised for the classification of explosives. Assignment may be on the basis of UN test series[10] results and other information supplied by the applicant, or by analogy with a similar explosive previously classified by HSE, or through documentary evidence of classification by the Competent Authority of another country. Additionally, in the UK, *for fireworks only*, a default classification may be claimed.

The default system (see Table 3) has been agreed upon by the HSE and the UK fireworks industry and provides a list of classifications of fireworks according to type. The classifications are those that the HSE would normally award

Table 3. UK Default Classification Scheme for Fireworks.

Description	Specification	UN Hazard Division if in UN Approved Package
Rockets (with or without sticks)	≤4 oz calibre or 25 mm motor inner diam.	1.4G
	>4 oz calibre or 25 mm motor inner diam.	1.3G
Roman candles: Type1 with bombettes or units containing only flash composition	≤30 mm inner diameter	1.4G
	>30 mm and ≤45 mm inner diameter	1.3G see note 1
	>45 mm inner diameter	1.1G see note 1
Roman candles: Type 2 with bombettes or units other than Type 1	≤30 mm inner diameter	1.4G
	>30 mm and ≤60 mm inner diameter	1.3G
	>60 mm inner diameter	1.1G
Gerbs	≤8 oz calibre or 26 mm inner diameter	1.4G
	>8 oz calibre or 26 mm inner diameter	1.3G
Wheels		1.4G
Set pieces/Batteries		See notes 2 and 3
Lancework on frames		1.4S
Lancework & effects	packaged	See note 4
Report Shells (not in mortars)	≤75 mm (see note 5)	1.3G
	>75 mm	1.1G
Star Shells (not in mortars)	≤125 mm	1.4G
	>125 mm	1.3G
Shells (in mortar)	All sizes and types (see also note 3)	1.1G
Mines	≤100 mm diameter	1.4G
	>100 mm diameter	1.3G
British Standard (BS) [11] Category 1		1.4S
BS Category 2 and 3 (other than types listed above)		1.4G
BS Category 4 (other than types listed above)		No default classification
Mixed Packs (Selection Boxes)		Highest individual type Hazard Division applies (i.e., 1.1>1.3>1.4>1.4S)

Note 1: These items contain bombettes or units containing only flash composition and no other composition such as stars.

Note 2: Default hazard depends on types of unit used in any set piece, combination or battery (e.g., batteries containing Roman Candles >30 and ≤45 mm inside diameter, with bombettes or units containing only flash composition default to 1.3G).

Note 3: Any combination, set piece or battery containing shell-in-mortar units default to 1.1G.

Note 4: Default hazard depends on effects (e.g., Lancework Battles with Roman Candles ≤30 mm inside diameter default to 1.4G).

Note 5: If only one report shell of this category is in a mixed box, the shell, provided it is individually packaged, can be regarded as 1.4G.

where information from specific UN tests or competent authority documents is not available. The publishing of the default list does not replace the requirement for HSE to classify all individual fireworks and should not be used as a basis for "self classification". Classification by the default route may be claimed where test results are not available or where no satisfactory documentary evidence of classification in the country of manufacture can be obtained. Classification on the basis of test results will take precedence over classifications derived by default. Classifications awarded by another competent authority may also be considered by HSE. Applicants may be asked to demonstrate that the fireworks as packaged are safe to convey by satisfactorily undergoing the UN Series 4(b) (ii) 12 metre drop test.[10] The default list may be reviewed from time to time in the light of further tests.

UK Hazard Type Scheme for Fireworks in Steel Containers

In recent years, UK licenses for explosives factories and magazines have referred to Hazard Types (HTs) and not Hazard Divisions (HDs). HTs have been defined in the terms of the licence by descriptions similar to those for the UN HDs employed in the classification of explosives (see Table 4). This move was prompted because there are certain conditions of manufacture and/or storage where a different hazard may be presented than that recognised and classified in accordance with the UN scheme. Such circumstances may occur for example, with the storage of fireworks in steel containers. Guidance on HTs for the storage of fireworks in steel containers has been generated and circulated to the industry[12] (see Table 4). This guidance is interim pending the results of further large-scale fire testing of fireworks in containers.

Bonfire Trials on Fireworks Stored in Steel ISO Containers

HSE has conducted three bonfire trials on fireworks held in 6.1 m long steel ISO containers and the results from this work will be reported in full in a separate paper.[3] Since one of the UK's recent fireworks incidents involved initiation of the fireworks inside an ISO container as a result of external heating by an adjacent burning car, stacks of wooden pallets, as high as the container, were positioned 0.5 m away from the container walls to simulate this external fire threat. The first two trials had relatively small quantities of fireworks stacked against one side of the container whereas the third trial was packed 70% full of fireworks, with the remaining space filled with boxes of wood shavings. The three trials were intended to be representative of the bulk storage of fireworks with low, medium and high Net Explosive Content (NEC). Tables 5 and 6 provide a summary and detailed breakdown of the fireworks used. The first two trials—arrangements with the containers only partly full—had limited confinement.

Table 4. UK Guidance on Hazard Types for Fireworks Stored in Steel Magazines.

Hazard Type 1 — having a mass explosion hazard:	
Shell in mortar	All sizes and types
Report shells/aerial maroons	Diameter >75 mm
Any items of UN HD 1.1	As classified by HSE under CLER
Hazard Type 3 — having a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard:	
Airbomb	Diameter >30 mm internal diameter
Battery	Gross mass >10 kg
Combination	Gross mass >10 kg
Fountain/gerb	>8 oz or 26 mm calibre
Lancework	Lancework containing fireworks of Hazard Type 3
Mine	Diameter >100 mm internal diameter
Report shell	Diameter ≤75 mm
Rocket	>4 oz calibre or 25 mm diameter
Roman candle	Diameter >30 mm internal diameter or including bombettes containing flash compositions
Wheel	Gross mass >1.5 kg (excluding any frame)
Selection boxes	Containing any items of Hazard Type 3
Shells	All types and sizes (see Note below)
Any items of UN HD 1.3	As classified by HSE under CLER, and not otherwise placed in Hazard Type 1
Hazard Type 4 — having a fire or slight explosion hazard or both, with only local effect:	
Airbomb	Diameter ≤ 30 mm internal diameter
Battery	Gross mass ≤10 kg
Combination	Gross mass ≤10 kg
Fountain/gerb	≤8 oz or 26 mm calibre
Lancework	Simple lancework or lancework containing fireworks of Hazard Type 4
Mine	Diameter ≤100 mm internal diameter
Rocket	≤4 oz calibre or 25 mm diameter
Roman candle	Diameter ≤30 mm internal diameter and not including bombettes containing flash compositions
Wheel	Gross mass ≤1.5 kg (excluding any frame)
Selection boxes	Containing only types of Hazard Type 4
Any items UN HD 1.4	As classified by HSE under CLER and not otherwise placed in Hazard Type 3 or Hazard Type 1

Note: All shells classified as UN HD 1.4 are considered to be Hazard Type 3 unless they are stored in accordance with the following conditions in which case they may be considered to be Hazard Type 4:

(a) They are kept in their closed transport packages.

(b) Within the container the storage of shells is limited to units or stacks holding a maximum number of 8 boxes of shells in each.

(c) Shell units/stacks shall be separated from each other in any direction by either:

  (i) a 1 m air gap or barrier of empty boxes or boxes containing low energy fireworks (i.e., relatively small items of low hazard such as those that may be sold to the general public under the Fireworks Safety Regulations 1997[13]).

  (ii) a 0.5 m barrier of boxes filled with sawdust or similar material.

Table 5: Summary of Firework Loads in ISO Container Bonfire Trials.

Trial No.	Summary of contents of load	% volume fill of container with fireworks.	Gross weight (kg)	NEC (kg)
1	BS Category 3,[11] 1.4G, small selection box fireworks (containing >85% Category 2 fireworks).	25	1,000	228
2	Mixture of UN 1.3G & UN 1.4G fireworks: (Chinese cakes, gerbs, 2 & 4oz rockets, mines, 30, 45 & 60 mm Roman candles, 75, 100, 125, 150 & 200 mm star shells).	32	1,684	823
3	BS Category 3, UN 1.4G, star shells (125 mm diameter).	70	4,050	2,600

Table 6. Details of Fireworks Loads in ISO Container Bonfire Trials.

Fireworks Trial 1					
Description	Gross mass of UN transport carton (kg)	NEC contained/ UN transport carton (kg)	Number of UN cartons	Total gross mass (kg)	Total NEC (kg)
British Bulldog Selection Boxes					
Saturn	15	3.26	18	270	58.7
Venus	15	3.26	31	455	101.1
Red Dragon Selection Boxes					
Jade	11.7	3	16	187.2	48
Ruby	12.6	3	7	88.2	21
Totals			72	1,000.4	228.8

Fireworks Trial 2				
Description	No. of UN packs	Total gross mass (kg)	Total NEC (kg)	Classification
Chinese cakes/crackle mines	15	345	90	1.4G
19 and 24 mm titanium gerbs	1	8	4	1.4G
2 oz sticked rockets (100)	1	30	10	1.4G
2 oz Rockets (100)	1	30	10	1.4G
4 oz Rockets (100)	1	60	20	1.4G
4 oz sticked rockets (100)	2	60	20	1.4G
30 mm comet candles (48)	1	50	23	1.4G
30 mm Bombette candles (48)	1	50	14.5	1.4G
45 mm comet candles (40)	2	56	29.6	1.3G
45 mm Bombette candles (40)	2	56	20	1.3G
60 mm candles (assorted) (30)	3	60	30	1.3G
Shell 75 mm diameter (288)	4	63.6	43.2	1.4G
Shell 100 mm diameter (216)	6	140.4	86.4	1.4G
Shell 125 mm diameter (198)	11	221.8	138.6	1.4G
Shell 150 mm diameter (117)	13	224.6	140.4	1.3G
Shell 200 mm diameter (40)	10	224	140	1.3G
Mines (colour) 75 mm (20)	1	4.4	3	1.4G
Totals		1683.8	822.7	

Table 6. Details of Fireworks Loads in ISO Container Bonfire Trials (continued).

Fireworks Trial 3				
Description	No. of UN packs	Total gross mass (kg)	Total NEC (kg)	Classification
Assorted 125 mm diameter chrysanthemum shells with perchlorate burst charges (18 shells per box, manufactured by Sunny)	270	4,050	2,600	1.4G

The results from Trials 1 and 2 indicated that the HD 1.4 fireworks tested presented only a limited hazard when the ISO storage container was exposed to an external fire source. There was no damage to the container in Trial 1 and, although the doors were blown open in Trial 2 and individual fireworks were ejected, there was no bulk effect.

For fireworks Trial 3 however, significant explosions were recorded and a large fireball 100 m in diameter was formed by the burning shells and ejected stars. Full details of the experimental configuration and the outcomes from the tests will be given in a future publication.[3]

Summary and Conclusions

- Large quantities of a whole range of materials, including fireworks, are moved around the world in steel ISO-containers, and in recent years UK manufacturers and retailers have used such containers to store fireworks. Recent incidents and trials have heightened concerns about the possible effects of confinement on the more energetic fireworks held in storage.
- The container of fireworks, which caused the most damage at Uffculme, is considered to have exploded violently rather than to have detonated. The packaging arrangements of boxed fireworks will generally suppress the rate of flame propagation through a mass of material, and the resultant pressure wave will initially be drawn out as the flame front propagates through the stack of fireworks. This long duration pressure wave, however, can quickly shock-up into a shock wave as it moves away from the source.
- A limited number of large-scale bonfire trials have been carried out on fireworks in steel ISO containers. The initial results suggest that:

a) A steel container approximately one-third full of very low hazard HD 1.4 fireworks presents no significant hazard outside of the container.

b) A steel container essentially full of a certain type of HD 1.4 125 mm star shells presents a significant fireball hazard.

- Concerns remain that

a) Other more energetic HD 1.4 fireworks might present either a HD 1.3 or a HD 1.1 type hazard when heavily confined.

b) Energetic HD 1.3 fireworks might present a HD 1.1 type hazard when heavily confined.

c) The presence of small quantities of very high-energy fireworks such as maroons or report shells might boost or drive adjacent energetic fireworks into an additive high-energy response.

- Further large-scale trials are required to fully investigate this matter. We are also beginning to develop a small-scale test method to rank fireworks in order of their confined mass burning rate.
- In the UK, the hazard division classifications, derived for transport via the UN scheme, have not been used automatically for defining the hazards of fireworks held in storage. The guidance currently followed by the industry for storage and li-

censing purposes will be revised as necessary following the results of further large-scale trials on fireworks held in confinement. Similarly, the UK default classification scheme used for fireworks will be reconsidered in the light of any new trials information.

- Questions arise concerning the adequacy of the existing tests in the UN Scheme for the classification of fireworks. In particular, there are questions regarding the proper characterisation of the hazards associated with fireworks held in steel ISO containers used for transport and, in some countries, for storage. In the longer term, there is need for the development of additional test methods for fireworks. For the latter, any consequential proposals will be submitted to the United Nations Committee of Experts on the Transport of Dangerous Goods (UNCOETDG).
- This work may also impact upon QD safety distances for existing and future stores.
- We intend to seek European collaboration regarding further research into this area.

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Thermal Techniques Used in the Hazard Evaluation of Pyrotechnics

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ABSTRACT

A hazard assessment provides important information for determination of safe conditions for the manufacture, storage and transportation of pyrotechnics. Sensitivity to thermal stimuli is an important aspect of an overall hazard assessment. This paper describes a number of laboratory techniques that can be used to determine thermal properties of pyrotechnics and other energetic materials. The experimental methods and variable parameters of thermogravimetry (TG), differential scanning calorimetry (DSC), accelerating rate calorimetry (ARC), heat flux calorimetry (HFC) and simultaneous TG/DTA (SDT, for simultaneous differential thermal analysis) are described, along with the information they provide. Experimental examples are provided in each case. All the techniques described are in use at the Canadian Explosives Research Laboratory. No single technique is without its limitations, and a combination of techniques, to provide complementary information, is often the best approach. Many of the methods employed are described in ASTM standards.

Keywords: thermal hazards, differential scanning calorimetry, DSC, thermogravimetry, TG, differential thermal analysis, DTA, accelerating rate calorimetry, ARC, heat flux calorimetry, HFC, simultaneous differential thermal analysis, SDT

Introduction

The production, transportation and storage of pyrotechnic mixtures are fraught with potential hazards. Many of these compositions are sensitive to mechanical and electrostatic stimuli, but thermal sensitivity is also of concern. The thermal activity, stability and thermal explosion potential of pyrotechnic mixtures must be well known, in order to identify any risk of thermal runaway reactions that could lead to catastrophic events.

A thermal runaway reaction occurs when the rate of heat generated by that reaction exceeds the rate of heat loss. Chemical reactions of pyrotechnics generally produce large amounts of heat and many of them generate a significant quantity of gaseous products. When confined in a closed system, a decomposing pyrotechnic can produce considerable pressures, resulting in vessel rupture and explosion. While most pyrotechnic mixtures deflagrate (burn) when ignited, many can undergo the transition to detonation (supersonic burning), especially when confined. A detonating material presents a severe hazard in many ways, with contributions from fragments, blast waves and heat.

Thermal techniques are often very useful for quality control purposes and can help avoid the malfunction of pyrotechnic devices. Poorly functioning devices can create significant hazards, either directly or indirectly.

Numerous experimental techniques are available to examine the thermal properties of materials, many of which are specifically useful for examining pyrotechnic compositions. An extensive review of the thermal analysis of pyrotechnics was published by Laye and Charsley in 1987.[1] The purpose of the present paper is not to provide an exhaustive review of thermal analysis as applied to pyrotechnics, but to highlight some of the techniques that can be of use in evaluating the thermal hazard properties of pyrotechnics and other sensitive energetic materials. All of the techniques described are currently in use at the Canadian Explosives Research Laboratory.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is the most widely used technique in the study of the thermal properties of pyrotechnics. DSC is a technique in which the heat flow in and out of the sample is monitored against temperature or time, while the temperature of the sample, in a specified atmosphere, is either ramped at a constant rate or held isothermal. If the sample undergoes an exothermic reaction, heat will flow out from it; endothermic processes cause heat to flow into the sample. A similar technique, differential thermal analysis (DTA) measures the temperature difference between the sample to be investigated and a reference sample as a function of temperature (or time). If the sample generates heat, its temperature will be above that of the reference and vice versa. Since the two techniques provide largely equivalent information, they can often be used interchangeably. It should be noted, however, that DTA only provides qualitative information on heat flow, so that DSC is the preferred method for quantitative heat flow measurements.

Experimental Parameters

A typical sample size for DSC measurements is of the order of a few mg, but for pyrotechnic compositions a sample size less than 1 mg is recommended, particularly when using sealed sample holders. Small sample size helps to reduce the risk of damaging the apparatus. A larger sample could be used if the temperature were kept well below the expected ignition temperature. Various sample holders, such as aluminum pans (open, hermetically sealed, or having a pinhole lid[2]), glass ampoules[3] and closed metal (non-aluminum) containers,[4] can be used for various purposes. Also, Teflon-coated pans are often used for compositions that react with aluminum, such as halogen-containing samples.[2]

If an open or hermetic pan is used for experiments with pyrotechnic compositions, limited quantitative information about the energetics of the decomposition is generally obtained because of venting of the gas products. However, quantitative data for non-gassy processes, such as phase transitions or thermite reactions, can be obtained.

A variety of purge gases can be used in DSC measurements, and selection of the type of purge gas may be for a specific purpose in an open system. For example, nitrogen is often used to avoid complication of the analysis by oxidation of the sample. In contrast, air can be used to determine whether there is a component of the sample that is easily oxidised. A pressure cell can be used to conduct measurements above or below atmospheric pressure. This cell can be used to measure vapor pressures[5] and the effect of pressure and different atmospheres on decomposition.

Generally useful heating rates in DSC measurements range from 2 to 20 °C min^{-1} although the lower end of the range is more commonly used for energetic compositions, to avoid uncontrolled reaction. Additionally, DSC can be conducted in a constant temperature or isothermal mode.

The instrument used for DSC should be calibrated under the same experimental conditions as those intended for the pyrotechnic composition using ASTM procedures.[6,7] This calibration must be carried out before conducting DSC measurements, if the results are intended to stand alone, in an absolute sense, and to be published. In contrast with heat flux calorimetry (see below), for which calibration is stable for up to a year, calibration for DSC measurements should be checked before each study.

Information Obtained by DSC

For pyrotechnic compositions or their individual components, DSC is used to measure onset temperatures and energetics of phase transitions,[8] to estimate purity, to determine heat capacities,[9] and to measure the enthalpy change (ΔH) and kinetic parameters of the decomposition process.[10,11] Studies using a series of isothermal temperatures yield kinetic parameters[12,13] that can be compared with those obtained using a variable heating rate method.[14]

DSC measurements can also “fingerprint” a component in a pyrotechnic composition (e.g.,

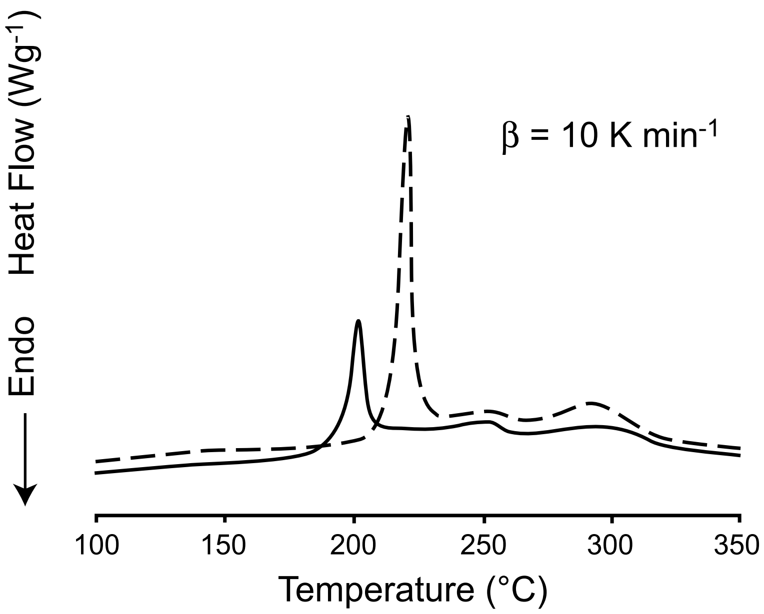

Figure 1. Effect of isothermal aging on the thermal decomposition of the primary explosive KDNBF. Solid line: with aging at 176 °C. Dashed line: without aging. Sample mass 0.2 mg. Nitrogen atmosphere.

Because of the small sample size required by DSC, sampling for heterogeneous pyrotechnic compositions should proceed as follows:

1) Select several samples at random from the composition
2) Conduct DSC experiments on each of the samples and use the variation in the results to estimate an experimental uncertainty
3) Conduct experiments on each pure component of the composition

A careful sampling methodology is necessary, as the material might not be well mixed on the scale of the sample.

The primary advantage of DSC is the rapid turn-around of experimental work, with single experiments lasting approximately one hour, much shorter than the timescales typical of accelerating rate calorimetry (ARC) and heat flux calorimetry (HFC) measurements (see below). DSC is therefore often useful as a preliminary characterization technique before other measurements. However, for pyrotechnic compositions, requiring a careful sampling program as described above, there may not be any significant savings in experimental effort. Laboratories that rely solely on DSC for characterization should commit, however, to such a sampling program. It should also be recognized that, because of the small sample sizes involved, DSC does not provide a meaningful indication of safe operating temperatures for full-scale manufacturing processes. Thermal onset temperatures measured by DSC can be substantially (several tens of degrees) higher than those measured by larger-scale experiments such as ARC.

Figure 1 shows DSC traces obtained for the primary explosive potassium dinitrobenzofuroxan (KDNBF), before and after thermal aging below its runaway decomposition temperature.[15] A strong exothermic decomposition is seen in both traces. However, the onset temperature is substantially lower in the sample that had been previously heated, increasing the thermal hazard.

that had been previously heated, increasing the thermal hazard.

Thermogravimetry (TG)

Thermogravimetry (TG) is a technique in which the mass of a sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is either ramped at a specified rate or held isothermal. Thermobalances used in TG experiments are highly sensitive, with mass resolution as low as 1 µg.

Experimental Parameters

Sample sizes in TG studies can be up to 50 mg, although with energetic compositions, such as pyrotechnics, the normal sample size is a few mg, to reduce the risk of damaging the equipment. As for DSC, it is important with such a small sample size to take precautions to obtain results that are representative of the bulk sample. Typical heating rates range from 2 to 20 °C $\min^{-1}$, with a typical temperature range from ambient to 1000 °C. Normally, TG measurements are conducted in an open system with a purge gas flow. The gas environment can be changed either during an experiment or in separate experiments. This feature can be useful in elucidating the oxidation of a component in an oxidizer/fuel system. Isothermal TG can be used to model pyrotechnic storage conditions, to estimate rates of volatilization and/or decomposition and to model the kinetics as in DSC.[16]

Mass and temperature calibrations are required prior to TG studies. A standard reference material is used for mass calibration and this material is checked against a precalibrated microbalance having a reproducibility of ±1 µg. The Curie point technique[17] for temperature calibration makes use of the apparent mass change that occurs when a ferromagnetic sample subjected to a magnetic field exhibits a definite transition temperature at which it becomes paramagnetic.

Information Obtained by TG

Changes in mass of a pyrotechnic composition with temperature or time (at constant temperature) can be determined from TG experiments. This information can help elucidate the nature of the reactions occurring in a pyrotechnic composition and can be used to determine the overall kinetics.[10] However, before investigating a pyrotechnic mixture, it is extremely helpful to carry out TG experiments on each of the components. Mass changes for the components may result from evaporation, sublimation, interaction with the purge gas, or decomposition. Characteristic thermal behaviour may be attributed to individual components and this property may be used to provide information about the environmental and thermal stability of the components as well as analytical information[18] for the pyrotechnic composition. Additionally, the kinetic parameters for the processes attributable to each of the components may be determined by a variable heating rate method[19] or an isothermal study.[10,15] Compositional analysis of a pyrotechnic composition for volatile and combustible matter and ash can be obtained using another ASTM procedure.[20]

Figure 2 shows an example of the sort of information that can be obtained by TG. Plotted are TG curves for two anthraquinone dyes used in the manufacture of pyrotechnic smoke compositions. The two dyes are nominally the same and do begin to vaporise at the same temperature. However, one of the dyes has a substantial non-volatile component, as can be seen from the residual mass. Of practical interest is the fact that one of the dyes gave rise to substantial performance problems in the final product. Although this is an example of the use of TG to perform quality control on components of pyrotechnics, there are often hazards associated with the malfunction of pyrotechnics devices.

Simultaneous Techniques

A significant improvement in characterization as well as productivity is achieved by combining DSC or DTA and TG in one apparatus. The union of DTA and TG, a technique known as simultaneous differential thermal analysis (SDT), offers the additional advantage that the temperature calibration in DTA also applies to the TG measurements. However, the experiment can only be done in an open system in a flowing gas environment.

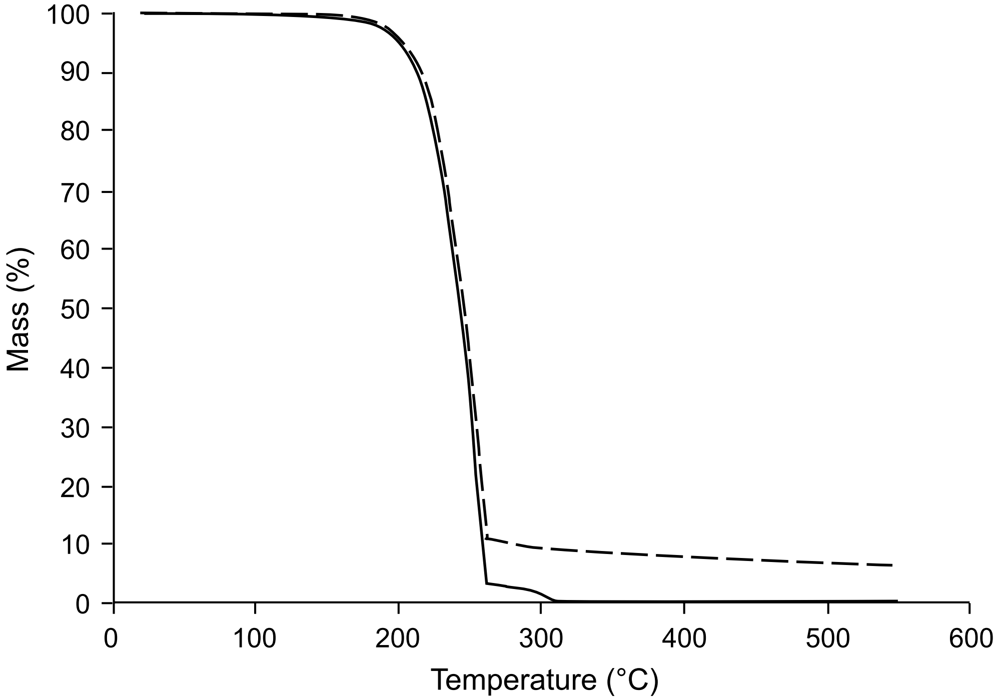

Figure 2. TG curves for two anthraquinone dyes used in the manufacture of smoke compositions. Heating rate 5 °C min^{-1} in nitrogen atmosphere. Sample mass 1.7 mg.

Research Laboratory, both MS and FTIR options are available. Combining these techniques with SDT produces the "hyphenated" technique TG-DTA-FTIR-MS. This powerful combination provides important information about the nature of the potentially hazardous gases produced on decomposition of an energetic material, as well as the associated heat and mass changes.

Figure 3 shows TG-DTA-FTIR results for a sample of Black Powder. The combination of the three techniques is very powerful. A full interpretation of these and other results on Black Powder will be given elsewhere[21] and only some illustrative points will be mentioned here. For example, the endothermic DTA feature at 130 °C corresponds to a phase change in potassium nitrate; there is no mass loss associated with the phase change, nor is there a concomitant evolution of a gaseous product. In contrast, the final stages of reaction above 350 °C give rise to an exothermic DTA feature, with a corresponding steep mass loss caused by the formation of gaseous products. By FTIR, both the major (carbon dioxide) and minor (e.g., nitrous oxide) products can be identified in the gas phase.

Accelerating Rate Calorimetry

The accelerating rate calorimeter (ARC) is a commercial, automated adiabatic calorimeter described by Townsend[22,23] and used for assessing the thermal hazard potential of chemicals. An ASTM Standard,[24] which uses this particular instrument, has been published. Figure 4 provides a cut-away drawing of the calorimeter vessel. An increase in temperature at the bomb thermocouple causes a mismatch with the zone thermocouples resulting in activation of the zone heaters to minimise heat flow out of the sample. This response ensures that heat losses are small and that the system mimics a much larger sample.

Experimental Parameters

Samples sizes of several grams are typical in ARC experiments with non-energetic materials. However, with pyrotechnic mixtures, where uncontrolled runaway and bomb rupture are possible, sample size is usually kept to 1 g or below, to minimize the risk of damage to the equipment. At this scale, the sample size is approximately three orders of magnitude greater

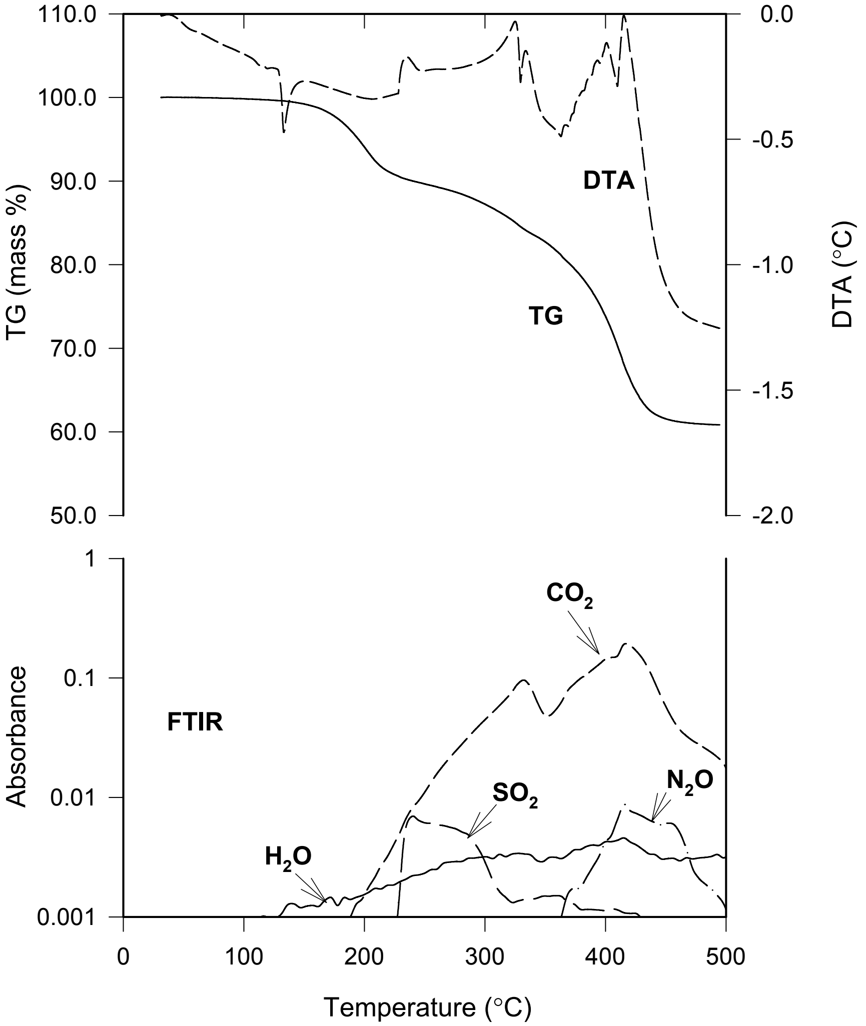

Figure 3. TG-DTA-FTIR traces for 5FA Black Powder in air. Heating rate 5 °C min^{-1}. Sample mass 5 mg.

sible, sample size is usually kept to 1 g or below, to minimize the risk of damage to the equipment. At this scale, the sample size is approximately three orders of magnitude greater than in DSC and TG experiments. A single sample, collected at random throughout the sample, will normally be quite representative of the bulk material.

In the standard ARC procedure of "heat-wait-search", the temperature of the calorimeter is raised by user-selected steps (usually 5 °C). The calorimeter is then maintained under adiabatic conditions until thermal transients have dissipated and while a "search" is made for an exotherm. The onset of an exotherm is the temperature at which the self-heating rate (R) exceeds a threshold value (generally 0.02 °C min^{-1}). If no self-heating is observed, the temperature is incremented again and the process repeated. In the instrument commonly used for ARC measurements, adiabatic conditions can be maintained provided R < 10 °C min^{-1}. ARC experiments can also be conducted in a quasi-isothermal mode, from which induction times may be obtained under a variety of conditions. The options of using an open or closed system and inert or reactive atmospheres are also available in ARC studies. In a closed system, a transducer (see Figure 4) continuously monitors the pressure. Spherical sample bombs (about 10 cm^3)

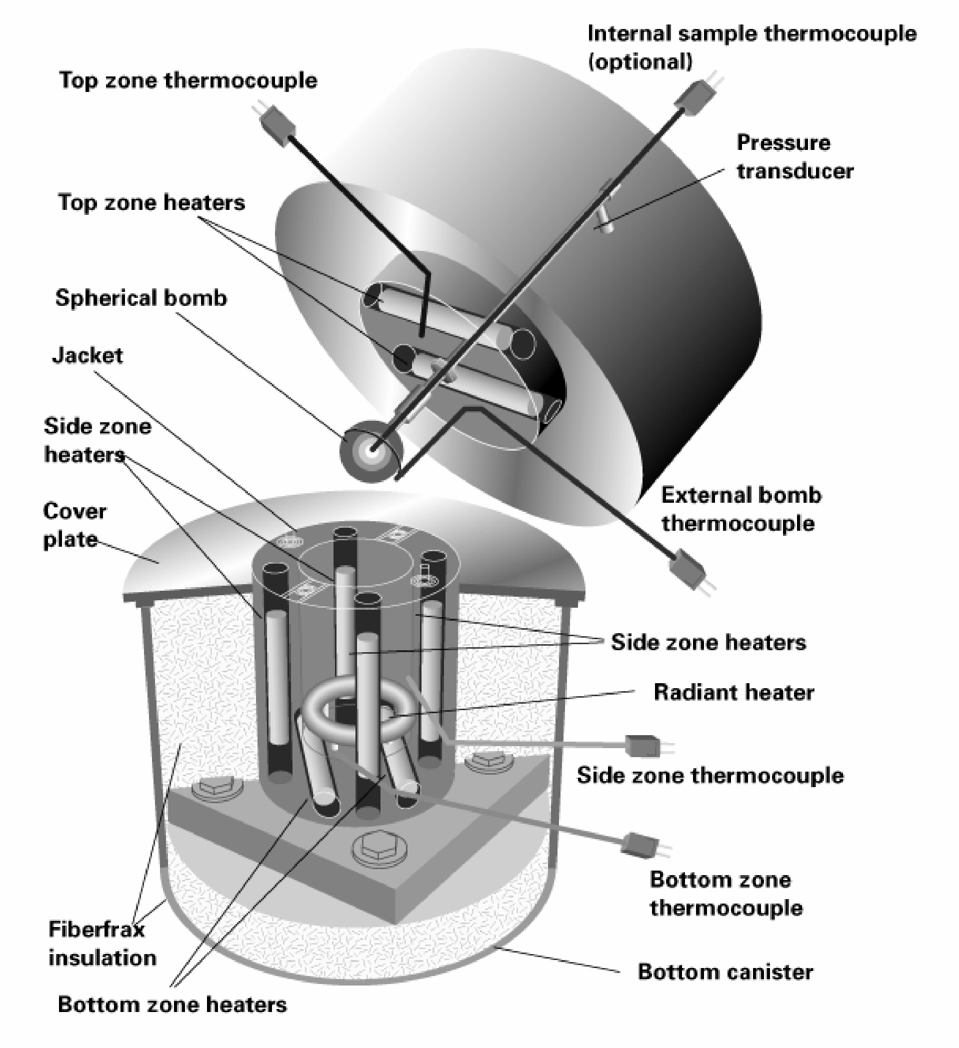

Figure 4. Cutaway diagram of the accelerating rate calorimeter.
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are available in titanium, stainless steel, glass and Hastelloy. Cylindrical ones are available in Hastelloy. Bomb selection and sample size depend on the purpose of the experiment and the type of sample.

Information Obtained by ARC

ARC is primarily used to derive information about exothermic events, although data for endothermic processes, such as phase transitions, can sometimes be obtained indirectly. Time, temperature and pressure data for a pyrotechnic composition prior to and during decomposition are obtained from a heat-step-wait-search experiment.

The information most commonly obtained from ARC experiments is the onset temperature for exothermic reaction. This value can be used to set limits on operating, storage and transport temperatures. Because ARC measurements are conducted adiabatically (i.e., no heat losses), the results can effectively simulate real bulk behaviour of an energetic material. However, because the heat generated by the sample is used to heat both the sample and the bomb, the effective rate of self-heating is reduced. The threshold temperature at which self-heating is observed can thus be slightly below that of a large bulk sample and may depend somewhat on sample size.

In addition to onset temperatures, ARC can provide information on the kinetics of decomposition, based on how quickly the self-heating takes place once detected. Overall, energetics can be obtained from the total temperature rise in the system due to self-heating, but DSC can usually obtain more precise values. Post-run residual mass and pressure measurements provide useful information about the volatile, non-condensable products of decomposition. It is also possible to collect gas samples for further analysis.

An ARC experiment takes at least one and more usually two or more days for completion, considerably longer than a single DSC experiment. However, owing to the large sample mass, it is not usually necessary to carry out experiments on several samples.

Results of an ARC experiment on 5FA Black Powder are shown in Figure 5. After a series of heat-wait-search steps, the onset temperature ($R > 0.02$ °C min^{-1}) is reached.

Heat Flux Calorimetry (HFC)

Precision heat flux calorimetry (HFC) can be undertaken using a Tian-Calvet instrument, as described in the literature.[25] This instrument, as depicted in Figure 6, consists of a massive aluminium block, with two identical cylindrical cavities located symmetrically about the centre; a thermopile surrounds each cavity. The design results in a sensitivity to heat flow that is significantly higher than for ARC and DSC measurements.

Experimental Parameters

HFC experiments are conducted in the same manner as for DSC (i.e., in a scanning mode or isothermally). However, the maximum heating rate is 2 °C min^{-1}, so that HFC measurements usually require a relatively longer period of time. Additionally, the instrumental design imposes a narrow temperature range (ambient to 300 °C), which is somewhat limited in comparison with that available from DSC (ambient to 600 °C), and ARC (ambient to 400 °C). Because energetic materials often decompose at temperatures well below 300 °C, the temperature range of HFC may not be limiting. Further, the onset of decomposition may be shifted to lower temperature by reducing the heating rate, albeit at the expense of prolonging the experiment.

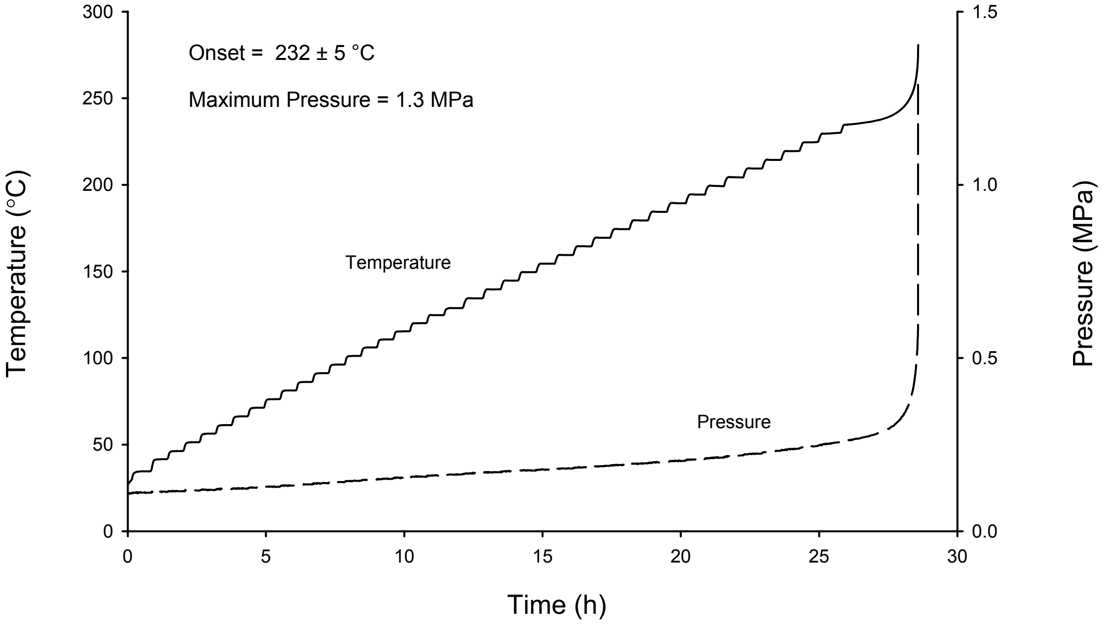

Figure 5. Temperature and pressure traces for ARC experiment on 0.5 g of Black Powder in air.

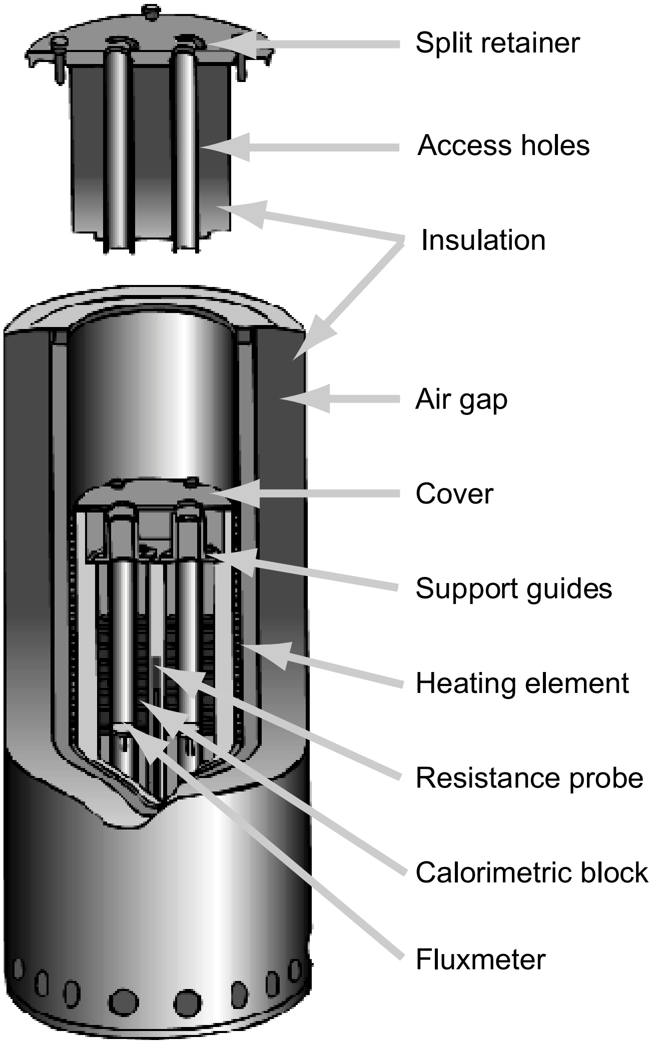

Figure 6. Cutaway diagram of heat flux calorimeter.

Samples sizes used in HFC experiments on energetic materials are on the order of 100 mg, a significant advantage over both DSC and TG where about 1 mg of an energetic material is commonly used. Sampling is not nearly as critical an issue, so that results for heterogeneous compositions are quite reproducible.

In preparation for HFC measurements, the instrument is calibrated for sensitivity using standard reference material (SRM) sapphire. Temperature calibration is similar to that used for DSC. HFC calibrations are valid for about a year, in contrast with DSC and ARC where more frequent calibrations are usually required. Verification of the calibration is conducted by means of an HFC experiment on another SRM, such as benzoic acid.

HFC measurements may be carried out in open or closed systems. In a closed system the cells may be connected to a manifold.[25] In this system, the pressure is measured simultaneously or, alternatively, the effect of pressure and/or atmosphere on thermal behaviour may be investigated. The manifold in use in our laboratory is designed to work at pressures up to 68 MPa (10,000 psi).

When using a manifold, the free volume is significant (i.e., >12 cm^3). To reduce the free volume, the energetic material may be enclosed in a sealed glass ampoule, the volume of which is about 0.7 cm^3. In using this technique, there is a loss of sensitivity as a result of the reduced thermal conductivity of glass, and no pressure results accompany the heat flow information.

Information Obtained by HFC

HFC is used to obtain the same information normally derived from DSC measurements but with significantly enhanced precision. Onset temperatures measured by HFC are lower than measured by DSC and comparable to those obtained by ARC, owing to the greater sensitivity and lower heating rates. HFC is capable of detecting weakly exothermic events not generally observed in ARC, because of the enhanced sensitivity of HFC equipment.

Figure 7 shows the results of a HFC experiment on a Black Powder sample. Of note are the strong exotherm above 230 °C, the endothermic potassium nitrate phase change at 130 °C and the two weak endotherms due to sulfur phase changes in the region of 120 °C (inset). Onset temperatures measured by HFC are close to those found by ARC, but there are substantial differences between the HFC and DTA (see Figure 3) profiles, owing to the very different sample sizes, atmospheres and degrees of confinement in the two experiments. This example demonstrates clearly the benefits of using several techniques to assess the thermal hazard properties of pyrotechnics. In particular, small-scale experiments can give very misleading results.

Conclusions

There are a number of thermal techniques that can be used to provide hazard information on pyrotechnic mixtures. Each of the techniques provides useful information, but none provide a complete picture. A powerful approach is to use a number of different, but complementary techniques to address the same problem. For example, DSC will provide the enthalpy change for an exothermic decomposition, allowing an assessment to be made of the heat that could be generated by a runaway reaction. Although onset temperatures can be measured by DSC, ARC would provide a much better estimate of the temperature at which thermal runaway will occur. Through pressure measurements, ARC can also be used to estimate the volume of gaseous products generated and the rate at which pressure is built up. Further useful information can be obtained by TG, which can be used to detect mass loss corresponding to the early formation of gaseous products. Coupling TG to MS or FTIR instruments can provide information on the nature of the gaseous products and their toxicity. By using complementary thermal techniques in this way, it is possible to make a very informed assessment of the thermal hazard of a particular pyrotechnic mixture.

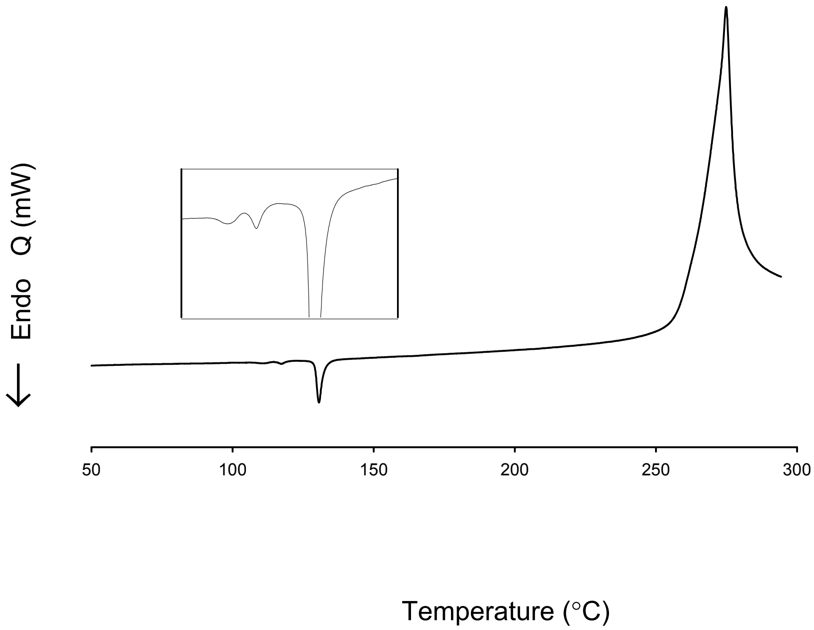

Figure 7. Heat flux calorimetry results for 5FA Black Powder in an argon atmosphere. Sample size 100 mg. Heating rate 0.3 °C min^{-1}

Acknowledgements

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Our Present Knowledge of the Chemistry of Black Powder

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ABSTRACT

Black Powder has been around for centuries and has had a profound influence on the history of the world. Over this time, a considerable amount of knowledge has been gained that not only sheds light on the chemistry of Black Powder but also on other pyrotechnic reactions. This knowledge cannot be considered complete, in spite of all the research that has taken place, and this article attempts to summarize the present understanding about Black Powder's ignition and propagation chemistry.

Keywords: Black Powder chemistry, ignition, propagation, Black Powder research

Introduction

From early times, when Black Powder came to the attention of the alchemists, researchers have wondered and speculated about its explosive power when ignited. Science has indeed come a long way since the mysticism of the alchemists and the phlogiston theory of combustion. Today our understanding of the chemistry of Black Powder's ignition and propagation is far more accurate and precise.

The speculation of bygone ages has been largely replaced with solid knowledge backed by solid data. However, there remain, to this day, areas of our knowledge about Black Powder that are sparse and even virtually non-existent. Having been around for so long, and studied so extensively, many have concluded that current knowledge about its ignition and propagation characteristics is virtually complete. This, however, is not true.

This paper attempts to summarize present knowledge of the chemistry of Black Powder. Specifically it examines the chemistry of ignition and propagation.

Problems Relating to Black Powder Research

Black Powder research has been hampered by several factors. Perhaps one of the most important of these is the waning interest in its use, with Black Powder having been replaced by other more efficient explosives and propellants. Traditionally Black Powder research (with its necessary funding) has been sponsored by the military. With declining military use came a corresponding decline in research, but not a total decline. Black Powder still has certain superior properties to the more powerful smokeless powers that have largely superseded it. For example: in military use, where Black Powder has been superseded by newer propellants, it still finds uses in fuses and as an initiator of other explosive materials. This utilization is largely due to its superior ability to produce a large percentage of hot solids after ignition. These solids are more efficient in igniting other substances than hot gases.

Some might suppose that Black Powder's use as a fuse or an igniter merits less study than its uses as explosives and propellants. This might be true from a fireworks maker's viewpoint but not from a military standpoint. Recent military research has focused on consistency in performance—a goal critical to Black Powder's role in igniting other propellants.

Another factor influencing the gathering of scientific data about Black Powder is its most important characteristic, its explosive power. To meaningfully study Black Powder's ignition and propagation characteristics, one needs to simulate its actual application as closely as possible. This means that the Black Powder usually needs to burn with explosive force. This force, unfortunately, tends to scatter the combustion components, making their collection and detection difficult. This explosive force is also dependent on its unique application. Thus far, less explosive force is generated in the tube of a fireworks mortar than in a barrel of a gun.

Lack of standardization has also hampered research. Different researchers at different times have used different methods of sampling and testing. This has resulted in "comparing apples with pears" scenarios where data has been misapplied and misinterpreted. The literature frequently refers to research that took place many years ago. And while some of this research may be very well documented, its authors and their associates are no longer available to share their insights through personal correspondence. Thus seeking clarification on many of the finer points in their research is very difficult, if not impossible. Again, this can result in "apples and pears" scenarios when recent experimental data is compared with much older data.

The Importance of Black Powder Chemistry

What is there to be gained from studying the chemistry of Black Powder ignition and propagation? To many the answer is—not much. Where their chief concern is having a powder with reasonably predictable explosive characteristics, many conclude that the study of its chemistry contributes little beyond mere academic interest. However, a lot can be gained from studying Black Powder chemistry. Here are a few reasons why such knowledge can be advantageous:

- Toxic gases may be formed when Black Powder ignites.
- Black Powder still does many unpredictable things.
- Black Powder has certain undesirable characteristics.
- Tighter control of variables is needed for critical applications.
- Knowledge of Black Powder contributes to the general pyrotechnics knowledge pool.

Parameters of this Investigation

There are many variables involved in both the production and utilization of Black Powder. Some of these variables may have a marked effect on the resulting chemical reactions when Black Powder is ignited. For the purposes of this discussion, it is assumed that the Black Powder in question has been made by a process that optimizes the incorporation of its ingredients. These ingredients are also assumed to be: potassium nitrate (KNO_3), sulfur (S) and charcoal (C) in the approximate percentages of 75, 10 and 15, respectively. Thus other Black Powder mixes with different ingredient ratios such as those used in gerbs, drivers and rockets are not examined here.

Here and elsewhere in this paper charcoal is represented merely as carbon (C). This convention is used to both simplify some of the discussions and to accurately represent the works of the various authors quoted. Many of these authors treated charcoal as pure carbon, ignoring its smaller percentages of other elements such as hydrogen and oxygen. So charcoal is represented just as carbon where deemed appropriate and as a complex of carbon and other substances where it is helpful to examine charcoal in greater detail.

Although this paper is mainly confined to the above-mentioned definition of Black Powder, it is useful to explore the properties of sulfurless Black Powder and Black Powder that substitutes sodium nitrate ($NaNO_3$) for potassium nitrate. Black Powder mixes that do not use sulfur give a clearer picture of the importance of sulfur in most Black Powder mixes. Sodium salts are similar enough chemically to potassium salts to merit serious study. In practice, sodium nitrate is used in Black Powder made for blasting applications. Thus, both sulfurless Black Powder and sodium nitrate powder form part of this discussion.

Reactions and Combustion Products

In the early 19th century, Guy-Lussac[1] proposed that the gases formed by exploding Black Powder comprised:

Carbon dioxide (CO_2)	52.6%
Carbon monoxide (CO)	5.0%
Nitrogen (N_2)	42.4%

These results were contested by Piobert[1] but the main disagreement appears to relate to gas volumes rather than content. Later research conducted by numerous other researchers shows that these conclusions concerning the types of gases produced were overly simplistic and that many other gaseous products could be formed. Notable is the extensive research done by Noble and Abel.[2] Nevertheless, these later experiments showed that the principle gases produced from exploding Black Powder are carbon dioxide and nitrogen.

Chevreuil[1] conducted experiments with Black Powder exploded in a gun barrel and also burnt in the open air. These experiments can be considered a milestone in our present understanding of Black Powder chemistry, for they showed that quite different results are obtained when Black Powder is ignited under different conditions. Later experiments by Noble and Abel[2] re-affirmed these results.

Chevreuil concluded that Black Powder exploded in the barrel of a gun reacted according to the following equation:

$$2\,KNO_3 + S + 3\,C \rightarrow K_2S + N_2 + 3\,CO_2 \quad (1)$$

Part of Chevreuil's reasoning points to the fact that this formula represents almost exactly the proportions found in Black Powder made with the 75:10:15 ratios. Substituting the atomic masses of KNO_3, S and C into the above formula gives:

KNO_3	74.8%
S	11.9%
C	13.3%

This explanation seems to have gained enough credibility in certain quarters that even more than a century later it was still accepted by some. This author has a chemistry textbook[3] dated 1936 that accepts the above theoretical explanation with the above formula modified only as follows:

$$4\,KNO_3 + S_2 + 6\,C \rightarrow 2\,K_2S + 2\,N_2 + 6\,CO_2 \quad (2)$$

Graham[1] accepted Chevreuil's view, and expanded on it by proposing that potassium sulfide (K_2S) is converted to the sulfate (K_2SO_4) when it is exposed to air.

Slower burning Black Powder, according to Chevreuil, yielded carbon and the following potassium compounds: sulfide, sulfate, carbonate (K_2CO_3), cyanide (KCN), nitrate and nitrite (KNO_2).

In 1857, Bunsen and Schischkoff published a classic paper on Black Powder research.[1,2] This research investigated the nature and proportions of the permanent gases generated when Black Powder explodes and the amount of heat generated by this transformation. From these experimental data, they deduced theoretically the temperature of explosion, the maximum pressure in a closed chamber, and the total theoretical work done on projecting a projectile. It is worth noting that these findings were theoretical in nature, as their experiments did not properly emulate the type of conditions typically found when Black Powder is exploded in a confined space. Their experiments were performed on Black Powder that was deflagrated by being allowed to fall into a heated bulb.[2]

From these observations, they concluded that the permanent gases represented only about 31%, by weight, of the powder and occupied a volume of 193 times that of the original unexploded Black Powder. Table 1 lists their results.[2]

It can be seen from Table 1 that the Black Powder used in this experiment was comprised of a slightly different formula than the commonly used ratio of 75:10:15. Here the approximate ratio is: potassium nitrate 79%, sulfur 10% and charcoal 11%. Also worth noting is their representation of charcoal as a substance comprising not only carbon, but also hydrogen and oxygen.

Berthelot[1] derived the following equation based on Bunsen and Schischkoff's investigations:

$$16\,KNO_3 + 6\,S + 13\,C \rightarrow 5\,K_2SO_4 + 2\,K_2CO_3 + K_2S + 8\,N_2 + 11\,CO_2 \quad (3)$$

Table 1. Results of the Bunsen and Schischkoff Experiments.[2]

Sample Size	Components before Ignition (in grams)		Components after Ignition (in grams)		
1 gram of Black Powder			Solids		
	KNO_3	0.7899	0.6806	K_2CO_3	0.1264
				$K_2S_2O_3$	0.0327
	S	0.0984		K_2SO_4	0.4227
				K_2S	0.0213
	Charcoal			KCNS	0.0030
	C	0.0769		KNO_3	0.0372
	H	0.0041		$(NH_4)_2CO_3$	0.0286
	O	0.0307		S	0.0014
				C	0.0073
			Gases		
			0.3138	H_2S	0.0018
				O	0.0014
				CO	0.0094
				CO_2	0.2012
				H	0.0002
				N	0.0998

He then developed the first theory about the explosion of Black Powder. Here he drew extensively on the experimental work of Bunsen and Schischkoff. Berthelot's theory assumes two limiting cases for the decomposition of Black Powder.

In Berthelot's first case, K_2CO_3 forms the chief product of decomposition and K_2SO_4 is a by-product.

In his second case, K_2SO_4 forms the chief product of decomposition and K_2CO_3 is a by-product.

In the first case, the decomposition proceeds according to the following three equations:

$$2\,KNO_3 + S + 3\,C \rightarrow K_2S + 3\,CO_2 + N_2 \quad (4)$$

$$2\,KNO_3 + S + 3\,C \rightarrow K_2CO_3 + CO_2 + CO + N_2 + S \quad (5)$$

$$2\,KNO_3 + S + 3\,C \rightarrow K_2CO_3 + 1.5\,CO_2 + 0.5\,C + S + N_2 \quad (6)$$

Berthelot further proposed that the above occurred in the ratios of 1/3 for equation 4, 1/2 for equation 5, and the remaining 1/6 for equation 6.

In the second case, the decomposition proceeds according to equations 4 and 6 above plus the following two equations:

$$2\,KNO_3 + S + 3\,C \rightarrow K_2SO_4 + 2\,CO + C + N_2 \quad (7)$$

$$2\,KNO_3 + S + 3\,C \rightarrow K_2SO_4 + CO_2 + 2\,C + N_2 \quad (8)$$

And the above are supposed to occur in the proposed ratios of 1/3 for equation 4, 1/2 for equation 6, 1/8 for equation 7, and the remaining 1/24 for equation 8.

A different conclusion was reached by Debus[1] who concluded that Black Powder burns in a two-stage process. In the first stage, oxidation occurs according to the following exothermic reaction:

$$10\,KNO_3 + 3\,S + 8\,C \rightarrow 2\,K_2CO_3 + 3\,K_2SO_4 + 6\,CO_2 + 5\,N_2 + 979\text{ kcal (4096 kJ)} \quad (9)$$

The resulting products are then reduced according to the following endothermic reactions:

$$K_2SO_4 + 2\,C \rightarrow K_2S + 2\,CO_2 + -58\text{ kcal } (-242.7\text{ kJ}) \quad (10)$$

$$CO_2 + C \rightarrow 2\,CO + -38.4 \text{ kcal } (-160.6 \text{ kJ}) \quad (11)$$

The resulting potassium sulfide may further undergo the following reactions:

$$K_2S + CO_2 + H_2O \rightarrow K_2CO_3 + H_2S \quad (12)$$

$$K_2S + CO_2 + 0.5\,O_2 \rightarrow K_2CO_3 + S \quad (13)$$

A part of the unburned potassium sulfide and sulfur gives K_2S_2.

Much later Kast[1] derived the following equation:

$$\begin{aligned} 74\,KNO_3 + 30\,S + 16\,C_6H_2O \text{ (charcoal)} \rightarrow \\ 56\,CO_2 + 14\,CO + 3\,CH_4 + 2\,H_2S \\ + 4\,H_2 + 35\,N_2 + 19\,K_2CO_3 \\ + 7\,K_2SO_4 + 2\,K_2S + 8\,K_2S_2O_3 \\ + 2\,KCNS + (NH_4)_2CO_3 + C + S + \\ 665 \text{ kcal/kg } (2782 \text{ kJ/kg}) \quad (14) \end{aligned}$$

From the foregoing, a somewhat confusing picture emerges concerning the chemical reactions (with resulting products) that occur when Black Powder is ignited. While it is tempting to give more credibility to chemical equations derived by more recent research, due caution should be exercised here. The number of resulting variables, after ignition occurs, precludes chemical equations that will be true under all ignition conditions.

Ignition conditions vary widely in practice from high-pressure ignition that occurs in guns (of both large and small caliber) to lower pressures found in fireworks applications such as mortars, Roman candles and mines. Environmental factors such as temperature and relative humidity might also come into play. Noble and Abel[2] found so many variations in their experiments that they concluded that no value could be attached to a general chemical expression relating to the burning of Black Powder. So there is no "one true formula" for the chemical reaction that occurs when Black Powder is ignited. Thus, any formula presented should be treated as an approximation of what happens when igniting Black Powder.

Another consideration is some variation in the formula used in Black Powder manufacture. While the traditional Waltham Abbey ratio of 75:10:15 can be regarded as a standard, some variations do occur in practice. Propellant powders used by the military and in fireworks usually stick quite closely to the 75:10:15 ratio. (This is illustrated in Tables 2 and 3).

Note that in Table 2 the percentage value of potassium nitrate includes tiny percentages of impurities such as potassium sulfate and potassium chloride.

The data in Tables 2 and 3, gathered approximately a century apart, indicate that the 75:10:15 ratio has been fairly closely adhered to, especially with the more modern powders. This is not only true for Black Powder produced in Britain and the USA, but for Black Powder manufactured elsewhere as well. For example, Shimizu[5] gives an analysis of Japanese Black Powder containing 74.20% potassium nitrate, 9.62% sulfur, and 16.18% charcoal.

However, much variation exists in powders used for blasting. Here, not only do the ratios of

Table 2. Analysis of Black Powders (circa 1875).[2]

Description	Potassium Nitrate (%)	Sulfur (%)	Charcoal (%)	Water (%)
Pebble Powder	74.76	10.07	14.22	0.95
Rifle Large-grain	75.1	10.27	13.52	1.11
Rifle Fine-grain	75.18	9.93	14.09	0.80
Fine-grain	73.91	10.02	14.59	1.48
Spanish Spherical Pebble Powder	75.59	12.42	11.34	0.65
Sporting Powder	77.99	9.84	11.17	—
Austrian Cannon Powder	73.78	12.80	13.39	—
Austrian Small Arms Powder	77.15	8.63	14.27	—
Cannon Powder	74.66	12.49	12.85	—
Russian Powder	74.18	9.89	14.83	1.10

Table 3. Analysis of Black Powders (circa 1975).[4]

Description	Potassium Nitrate (%)	Sulfur (%)	Charcoal (%)	Water (%)	Ash (%)
Du Pont 3814	73.88	9.97	15.71	0.30	0.14
Du Pont 7625	73.59	10.61	14.84	0.82	0.14
CIL 1-Keg-A	73.13	10.83	14.61	0.64	0.79
CIL 1-Keg-B	73.13	10.83	14.61	0.64	0.79
GOE 76-3	74.34	10.25	14.66	0.48	0.27
Du Pont 7846	74.01	9.92	15.01	0.79	0.27
GOE 78-1	74.43	9.95	14.54	0.49	0.58
GOE 78-2	74.45	9.88	14.88	0.20	0.59
CIL 8-2-73	72.92	10.83	14.78	0.65	0.82
CIL 4-23	73.93	10.63	14.05	0.63	0.48

the three principal ingredients differ, but also it is common to find additional ingredients in such powders. Blasting powders also tend to substitute sodium nitrate for potassium nitrate and some use both oxidizers. Substitutes for charcoal are also found in some blasting powder formulas. Tables 4 and 5 show some of these variations.

Further consideration should be given to other variations in manufacture such as the degree of incorporation and the resulting density of the powder. Also, a major factor that often is not given the consideration it deserves, is the type of charcoal used.

Charcoal's Significant Influence

While little variation is found in potassium nitrate of high purity and minimal variation in sulfur, significant differences can be found in the different charcoals used in Black Powder. These differences can be largely attributed to the fact that charcoal is derived from organic

Table 4. Blasting Powder Compositions (Potassium Nitrate Based).[1]

Description	KNO_3 (%)	Sulfur (%)	Charcoal (%)	Ammonium Sulfate and Copper Sulfate (%)
Strong Blasting (French)	75	10	15	
Slow Blasting (French)	40	30	30	
No. 1 Blasting (German and Polish)	73–77	8–15	10–15	
No. 1 Bobbinite (with 2.5–3.5% paraffin) (British)	62–65	1.5–2.5	17–19.5	13–17
No. 2 Bobbinite (with 7–9% starch) (British)	63–66	1.5–2.5	18.5–20.5	

Table 5. Blasting Powder Compositions (Sodium Nitrate Based).[1]

Description	$NaNO_3$ (%)	KNO_3 instead of $NaNO_3$ (%)	Sulfur (%)	Charcoal or substitutes (%)
No. 1 Black Blasting (German)	70–75	up to 25	9–15	10–16
Blasting (American)	70–74	—	11–13	15–17
No. 3 Black Blasting (Petrolastite or Haloclastite)	71–76	up to 5	9–11	15–19 of coal-tar pitch
No. 2 Black Blasting	70–75	up to 5	9–15	10–16 of lignite

Table 6. The Effect of Carbonization Temperature on Charcoal's Chemical Composition.[1]

Carbonization Temperature (ºC)	Charcoal Color	Yield (%)	Composition of Charcoal (%)		
			C	H	O + N
280–300	brown	34	73.2	4.3	21.9
350–400	black	28–31	77–81		
1000	black	18	82.0	2.3	14.1
1250	black	18	88.1	1.4	9.3

matter, this matter being either animal or vegetable in origin. Black Powder appears to have been made exclusively with vegetable charcoal. Any possible experiments with animal charcoal are not on record, at least not in any prominent literature in the English language. And even if it could be proven that certain animal charcoals exhibited superior properties, cost and other practical considerations would preclude their use in Black Powder.

The two most influential variables in charcoal are:

- The type of material from which the charcoal is derived.
- The method used to make the charcoal.

Charcoal Varieties

Given the abundant variety of vegetable matter in existence, the potential exists to create an endless variety of charcoals. In practice, Black Powder manufacturers have focused on materials that were readily available and suitable for Black Powder manufacture. Typically, softer woods such as willow, poplar and alder have been used. Specifically the "white wood" from such sources is preferred.[1]

In willow trees alone, many different species exist throughout the world. Even within the same species of willow, variations in its wood exist due to such factors as weather, soil conditions, the age of the tree, and the part of the tree from which the wood is taken.

Research on maple charcoal has also indicated that differences in charcoal properties can exist even within batches of charcoal obtained from the same supplier.[6]

Charcoal Manufacture

Different methods of charcoal manufacture can impart different properties to the charcoal. Even variations in the same method can yield different results. For example, charcoals produced at lower temperatures retain meaningful percentages of volatiles. Higher temperatures drive these volatiles out of the charcoal. Excessively high temperatures can cause the charcoal to transition into graphite.

For centuries, charcoal used in Black Powder was made using traditional methods such as igniting a large pile of wood and then covering it with earth to exclude oxygen from the air. Typically, a kiln was used, consisting of a pile of wood covered with earth or other material. Modern variations use metal covers and are more efficient.[7] But these are still not optimal for charcoal used in Black Powder. At the end of the 18th century, an Englishman, Richard Watson, invented a new method that revolutionized charcoal manufacture.[8] This method used metal cylinders that were filled with wood and sealed prior to heating. Ballistic tests on Black Powder made with this charcoal showed an increase in range of about 60%.

Temperature Considerations

The temperature at which charcoal is made has a very large influence on the temperature at which it burns. This property of charcoal was explored by Violette in 1848.[1,8] Violette prepared charcoals in a retort, using different types of wood, and subjecting the woods to different temperatures of carbonization. Violette's work was a milestone in research on the properties of charcoal. Some of his findings are reflected in Tables 6 and 7.

Table 7. The Relationship between Carbonization Temperatures and Ignition Temperatures.[1]

Carbonization Temperature (ºC)	Ignition Temperature (ºC)
260–280	340–360
290–350	360–370
432	400 (approx.)
1000–1500	600–800

Thus, Black Powder made with charcoal carbonized at lower temperatures will ignite at lower temperatures, and it burns at lower temperatures. This could be advantageous or disadvantageous, depending on the application. Typically, blasting powders are designed to burn at lower temperatures. Highly carbonized charcoal tends to absorb moisture less readily than less carbonized charcoal. Thus, certain tradeoffs exist in charcoal made for Black Powder manufacture, and thus it is wrong to describe any charcoal as ideal.

Volatiles

Volatiles in charcoal noticeably affect the burn rate of Black Powder. Generally, it is desirable to use such charcoal rather than charcoal where the volatiles have been driven out. Sassé[6] determined that a 25% volatile content was about the optimal amount for Black Powder use. This figure came from his own research, which correlated with research done by others who are referenced in his paper.[6]

Charcoal Variations

The many variations in charcoal have influenced research by the US military. Notable is the research done by Rose[9] at the Naval Ordnance Station at Indian Head, Maryland and by Sassé at the US Army Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland. Both research projects aimed at producing more uniform powders by establishing more exacting standards for charcoal. Rose's research compared charcoal made from different species of trees, while Sassé[6] focused on maple charcoal. Even within the narrower confines of Sassé's research, notable variations in properties were found between charcoal samples. One example is the variation in volatile content of between 21 and 29%. Sassé concluded that the properties could vary even between different samples in the same lot obtained from a single supplier. He suggests that these variations are due to variations in the wood used and differences in temperature in different parts of the kiln. His proposed solution to this problem is to preblend such charcoal to obtain a more predictable Black Powder.

Chemical Analysis

Charcoal should never be regarded as pure carbon, but rather as an organic hydrocarbon compound. Just as there is no one true equation for Black Powder's chemical reaction, there is no one true formula for charcoal. Again, some authors of textbooks and technical papers have erred here. The formula for charcoal depends on which charcoal it is meant to represent. Often this representation is approximate and not exact. Table 8 shows that even charcoal obtained from the same type of wood may have variations in chemical content.

The data in Table 8 is extracted from experiments conducted by Sassé[6] in trying to determine the characteristics of maple charcoal. These data demonstrate that noticeable differences in chemical composition are to be found in charcoal made with the same type of wood.

Table 8. Chemical Characteristics of Roseville Maple Charcoal.[6]

Sample	O_2 (%)	C (%)	H_2 (%)	N_2 (%)	S (%)	Ash (%)
1	12.71	78.40	3.26	0.44	0.68	5.11
2	13.10	78.40	3.24	0.35	0.01	4.90
3	14.20	75.83	3.15	0.35	0.02	6.45
4	14.14	75.41	3.24	0.34	0.02	6.85
5	16.03	76.87	3.49	0.32	0.01	3.30

These values, however, are close to the empirical formula of C_8H_4O. Sassé[10] also refers in a later paper to other empirical formulas for charcoal:

- $C_{14.57}H_{7.17}O_{1.00}$
- $C_{8.68}H_{4.96}O_{2.00}$

Charcoal Substitutes

Charcoal substitutes have been investigated by researchers seeking Black Powder with characteristics that are more predictable. Notable is the research conducted by Wise, Sassé and Holmes,[11] which was followed by research done by Weber.[12] Many different crystalline organic compounds were tested by Wise, et al., who concluded that some of these compounds showed promise as viable alternatives for charcoal. Their research, however, did not exhaustively test the properties of the powders produced, and they concluded that such tests were necessary before claims of a viable charcoal substitute could be considered conclusive.

Weber focused on a process that used phenolphthalein as a charcoal substitute, with promising results. His findings, however, were not subjected to all the test criteria outlined by Wise, et al.[11]

None of these findings has resulted in a large-scale commercially viable production process. Possibly the cost of alternate substances such as phenolphthalein is in itself prohibitive. However, there may be niche applications of these alternate formulations where cost and large-scale manufacture are not major factors.

The foregoing discussion focused on the resulting products produced when Black Powder is ignited and its ignition allowed to go to completion. While some of this discussion has involved intermediate reactions in the combustion process, it has not attempted to explain the ignition process itself (i.e., what happens when heat of sufficient intensity is applied to the powder, causing it to ignite).

The Ignition Process

The following discussion examines the ignition process itself.

Principal in importance in Black Powder ignition is its oxidizer, potassium nitrate. Here, as with other oxidizers, potassium nitrate supplies oxygen to the reaction. This oxygen, if supplied with sufficient heat, causes the two other components to burn. Given the right combination of the ratios of the ingredients and an efficient method of manufacture, the resulting Black Powder will burn very rapidly. This rapid burning makes it useful as an explosive or propellant.

While the potassium nitrate supplies most of the oxygen to the reaction, a small percentage of oxygen is contributed by the charcoal and also possibly by the atmosphere. Charcoal itself contains oxygen atoms in its chemical composition and may contain absorbed oxygen and other atmospheric gases.

Ignition Phases

Although Black Powder ignites very rapidly, its ignition can be separated into several distinct phases. The most important phase is the decomposition of the potassium nitrate, which is preceded by a pre-ignition phase. This decomposition of the potassium nitrate is essential for it to yield its important oxygen component to the process. The decomposition starts with the melting of the potassium nitrate.

Potassium nitrate melts at 334 °C. Its counterpart, sodium nitrate, used in various blasting powders, melts at 307 °C. This suggests that sodium nitrate powders ignite at lower temperatures, which indeed they do. Interestingly, a eutectic mixture of potassium nitrate and sodium nitrate melts at 220 °C.[1]

Experiments performed by Hoffmann[1] have shown, however, that the Black Powder ignition process begins at a much lower temperature. This is due to the influences of the charcoal and sulfur. An important factor here is the melting point of sulfur, which is about 115 °C. Thus at about 150 °C, molten sulfur reacts with hydrogen to form hydrogen sulfide (H_2S). This H_2S then reacts with the KNO_3 to form potassium sulfate (K_2SO_4). This reaction generates heat, causing the KNO_3 to melt. This process is often referred to as the pre-ignition process.

Sulfur's Importance

The importance of sulfur has been demonstrated in experiments performed by Hoffmann.[1] These experiments showed that sulfur did the following:

- Facilitated an increase in the quantity of gases evolved on explosion
- Reduced initial decomposition temperature and temperature at which explosion occurred
- Intensified the sensitiveness of mixtures to impact
- Counteracted the formation of carbon monoxide

The above conclusions were drawn in part from some of Hoffmann's following experimental data:

- Potassium nitrate ignited with carbon produces only K_2CO_3, but in the presence of sulfur produces CO_2, K_2SO_4 and K_2S. Thus, more gases are created by exploding Black Powder that contains sulfur than Black Powder that does not.
- A mixture of two moles of KNO_3 and three moles of carbon (charcoal with a 71% carbon content) begins to decompose at 320 °C and explodes at 357 °C, while a mixture of two moles of KNO_3 and one mole of sulfur begins to decompose at 310 °C and explodes at 450 °C. A mixture of KNO_3 with both sulfur and charcoal yields both lower decomposition and explosive temperatures as shown in an experiment where a mixture of two moles of KNO_3, one mole of sulfur and three moles of carbon begins to decompose at 290 °C and explodes at 311 °C. This latter experiment is very significant in that it shows that sulfur does not only reduce decomposition and explosion temperatures, but it greatly narrows the gap between initial decomposition and explosion temperatures.
- Sulfur increases the sensitiveness of Black Powder mixes to impact while carbon (charcoal) reduces it. This is shown by the following experimental data. A 2 kg mass dropped from 45–50 cm caused a mixture of KNO_3 and sulfur to explode while a mixture of KNO_3 and charcoal was unaffected. A mixture of KNO_3 with both sulfur and charcoal exploded when a 2 kg mass was dropped on it from a height of 70–85 cm.

Hoffmann[1] also concluded that sulfur counteracts the formation of carbon monoxide when Black Powder explodes and also has an impact on the amount of potassium cyanide (KCN) gas produced. This is because the addition of sulfur causes K_2SO_4 to be formed in addition to K_2CO_3. Thus, the amount of potential K_2CO_3 is reduced. The formation of K_2CO_3 causes both carbon monoxide and potassium cyanide to be formed as follows:

$$K_2CO_3 + 2\,C \rightarrow 2\,K + 3\,CO \qquad (15)$$

$$2\,K + 2\,C + N_2 \rightarrow 2\,KCN \qquad (16)$$

The decomposition of K_2SO_4 does not result in either carbon monoxide or potassium cyanide gases forming, as shown in the following equation:

$$K_2SO_4 + 2\,C \rightarrow K_2S + 2\,CO_2 \qquad (17)$$

The importance of sulfur in Black Powder is further emphasized by experiments in trying to find a substitute for charcoal. Such experiments were conducted by Wise, et al.[11] Their research demonstrated that sulfur has a profound effect on combustion when phenolic materials were used as charcoal substitutes. However, their experiments did reveal opposing trends when different types of phenolic materials were used. For example, quinizarin and anthraflavic acid both produced more rapid burning powders with the absence of sulfur. Other polyphenols exhibited the opposite trend but to a lesser degree. These data challenged the perceived importance of the sulfur being reduced by organic compounds and strengthened the hypothesis that the influence of sulfur is more marked in its role in the flame-spread rate after ignition occurs. Wise, et al. concluded that this hypothesis needs to be explored further using both charcoal and charcoal-substitute mixes.

Sulfurless Black Powder

No discussion about the role of sulfur in Black Powder would be complete without examining useable Black Powder that does not contain any sulfur. Here the term “useable” denotes Black Powder that performs adequately as an explosive, propellant or igniter. Probably the most famous type of sulfurless Black Powder was the so-called “Cocoa” powder, which used incompletely carbonized charcoal.[1] This charcoal, known as “Cocoa” or “Red” charcoal, was typically manufactured at a temperature of 140–175 °C. It had a carbon content of 52–54%, which is much lower than other charcoals used in Black Powder. Its major drawback was its sensitivity to friction, which easily ignited it.

A stoichiometric mixture of sulfurless Black Powder comprises 87.1% potassium nitrate and 12.9% charcoal. The decomposition occurring after ignition can be represented theoretically as follows:

$$4\,KNO_3 + 5\,C \rightarrow 2\,K_2CO_3 + 2\,N_2 + 3\,CO_2 \qquad (18)$$

In practice, sulfurless Black Powder mixtures are generally not used for propellants, but rather as igniters. These have a potassium nitrate content of between 70–80% and a charcoal content of between 20–30%. Some “sulfurless” powders actually do contain a small percentage (about 2%) of sulfur, which is far below the normal percentage.

Binary Mixtures

Blackwood and Bowden[1] made extensive studies on the ignition of Black Powder and also on the following binary mixes:

- potassium nitrate + sulfur
- sulfur + charcoal
- potassium nitrate + charcoal

Amongst their findings, they concluded that ignition could take place as low as 130 ºC, depending upon the pressure to which the Black Powder was subjected. They also confirmed the importance of having charcoal with the right constituents. In their opinion, it was advantageous to remove the constituents that could be dissolved with organic solvents. This, they said, made ignition easier and gave a faster burn rate.

Blackwood and Bowden formulated the mechanism for Black Powder’s ignition and subsequent burning reactions. Accordingly, sulfur reacts first with the organic substances in the charcoal:

$$S + \text{organic compounds} \rightarrow H_2S \qquad (19)$$

Potassium nitrate reacts almost simultaneously with these organic compounds:

$$KNO_3 + \text{organic compounds} \rightarrow NO_2 \qquad (20)$$

The following reactions may also occur:

$$2\,KNO_3 + S \rightarrow K_2SO_4 + 2\,NO \qquad (21)$$

$$KNO_3 + 2\,NO \rightarrow KNO_2 + NO + NO_2 \qquad (22)$$

$$H_2S + NO_2 \rightarrow H_2O + S + NO \qquad (23)$$

This last reaction proceeds until all the H_2S is consumed. The remaining NO_2 then reacts with the unconsumed sulfur according to the following reaction:

$$2\,NO_2 + 2\,S \rightarrow 2\,SO_2 + N_2 \qquad (24)$$

The SO_2 formed in the above reaction may then immediately react with the KNO_3 as follows:

$$2\,KNO_3 + SO_2 \rightarrow K_2SO_4 + 2\,NO_2 \qquad (25)$$

Reactions 23 and 24 are endothermic while reaction 25 is strongly exothermic. Reactions 19 to 25 constitute the ignition process.

Blackwood and Bowden concluded that the chief reaction is the oxidation of charcoal by the potassium nitrate. This is when the Black Powder starts to burn.

Flame Spread Rates

The flame-spread rate of Black Powder is firstly dependent on the solid salts produced after ignition has commenced. These tiny hot pieces of solid matter are driven into the surrounding Black Powder, causing it to ignite and the flame to spread until all the powder is consumed. While the production of solid hot particles produced by different chemical reactions is an important factor in Black Powder’s flame spread characteristics, other physical attributes are also important.

Many processes have been tried over the centuries to improve and control the flame-spread attributes of Black Powder. Essential to these attributes is the process of granulation or corning where the Black Powder is formed into solid grains. Recent research on the influence of physical properties on the burn rate has been done by Sassé[13] and also by White and Horst.[14] Sassé's research showed flame spread to be dependent on density, surface area and free volume. White and Horst found that grain position and the ability of grains to move was important.

Thus, the flame-spread rate of any sample of Black Powder is dependent both on the chemical reactions that take place and on the physical attributes of the powder grains.

The Influence of Moisture

Most Black Powder contains some moisture, and this property does have an effect on the powder's ignition and explosive properties. Nearly every Black Powder manufacturing process uses water, some of which remains in the powder. Black Powder may also absorb moisture from the atmosphere. There remains a certain amount of controversy as to whether a certain small percentage of moisture aids ignition. The author's own observations indicate that it might. Some have made similar claims that have been refuted by other authorities. Shimizu[5] refers to an optimal moisture content of about 1%, but this statement in itself appears based more on hearsay rather than empirical evidence from experimentation.

Where there is agreement, is the fact that moisture does have an effect and that variations in moisture content do produce variations in ignition. So, where uniformity in performance is critical, the challenge is to find a range of moisture content where performance can be regarded as sufficiently uniform and then, to control this moisture range.

One suggested range is 0.3 to 0.5%.[15] Here the challenge is to keep the moisture level above 0.3% while not allowing it to exceed 0.5%. This is far more difficult to achieve than merely aiming at a specified upper moisture limit.

The Effect of Aging

Another area of controversy is the effect of aging on Black Powder. Black Powder has shown itself to be far less susceptible to aging than many other explosives, but the question is: Does it actually (like a good wine) improve with age? And if it does improve with age, under what conditions? And why does it improve with age? One possibility is that the charcoal in the Black Powder absorbs oxygen from the atmosphere over a period of time. Some tests have, however, been done on aging Black Powder. Notable among these are the tests performed by Kosanke and Ryan[16] on US Civil War vintage Black Powder (ca. 1865). These tests showed that such powder performed very well in spite of its age.

The question of aging is a difficult one to answer as the aging process itself, by its very nature, takes a long time. A proper objective test would be to determine the properties of a batch (or batches) of Black Powder and then perform the same tests after an aging period. Practically speaking, this would be difficult to achieve.

Conclusion

Over several centuries, a considerable amount of knowledge has been gained concerning the chemistry of Black Powder. Some of this knowledge comes from extensive research done under tightly controlled laboratory conditions and supplemented with field research in practical applications. But there is still a lot that is not known. And there is still a lot to be gained from further research and experimentation.

A big challenge still is in achieving consistency in performance. Even with modernized, tightly controlled manufacturing techniques, there is still one major variable in the equation—charcoal. Perhaps one day a viable alternative to charcoal will be found, or a method to produce charcoal with very tightly controlled specifications.

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A Brief Introduction to Noise and Data Filtering

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ABSTRACT

This brief article examines some aspects of noise and the effects of filters applied to data.

Keywords: signals, data acquisition, noise, data filter, digital filter, pyrotechnic, experimental design

Introduction

Filtering as used herein, is the removal of noise from the signal under examination

Noise, as defined herein, is any portion of a measured signal that is not desired. The noise may result from fluctuations in the event, from mechanical sources that are not being measured, from inherent electronic sources, from unwanted electromagnetic interactions with the electronics or wiring, or just something that is interfering with what the investigator thinks the signal should look like. (However, as someone famous once said—No data is completely useless, it just isn't quite what you had in mind before you took it.)

Background

The fundamental process of data acquisition, reduction, and analysis is as follows:

- A physical event occurs.
- A transducer changes some physical manifestation of the event into a form that may be recorded.
- A record is made.
- The record is examined and useful information is obtained.

In an ideal world, one would be able to directly record every physical manifestation of any event with perfect fidelity, assign correct values, and obtain all the information that is desired. In the real world, however, things are a bit different.

There Are Two Significantly Different Ways of Filtering: Analog and Digital

Analog filtering removes some frequency(s) portion of the signal by means of passive, active, or both passive and active electronic components. A very common analog filter is the "crossover" used in multi-driver speaker systems. In this application various bands of frequencies are either blocked, or passed, to the speakers, because some speakers are better at reproducing low, mid range, or high frequencies. Since the speakers are transducers (electrical energy to sound energy) and since the filters are (usually) comprised of capacitors, inductors, and resistors, one can readily see how the process would work in reverse.

Imagine that there are two sound-energy to electrical-energy transducers (microphones) with one having good linear response at low frequency and the other, good linear response at high frequency. If a sound, comprising both high and low frequencies excites these transducers, one will produce an electrical signal that is a good representation of the low frequency component of the sound, but with a superimposed poor representation of the high frequency component, and vice versa. The filter, in this case would serve to block the high frequency electrical signal produced by the transducer having good low frequency response, and vice versa.

However, in modern digital data acquisition, the main use for an analog filter is solely to block frequencies that are above the Nyquist Limit. The Nyquist Limit is that data acquisition rate which will allow at least two data points per Hz. [a] (A signal having a maximum frequency component of 50 KHz *must* be digitized at a rate of at least 100,000 samples per second, a 25 KHz signal must be digitized at a rate of at least 50,000 samples per second, and so forth), although a higher digitizing rate is desirable. If this is not done, an effect called aliasing[b] may/will occur. This causes the appearance of spurious data and must be taken into account.

Frequently, either the transducer or the associated electronics will take care of this problem. If a transducer, or its signal conditioner, only has a frequency response of 10 KHz one need never digitize the data from that transducer at (much) over 20,000 data points per second. One must also be aware of frequency response nonlinearity in transducers as areas of potential problems. As an example, some transducers may have a stated frequency response of 100 KHz, but a resonance at 200 KHz. In this case, one would have to make sure that no frequency over 100 KHz was digitized.

It is very desirable to not introduce any additional analog filtering before digitizing the signal of interest. While it may be nice to show a "clean" waveform on an oscilloscope, once analog filtering has been performed, it is not possible to recover any information, or frequencies, that might have been present in the signal but have been removed by the analog filtering.

The investigator will frequently discover that upon re-examining data that an "interesting" shape in a curve is noticed. If the data, showing the event of interest, has only been digitally filtered, the data may be re-presented with either no, or different, filtering applied in an effort to emphasize/clarify the "interesting" event. However, if the data had been analog filtered prior to digitizing, no frequency that had been filtered may be recovered.

Conceptually, all filtering may be viewed as a series of steps. These steps, in their most fundamental form, are the following:

- transformation of the time domain data to frequency domain data
- reduction of unwanted frequency data
- transformation of the altered data back to the time domain

The simplest, probably best-known, and most intuitive, low pass filters are the basic "square" smoothing methods. Consider the following example given in the Qbasic[c] computer language:

```
Dim Arr1(1000)        ' create two arrays,
                      capable of holding
                      1000 data
Dim Arr2(1000)        'points each
For I = 1 to 1000
   Arr1(I) = Data(I)  'fill the first array with
                      the raw data
Next I
For I = 2 to 999      ' this is where the
                      smoothing takes
                      place
   Avg = 0
   For J = -1 to 1
      Avg = Avg + Arr1(I+J)
   Next J
   Arr2(I) = Avg/3
Next I
```

This bit of code performs a three-point average smoothing on the data contained in Arr1, and places the smoothed data in Arr2. One might wish to note that the data contained in Arr2(1) and Arr2(1000) has the value of zero. It is obvious that any odd number of data may be smoothed using the above code with minor modifications, and even numbers with only a bit more of a change.

From this simple "square" smoothing, one may extend to a more complex method in which the data points are weighted. For example:

```
Dim Arr1(1000)        ' create two arrays,
                      capable of holding
Dim Arr2(1000)        '1000 data points each
Dim H(-2 to 2)        'this array will hold 5
                      filtering coefficients
H(-2) = 0.1
H(-1) = 0.2
H(0) = 0.4
H(1) = 0.2
H(2) = 0.1            ' note that the sum of
                      the coefficients = 1
For I = 1 to 1000
   Arr1(I) = Data(I)  ' fill the first array with
                      the raw data
Next I
For I = 3 to 998      ' this is where the
                      smoothing takes place
   Avg = 0
```

```
    For J = -2 to 2
       Avg = Avg + Arr1(I+J) * H(J)
    Next J
    Arr2(I) = Avg
Next I
```

In this case, we have applied a “triangular” low pass filter to the original data.

Most importantly, this introduces the concept of using a set of coefficients that are multiplied with the original data to form a new set of data.

$$FilteredArray(I) = \sum_{j=-n/2}^{j=n/2} DataArray(j+I) \times Coefficient(j)$$

Fortunately, and especially because this author is unqualified to properly explain the theoretical background for this area, workers in the field have written readily available programs to generate useful sets of coefficients. These programs are available as commercial software, shareware, and freeware.[d]

By using suitable sets of coefficients, one may obtain low-pass, high-pass, band-pass, band-stop, and differentiated data sets without ever permanently changing the original stored data.

It should be noted that the above method does not incorporate any output terms as an input to a later step, as with recursive filters. Perhaps the simplest recursive filter that the author is aware of[e] is shown in this example:

```
Dim Arr1(1000)  'create an array, capable
                of holding 1000 data
                points
C1 = .7         'a selected value 0 < C1
                < 1
C2 = 1 – C1
For I = 2 to 1000
   Arr1(I) = C1 * Arr(I – 1) + C2 * Arr(I)
Next I
```

Notice, that in this method, any data (after the first) is dependent on earlier data.

A more exact, and flexible, method to accomplish this filtering is to perform a Fourier[f] transform of the time domain data to the frequency domain, remove the unwanted frequencies, and then perform an inverse transformation back to the time domain. There are capabilities to perform these operations in many data analysis programs.[d] However, they are not so quick and easy to incorporate in small programs written to accomplish some task at hand.

As an example, Figure 1 shows the results of a test intended to measure the force exerted by a small pyrotechnic piston actuator. The data was acquired at a rate of 5E-6 seconds per point. Each of the data presentations includes a baseline and an arbitrary upper reference line. The first waveform shows the “raw” data as acquired. The successive waveforms show the effect of increased (lower frequency – low pass) filtering, while the last waveform shows the result of subtracting the 250 Hz filtered data from the raw data. This would represent only the “noise” above 250 Hz in the raw data, and it appears to be caused by two different excitation modes of the test fixture at approximately 3000 and 200 Hz. These two modes were thought to be caused by the vibration of a large mounting plate for the low frequency component, and a much smaller plate mounted at right angle to the large plate for the higher frequency. If desired this could have been determined by mechanically exciting the fixture, or parts of the fixture, using some small impact device to simulate the shock/impulse caused by the pyrotechnic actuator.

The effect of the digital filter before time “zero” is evident in the 500 and 250 Hz filtered waveforms. This could be eliminated/minimized by prefixing additional baseline data to the waveform prior to filtering it.

Inspection of these waveforms will make clear the importance of specifying how data is to be treated along with a set of requirements for the performance of an item. In this case, perhaps, the “time to function” might be specified to be determined from “raw” or “2000 Hz filtered” data, while the “peak effective force” might be required to be determined from a “500 Hz filtered” data set.

While the use of filtering will always have an effect on the magnitude, phase, and absolute time represented by the filtered data, in practice, and with judicious care, these effects will usually be found to be within an acceptable range when making physical measurements. However, one must always keep in mind the possibility that filtered data, under certain cir-

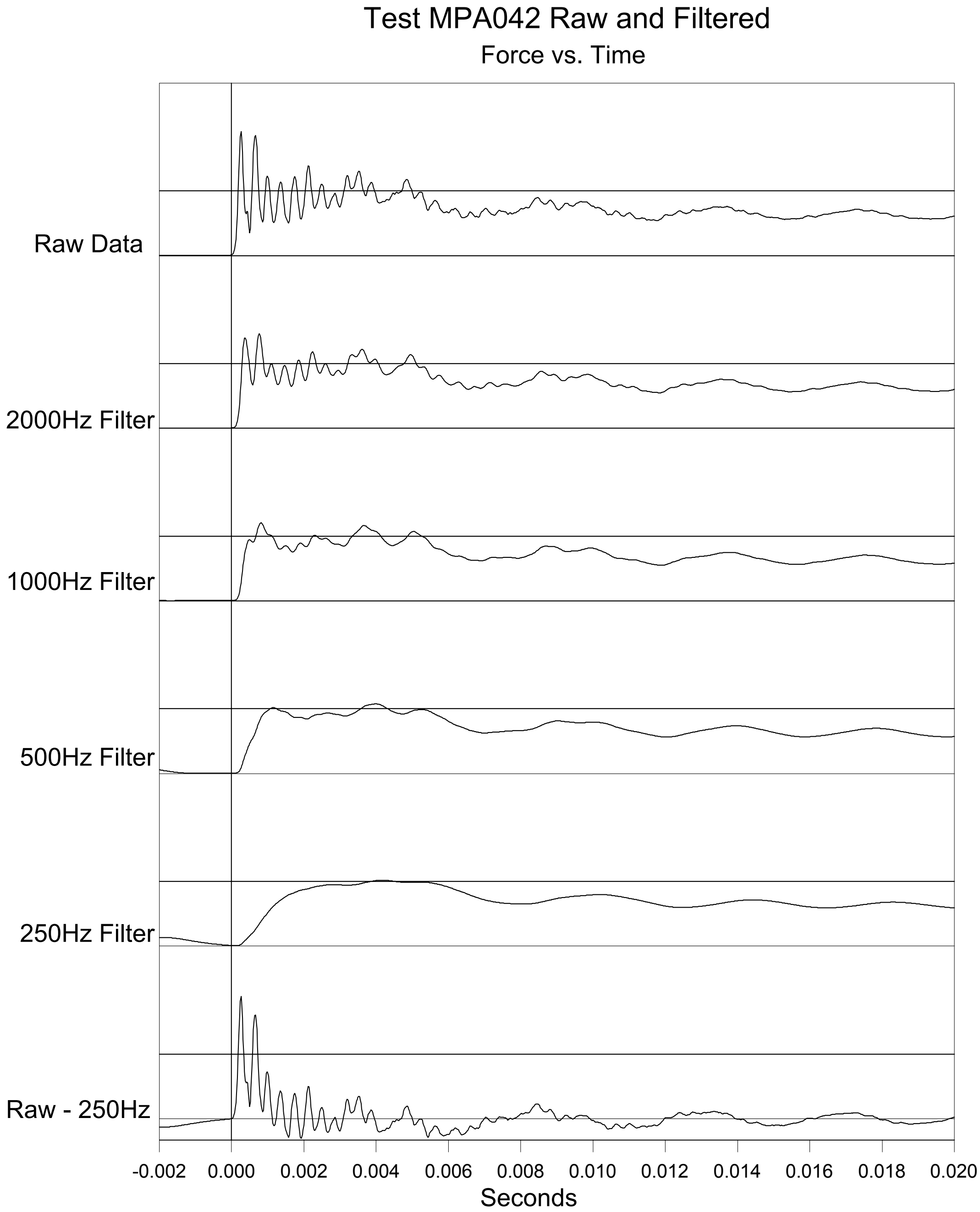

Figure 1. Data Filtering Examples.

cumstances, may not be a sufficiently accurate representation of the actual physical event.

Notes

a. Nyquist Limit: F_s = frequency of sampling, $Y(t)$ has a band limited spectrum

$$F_0 = \frac{\omega_0}{2\pi}\text{, then } F_s > 2F_0$$

b. If sampling is done at a frequency less than the Nyquist Limit, then some high frequency information in the analog signal will be shifted into the lower frequencies giving spurious data.

c. Qbasic can be found in the directory OLDMSDOS on Windows 95 and 98 disks.

d. The author suggests a search of the World Wide Web for finding such software and other available information.

e. Wm. Mattox, personal correspondence.

f. The forward and inverse Fourier transforms are:

$$Y(\omega) = \int_{-\infty}^{\infty} y(t) e^{-j\omega t} dt$$

$$y(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} Y(\omega) e^{j\omega t} d\omega$$

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Applying Explosives Testing Techniques To Obtain Insight into the Explosion (Or Is It Detonation?) Phenomenon of Piles of Fireworks

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ABSTRACT

There are times when the legal system requires so-called expert witnesses. Whether it is with regard to terrorist or criminal activities or accidents, the expert is often confronted with explaining the dreaded term "detonation". The attempt to explain such a catastrophic event often brings about the use of similes. In this paper, the author will provide arguments to support the use of a modified Height-to-Detonation and other steel pipe tests to generate data that may be useful in differentiating explosive reactions, including detonation, within a pile of fireworks. Work continues in this vein and test results will be published in a future article.[1]

Keywords: explosion, detonation, aerial shell, height to detonation output testing

Introduction

What is the duration of the explosion of a pressure vessel? Similarly, what is the duration of a dust explosion in a 500 m coalmine shaft? What is the duration of an explosion of a 500 m long pipe filled with natural gas? How long does it take from ignition to total consumption of 1 kg of Black Powder? How long does it take to totally consume a stick of dynamite from the time that the detonator is functioned? To many, these events are all "instantaneous" or that "they" explode "en masse". That is, they happen so quickly that for most, the duration of these events is too short to measure and therefore is deemed to be instantaneous. However, if one habitually measures in the region of femtoseconds (10^{-15} s), as in high-energy physics interactions, then the above events are of fairly long duration and far from being instantaneous.

How, then, does one explain that the explosion of a pressure vessel is different from the explosion of a pile of fireworks, is different from the explosion of a pile of pyrotechnic compositions, is different from the explosion of a pile of propellant, is different from the explosion of a pile of ANFO, or is different from the explosion of a pile of HMX? Should one be satisfied to state that all these explosions are the same because they are "perceived" to be instantaneous or that some are different because they don't simply explode but "detonate"? Or, is all that matters, is the simultaneity of the event as perceived by the human ear?

Energetic materials are often characterized through a measure of their output, including their rate of reaction, (velocity of detonation) and their power (TNT equivalency). As examples, see references 2–6, which deal with the output of fireworks shells and pyrotechnic compositions, TNT equivalency, relative effectiveness and blast pressure. One must recognize that a major parameter effecting the output of an energetic material is its "packaging". This can take the form of simple packaging used in shipping the material, a pipe used in the manufacture of a pipe bomb for increasing the material's damaging effects, and/or the casing of fireworks shells used to deliver the designed effect. Reference 7 contains more rigorous arguments and theory related to these topics.

Evaluation Tests

This paper suggests that a series of tests could be performed to obtain information on the behaviour of fireworks shells when subjected to thermal and blast stimuli. These tests can include *unconfined burns, height-to-detonation tests,* and *open and closed end pipe tests.*

Unconfined Burns

Unconfined burn trials are very common and are typically used to determine if a transition can occur from burning to explosion by varying the heat source and/or the size of sample. Data based on these tests will be the subject of a future paper.

Ideally, the plan would be to form hemispherical piles of firework shells on level ground with an ignition source located on the ground at the centre of the pile. The tests would be instrumented with continuous velocity of detonation probes radiating from the ignition source to various points on the surface of the hemisphere. On ignition, if the pile explodes, the probes would measure a reaction rate. To improve the probability of a reaction, the size and the bulk density of the pile would be increased. Additionally, blast pressures can be used to establish a TNT equivalency if the pile were to explode.

A modification of these hemispherical burns would be performed in large diameter, construction cardboard tubes, which could be filled with various sizes of shells or Roman candles. They would be initiated by flame at their base.

Height-to-Detonation

The less common test, the Height-to-Detonation (HtD) test, makes use of steel pipes with a sealed bottom. The test requires a series of pipes with different diameters and lengths. In the test, a pipe is set vertically to simulate a cylindrical core taken vertically within a conical pile of energetic material. Given this conical pile, the height of the core would increase as one moves from the edge to the center of the pile. See Figure 1.

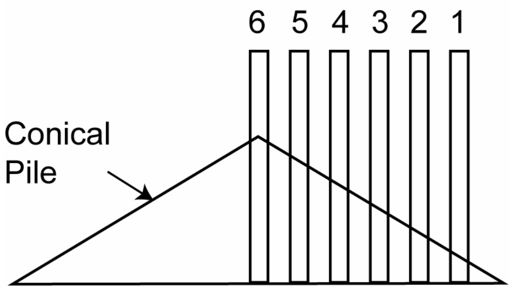

Figure 1. Showing how the height of the sample in the pipe would increase as it moved from the edge of the pile toward the center.

Assuming an ignition source at the bottom of the core, then the confining effect from the mass of the energetic material increases as the height of the core increases. The radial confinement is mostly due to the pipe wall. Increasing the diameter of the pipe/core will ensure that tests are performed in the region of the critical diameter of the energetic material under test, given the confining effect of the pipe. (Note that the wall thickness of the pipe will also play a role.) Ignition takes place at the bottom of the pipe, usually using an ignition source such as Black Powder. The pipe diameter and the height of the material under test are varied, altering the static pressure and the inertial resistance to the combustion products, until an ignition-to-detonation (explosion?) occurs.

The HtD test is often used to evaluate hazards in propellant processing.[8–10] Propellants are quite sensitive to confinement, therefore, it is important to know what amounts and/or thicknesses can be safely manipulated. To prevent catastrophic events, the amount and/or thickness of the propellant being handled should be less than a critical amount as determined in the HtD test performed with a relevant ignition source.

Conical piles of pyrotechnic compositions may be common in a process and the HtD test with a relevant ignition source can be relevant in establishing the safe size of a pyrotechnic composition. Firework articles and more specifically, fireworks shells may also be found in piles in factories and at display sites. Can the HtD be used to establish a safe limit below which an ignition would not result in what is perceived to be an explosion “en masse” or a “detonation”?

Figure 2 shows the set-up for a HtD test where the internal heat source normally used in these tests has been replaced with an external diesel fuel fire in a steel pan below the pipe.[11] (In this case, the modification to the standard

Figure 2. Height-to-Detonation test configuration.

test was made to better reflect the conditions at an accident site.) The external fire represents a relatively slow thermal stimulus requiring a period of minutes to raise the temperature of the energetic material. In contrast, the internal ignition method produces an extremely rapid heat source of short duration.

In this example, the HtD tests were performed by suspending different-sized pipes, with varying amounts of ANFO, approximately 50 cm above the burning pan of diesel fuel. HtD tests were performed to simulate the internal ignition of piles of ANFO with heights up to three metres. Typical instrumentation included three thermocouples within the pipe at 2.5, 15, and 45 cm from the base. See reference 11 for further details.

An example of the data obtained on ANFO[11] from thermocouples located at the bottom section of the pipe is shown in Figure 3. Typically, a mild decomposition begins, producing white smoke that then accelerates to eject most of the mass from the pipe. The reaction often ended with mild "popping" sounds, possibly due to the ignition of flammable gases escaping from the top of the pipe. The thermogram of Figure 3 indicates the characteristic ammonium nitrate (AN) phase change temperatures, specifically, those at 32 and 84 °C. Other higher peaks are in the neighbourhood of the melting and the decomposition temperatures of AN.

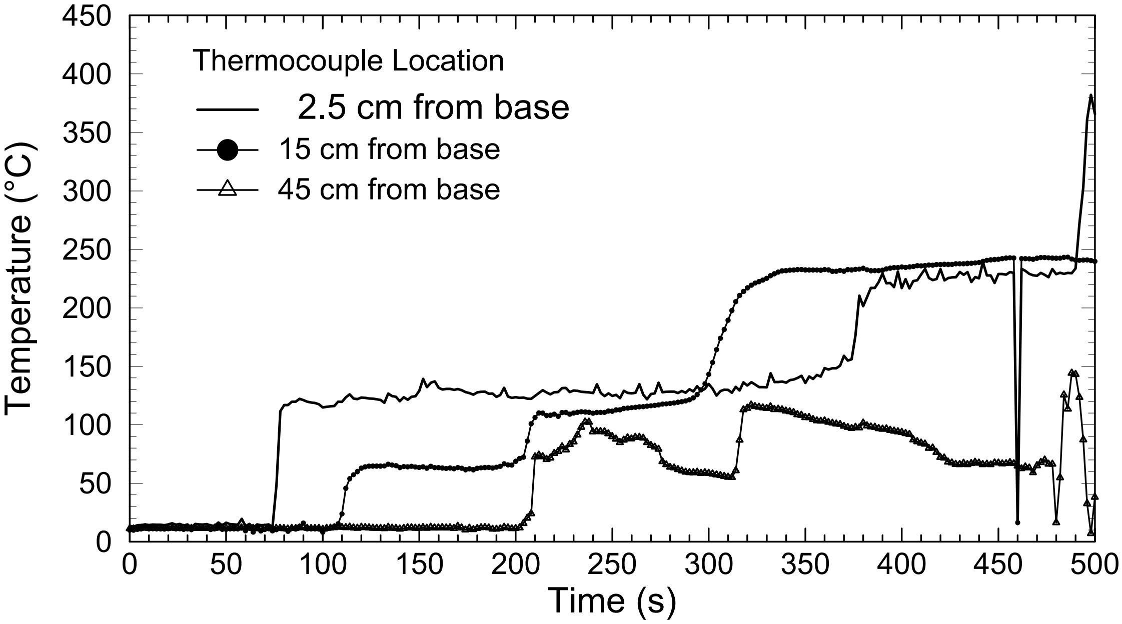

Figure 3. Details of the first 400 seconds of temperature profiles for HtD Test 5.

Figure 4. Preparation of plastic shells (no lift charge). Note steel pipe at top right of photo.

These series of HtD tests with ANFO indicated that it is unlikely that a pile of this explosive, under normal conditions, can provide the confinement required to lead to a detonation. The 3 m maximum test height was insufficient to cause a transition to explosion. It is possible that a taller pile of ANFO, with more confinement and/or a more energetic stimulus, could result in the transition.

If one were to perform HtD tests in this configuration with fireworks shells, (the fit being the same as with shells in standard mortars), the fire would heat the pipe and cause immediate initiation of the lift charge of the shells in the hot area (lower end of the pipe). The flame from the lift charge from these shells would not only ignite their respective delay elements but would jet by their respective shells to possibly ignite shells further up the column. However, with initiation occurring at the base of this closed-end, 3 m long, HtD pipe, it is very unlikely that the ignition of the lift charge of the shells in this region will be able to propel the column of shells out of the pipe. The lack of movement in the bottom shells will result in such high pressures that the shell or shells in this region will explode and burst the length of pipe in their vicinity. Additionally, if flames from the lift charge(s) traveled sufficiently far in the clearance volume between the column of shells and the inside wall of the pipe, the uppermost shell or shells could be ejected out of the open end of the pipe.

Figure 5. Shells (with lift charge) being wrapped in cardboard. Note velocity of detonation probe cable along shell surface.

Pipe Tests

Pipe tests are often used to determine the effect of confinement on the reaction rate and/or detonation velocity of energetic materials. The containment parameters include the pipe material (most commonly steel), diameter, and wall thickness. The length is usually fixed to a predetermined value. The pipe ends are either capped or left open, and the pipe may be either partially or completely filled with the test material. The tests performed in a pipe with one closed and one open end will simulate the HtD tests.

At this stage of the test program, some tests have been performed with nominal 1 and 3 m lengths of pipe filled with fireworks shells and Roman candles. Different pipe diameters will be used to accommodate shells up to 305 mm (12 in.). Figures 4 and 5 show two different shells being prepared for insertion into a steel pipe.

The fireworks shells were initiated with different stimuli. Electric matches were usually, simply inserted into the lift charge of the first shell. To initiate those shells with lift charge removed, a separate Black Powder charge was prepared with an electric match. Also, tests will be performed with explosive boosters to overdrive the initiation process. A resistive cable will be used to witness the reaction rate of the fireworks shells within the pipe and high-speed video will track the event. In case of an explosion, the pipe fragments and surviving shells will be recovered. The fragments will be used to classify the explosion and relate it to a detonation event.

Conclusions

In Reference 1, details of the tests being performed will discuss results such as the type and size of fragments produced from fireworks stars and fireworks shells caused to burst in steel pipes. Also, the reaction rates, as measured with velocity of detonation probes will be presented as a means to elucidate the mechanism of a pile of fireworks exploding. The data will also reference previous data including tests for classifying explosives[12] to establish a relationship between fireworks explosions and explosives detonations.

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A Ground Test Rocket Thrust Measurement System

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ABSTRACT

A strain gauge thrust measurement system is described for rocket motor ground testing. The unit uses sigmoid beams to hold the rocket motor in place, with the strain gauges mounted on these beams. The theory and usage of strain gauges is briefly discussed, along with all circuit and other information necessary to build a similar system. The system was calibrated for the 50 lb thrust level and applied to the UALR Hybrid Rocket Facility. Its performance characteristics are discussed. The system was found suitable for continuous monitoring in such a ground testing environment, and indicated that the hybrid thruster utilized in the facility develops 41 lbf thrust at an oxidant mass flow of 0.125 lbm.

Keywords: rocket ground testing, thrust sensor, combustion diagnostics, strain gauge, hybrid rocket

Conversions from English to Metric Units:

1 lbm = 1 pound mass = 454 g
1 lbf = 1 pound force = 4.45 N (Newtons)
1 lb = 1 pound = 454 g
1 psia = 1 pound per square inch = 0.145 kPa

Introduction

One of the most important parameters of rocket design is the time-thrust profile that the rocket is capable of producing. It is important in the developmental testing of rockets to determine the effect of nozzle design, fuel/propellant mixtures, additives, and changing other parameters of the motor or engine system on performance. While regression rates are often measured and used to determine a rate of performance, thrust measurement during ground testing allows the direct comparison of various motor and fuel/propellant configurations.

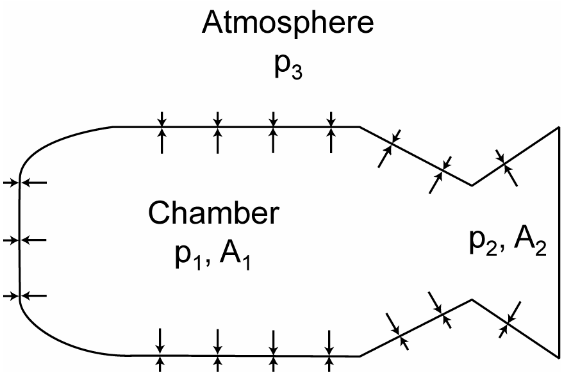


Figure 1. Simplified Schematic of a rocket motor.

Rocket propulsion is one type of jet propulsion. A rocket is propelled by the ejection of stored matter (propellant). The force produced by the ejection of the high-velocity matter is the thrust force (F). Thrust is defined as the sum of two terms, a momentum term and a pressure term. With reference to Figure 1, the equation for thrust is:

$$F = mv_2 + (p_2 - p_3)\, A_2 \qquad (1)$$

Momentum is the product of the mass and velocity of an object. For rockets, the momentum term is the product of the mass flow rate (m) and the exhaust velocity relative to the vehicle (v_2); it is the ejection of low mass gases at very high velocities. The pressure term is the product of the cross-sectional area of the nozzle exit (A_2)and the difference between the exhaust pressure (p_2) and the ambient fluid pressure (p_3).

The amount of thrust is determined, in part, by the amount of fuel and oxidizer in the combustion chamber. For a solid motor, neither the fuel nor oxidant can be varied during a burn, so the thrust is dependent on the original mixture and the grain physical configuration. In a liquid engine system, both oxidant and fuel can be varied to achieve start/stop and variations in thrust output. In a "normal" hybrid motor (as opposed to a reverse hybrid) as used here, the fuel is fixed, but the amount of oxidizer delivered to the chamber can be varied, thus varying the thrust.

The design of the nozzle is also critical to the thrust output. Briefly, if the nozzle is designed so that the exit pressure is greater or less than that of the surrounding medium, it will have a detrimental effect on the total thrust. The optimum expansion ratio will result when a nozzle is designed so that it expands the propellant products to the pressure that is exactly equal to the surrounding fluid pressure. While nozzles may be modeled analytically, each can be tested and fine-tuned for the desired performance through ground test thrust measurements.

This paper discusses a useful thrust sensor system of moderate cost that can be used with all types of rocket propulsion systems. In this case, the University of Arkansas at Little Rock (UALR) Hybrid Rocket Facility thruster, designed for 50-lbf thrust, is so instrumented. Solid propellant motors could easily be monitored using this type instrumentation, as can liquid engines with modifications to allow for the more complex fuel/oxidant feed system.

The Hybrid Rocket Facility

The Hybrid Rocket Facility has been described in detail elsewhere,[1] but is described briefly here for clarity. The facility utilizes a ground test 2×10-inch (51×254-mm) hybrid rocket thruster, designed to achieve approximately 50-lbf thrust. The unit uses a solid fuel grain of hydroxyl-terminated poly-butadiene (HTPB) and a gaseous oxidizer in the form of high pressure welding oxygen. The unit was designed to enable plume spectral studies,[2] fuel additive studies,[3] rocket materials research, and investigations of hybrid rocket instabilities.[4]

$$\begin{aligned}
\Sigma F_H &= F_B - F_A = 0 \\
F_B &= F_A \\
\Sigma M_B &= -M_A - M_B + F_A L \\
M_A &= M_B \\
M_A &= \left(F_A L\right)/2
\end{aligned}$$

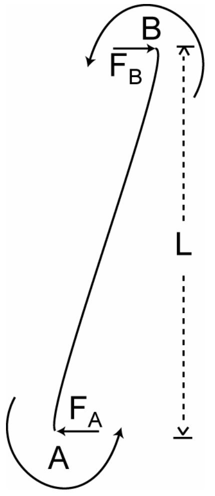
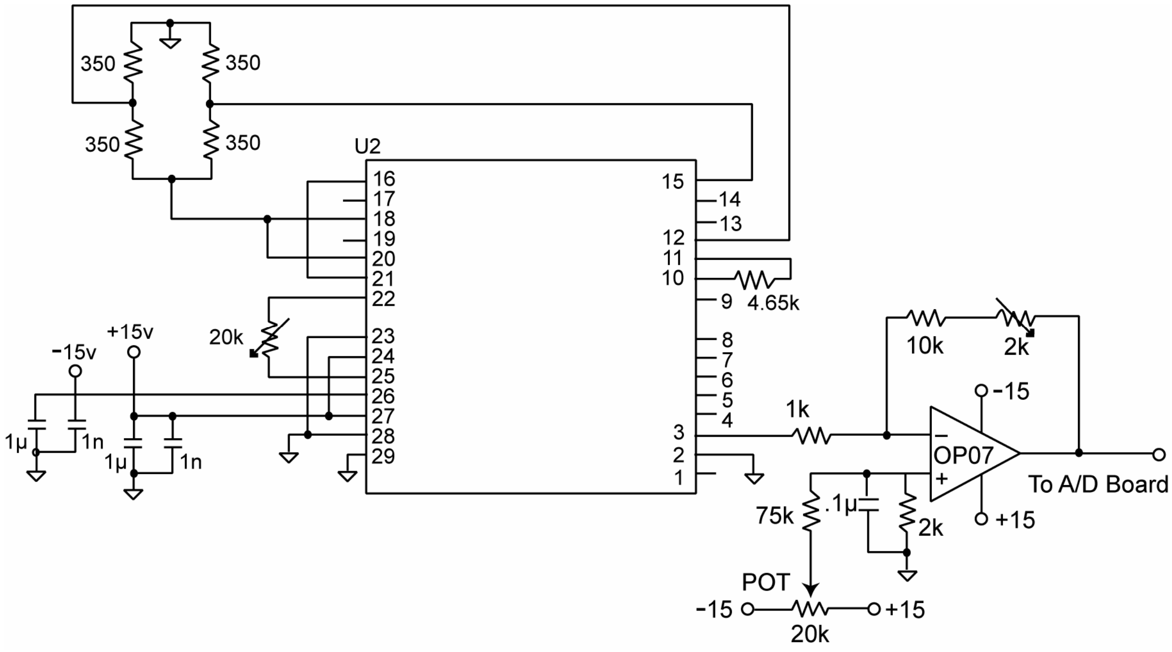


Figure 2. Diagram of a sigmoid beam.

The Thrust Sensor

Strain gauges basically consist of thin film resistors that are affixed to a surface of an object in which we wish to measure the strain caused by an event. For example, a simple wrench might have a strain gauge mounted to one of its surfaces. When the wrench is used, the deformation of the wrench material (strain) is measured by the change in resistance in the gauge that occurs upon tightening a nut or bolt. By accurately calibrating the wrench, and then monitoring its output upon tightening actual fasteners, one has a very accurate torque wrench. For our purposes in this study, the motor system could be mounted using four beams. These beams gave a surface that one could easily affix the strain gauges of the proper type for our thrust measurement.

The thrust sensor was designed and constructed so that the motor was supported on these four beams. Each of the beams were fixed on both ends, one end to the motor, one end to the ground-test frame, which forced them to deflect in the shape of a sigmoid curve (Figure 2) during a firing. The flexing beams were made from 2024-T81 aluminum with a yield strength of 65 kpsi. Strain gages were placed on the beams to convert strain to a voltage proportional to the thrust force. The sigmoid beam is often used in the design of transducers because of its predictable nature and known shapes of deflection. This makes the solution to the problem of how to



1	Output – 1	11	R-gain	21	Exc-sel-2
2	Fine-gain	12	– input	22	Ref-out
3	Fine-gain	13	Input-trim	23	Sense-low
4	Filter-trim	14	Input-trim	24	Regulator
5	Filter-trim	15	+ input	25	Ref-in
6	Bandwidth-3	16	Exc-sel-1	26	–vs
7	Output – 2	17	I-sel	27	+vs
8	Bandwidth-1	18	V-exc-out	28	Common
9	Bandwidth-1	19	I-exc-out	29	Out-trim
10	R-gain	20	Sense-high		

Figure 3. Circuit diagram of the thrust transducer.

calculate the stress and strain simple. To perform the calculations, the beam is split into two equal length beams in simple deflection. Using one of the beams, the stress on the beam and the maximum deflection are determined. The rocket design thrust was 50 lbf maximum, but the transducer system was initially designed for a 30 lbf maximum due to the less than optimal nozzle design that could cause a decrease in thrust output.[5] A computer program was written to perform the iterative calculations to determine the dimensions of the support beams to give approximately 1 mV/V sensitivity for the bridge circuit.[6] Total load, overall beam length, gage to gage distance, width of the beam, modulus of elasticity, and gage factor were input into the program along with a starting and ending thickness and an increment for the thickness. The beams of the transducer were designed such that even with overload, the beams would not plastically deform. At 100-lbf load, the maximum stress in the beams would be 19.2 kpsi, which is much less than the yield strength of the material. Calculations were performed to determine if the beams would deform under the load of the rocket itself. However, the weight of the rocket is well below the weight at which measurable deformation would occur.

Two fully active Wheatstone bridge circuits were used to measure the strain. Full bridges were used because they provide temperature compensation and are more sensitive than other bridge arrangements. A general-purpose strain gage from Measurements Group (CEA-13-

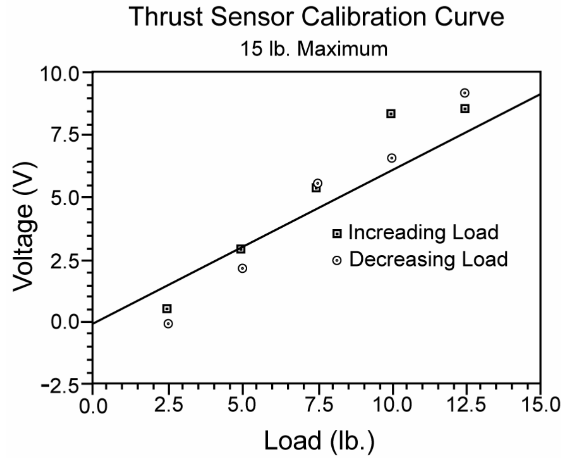


Figure 4. Plot of the hysteresis and linearity for the thrust sensor [V = 0.6144 × (Load) – 0.0482] 20 times the error is plotted.

125UW-350) was used in the bridges. Using M-Bond AE15, the gages were applied to the beams according to the manufacturers specifications.[7] A fixture was built to clamp the gages with the specified pressure to the beam during the curing process. The power density was calculated to be 3.17 W/in.^{2} which is considered to allow high accuracy when used on aluminum.[8]

To accommodate the frequency and gain requirements, a two-stage amplification circuit was built (Figure 3). The first stage consisted of a 2B31J Strain Gage Conditioner and the second stage was an OP07 Op-Amp, both from Analog Devices. After construction of the circuit, it was tested to determine its linearity using a DATEL voltage standard for input and measuring the output with a digital voltmeter. Next, the linearity of the entire system was determined by hanging weights off the end of the rocket and stand and recording the amplifier output voltage with the A/D converter (Computer Boards CIO-AD16F into a 486 DOS PC). The system produced 0.33 V/lb. The linearity of the transducer was determined to be +1.15% and –0.80% (Figure 4).

The original design called for measuring the thrust using two bridge circuits. This proved to be difficult in practice, due to the way the rocket was mounted. Both bridge circuits behaved linearly with respect to load, but the nozzle end bridge was highly influenced by pre-loading, depending on how the motor rear clamp was secured. The bridge on the injector head end was not influenced to any great extent by pre-loading, so it was decided to use only the head end circuit to record the thrust measurements. The clamp position on the chamber's nozzle end was not changed during all experiments, following system calibration, further minimizing offsets and error. This clamp was not tightened, allowing that portion of the mount to simply ensure that the motor could not come loose during firing. This placed all strain in the forward, injector head beams. The experimental protocol was changed to result in the forward, head end sensors measuring a maximum of 60 lbf, since the nozzle end beams were not taking any load. This was accomplished by changing the gain resistor in the circuit, and the system was recalibrated.

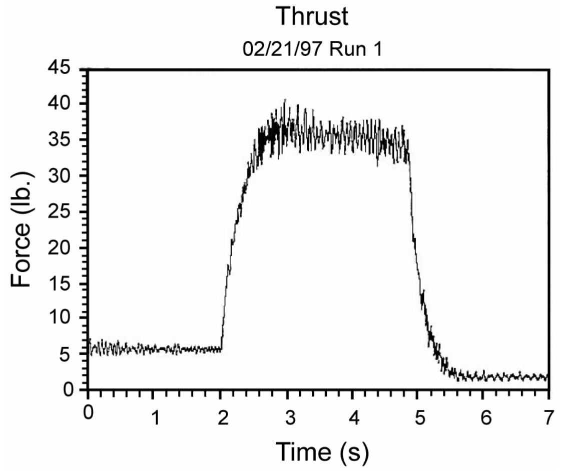


Figure 5. Plot of typical thrust data.

Experimental Matrix

A sequence of firings was designed to measure the thrust output of the rocket using the sensor system. HTPB cured with N100, the most well characterized fuel/curative formulation, was used in the fuel grains to produce a thrust vs. oxidizer flow curve. The fuel grains were made according to the methods already developed.[1,3,5] Oxidizer flow rate was varied from 0.04 to 0.12 lbm/s, in increments of 0.02 lbm/s. Two firings were performed at each flow rate.

At 0.06 lbm/s there were four firings to test the repeatability of the sensor.

Thrust Measurements

Changes in the hybrid rocket oxidizer flow rate will produce changes in the motor thrust, as will changing the diameter of the nozzle. The thrust sensor was sampled at 2 kHz. Figure 5 is a sample of the thrust vs. time data. Since the sensor was being proven, the diameter of the nozzle was not changed during the experiment, so effects from a change in nozzle size were not determined. The rocket produced a maximum of 41 lbf at 0.12 lbm/s flow rate. Figure 6 is the characteristic oxidizer flow rate curve for HTPB/N100, the values for the flow rate were calculated by the control computer[1,5] and thrust values were an average of the thrust produced during the steady state combustion (from 3 to 4.75 seconds).

Conclusions

Addition of the thrust transducer provided the thrust output of the Hybrid Rocket Facility motor for the first time. It showed that our rocket motor did produce a maximum of 41 lbf at 0.125 lbm/s oxidizer flow rate during this testing, verifying the design thrust max of 50 lbf.[1,5] The system, or variants thereof, can be used on small to medium hybrid motors, solid motors, and on certain liquid engine systems, depending on fuel/oxidant feed line and mounting considerations. The system can be scaled up by using mounting beams of a larger size to achieve higher thrust capacity, and should be usable to at least several hundred pounds thrust. Also, the system can be left in place over several weeks and remain calibrated, and so it is stable. For greater periods of time, re-calibration is suggested. Over a several month period, the bonding materials may decompose or soften, especially if the system is left in the elements. Since the actual strain gages are inexpensive, a new set can be bonded to the beams, renewing the measurements sensors when necessary.

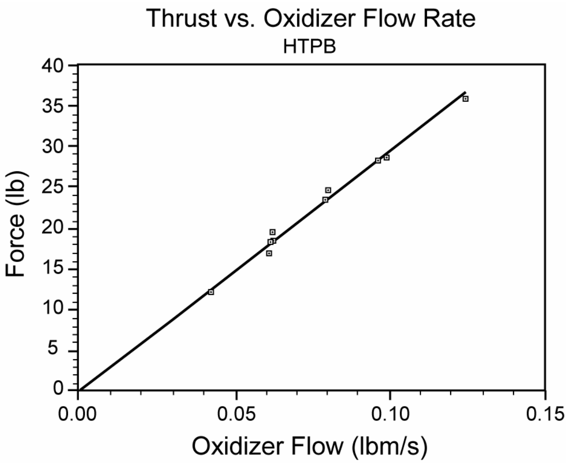


Figure 6. Plot of the thrust vs. oxidizer flow rate for HTPB.

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Articles accepted for publication in the *Journal of Pyrotechnics* can be on any technical subject in pyrotechnics. However, a strong preference will be given to articles reporting on research (conducted by professionals or serious individual experimenters) and to review articles (either at an advanced or tutorial level). Both long and short articles will be gladly accepted. Also, responsible letters commenting on past Journal articles will be published, along with responses by the authors.

All many body articles are peer reviewed by at least two technical editors. The author then has the final say about acceptance of reviewer suggestions.

Hypotheses Regarding “Star-Shell-Detonations”

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ABSTRACT

Fireworks star shells occasionally explode upon firing while they are still inside the mortar. Most often, this occurs with approximately the same level of violence as when the shell explodes after having left the mortar, and often even relatively weak mortars survive the experience intact. While unnerving to the firing crew, this represents relatively little hazard for crew or spectators. However, on rare occasion, the in-mortar star shell explosion achieves a level of violence substantially greater than normal. These more powerful explosions represent a potentially life-threatening hazard for both the firing crew and spectators. Unfortunately, the cause for these more violent explosions has not been established, and without knowing the cause, little can be done to prevent them from happening. In this article, two hypotheses are suggested as possible explanations for these dangerous malfunctions. Basic information and some empirical evidence are presented in support of two potential theories.

Keywords: aerial shell explosion, aerial shell malfunction, in-mortar explosion, flowerpot, star-shell-detonation, VIME

Preface

A large number of explanatory notes are included at the end of the text. These are indicated in the text using superscript letters. (Literature references are designated by superscript numerals.) Hopefully putting the supporting and supplemental information at the end of the article will make the text easier to read by allowing readers to skip this information if they wish.

Introduction

Occasionally upon firing, a fireworks aerial shell explodes while it is still within the mortar. Of course, when the shell in question is a salute (maroon), the result is always a powerful explosion, generally with the potential to fragment even a steel mortar. However, for star shells, the vast majority of in-mortar explosions produce the malfunction generally known in the US as a flowerpot. This results in a relatively mild explosion with an eruption of the burning contents of the shell projected upward from the mouth of the mortar. Typically, for small diameter, single-break shells the mortar remains intact and produces a display appearing much like a fireworks star mine. For large diameter, single-break star shells, depending on the strength of the mortar,[a] the display may again appear much like a normal star mine. (However, if a relatively weak mortar fails to withstand the explosive forces, a mortar failure may allow some of the burning stars to proceed in directions other than upward.)

For star shells, another more malevolent in-mortar explosive malfunction may occur, fortunately only on fairly rare occasions. In this case, the power of the explosion is much greater than that produced by a flowerpot, and most mortars will fail to withstand the explosive force, thus potentially producing dangerous mortar fragments. Traditionally, the accepted term for this malfunction is a *star-shell-detonation*. However, it is unlikely such explosions actually are detonations in the true high explosive sense. In recognition of this, some pyrotechnists are beginning to refer to this malfunction as a VIME (violent in-mortar explosion). In an attempt to be more generally correct, that usage has been adopted in this article. It is generally believed that the reason for the great power of these explosions is that most of the pyrotechnic content of the star shell is consumed in a much shorter span of time than is the case when the same type of shell flowerpots.[b] Because the shell's stars are apparently consumed in producing the explosion, they are not seen as a display being projected from the explosion.[c]

Some information in the literature[3,4] suggests that the cause of star shell flowerpots is the fairly catastrophic failure of the shell's casing upon firing, due to the reactive forces produced by the shell's rapid acceleration.[d] Unfortunately, however, little information suggesting the cause of VIMEs has appeared in the literature. There is the important suggestion by Brock,[6] based on research conducted in the late 19th century, that at least one cause for VIMEs was the result of using "badly made" ("crumbly") stars made with a chlorate oxidizer. The implication that chlorate-based stars contribute to the cause of VIMEs is consistent with much of the speculation regarding their cause even today. Potassium and barium chlorate oxidizers decompose exothermally, a property shared with explosives in general.[e] Further, potassium chlorate has been used to produce truly detonable explosives in simple combination with small percentages of organic fuels.[f]

In contrast to potassium and barium chlorate, the decomposition of potassium perchlorate is approximately energy neutral, and the decomposition of potassium, sodium, barium and strontium nitrate are all substantially endothermic.[7] Nonetheless, there have been anecdotally reported VIME incidents thought[g] to have been produced by shells containing stars made using potassium perchlorate, and still other incidents were thought to have involved stars made using a nitrate oxidizer with a metal fuel. Accordingly, while chlorates may make it somewhat more likely that a mild in-mortar explosion (flowerpot) may transition into a much more violent explosion (VIME), it would seem that the presence of a chlorate is not essential.

Another clue to a possible cause of VIMEs was revealed recently during the investigation following a serious fireworks accident. During the course of testing, the open burning of some large comets occasionally produced extremely powerful explosions.[10] These comet stars had previously been radiographed to confirm that they were composed of a single, substantially solid block of pyrotechnic composition (i.e., they did not contain internal explosive elements such as might be present in an intentionally exploding comet such as a crossette). The explosion of these comets while burning completely unconfined, and in particular the extreme violence of these explosions, was quite unexpected. While attempting to formulate an explanation for these observations, an additional possibility regarding possible causes of VIMEs was formulated. (A more complete accounting of the conditions and observations of this and other testing will be forthcoming in various reports and articles now in preparation.[10])

Two possible causes of VIMEs are presented below, along with brief supporting discussions. About 10 years ago, the necessary test equipment and rough protocol for testing the first of these hypotheses were developed; however, to date, time constraints and other research projects have prevented pursuing this project. In addition, current research interests make it unlikely that the causes of VIMEs will be studied in this laboratory in the near future. Accordingly, and in the hope that someone else may be encouraged to pursue such a study, this article was written.

Weak Star Collapse Hypothesis

Most commonly, the individual particles in a fireworks star composition adhere to one another as a result of a binder that has been activated by the addition of a suitable solvent.[h] As a practical matter, all fireworks stars contain void spaces between the individual grains of the components in the mixture.[i] Figure 1 illustrates the porosity of two typical fireworks stars. The upper micrograph is of a rolled spherical color star; below that is a pressed aluminum comet star. Even though the two stars are substantially different in both their composition and method of manufacture, note the grain structure and void spaces (dark recesses) in both.

If something were to happen that would suddenly collapse these void spaces, the gas within the spaces would increase in temperature as a result of the mostly adiabatic compression.[j] (This is the same process the causes the ignition of the fuel in the cylinder of a diesel

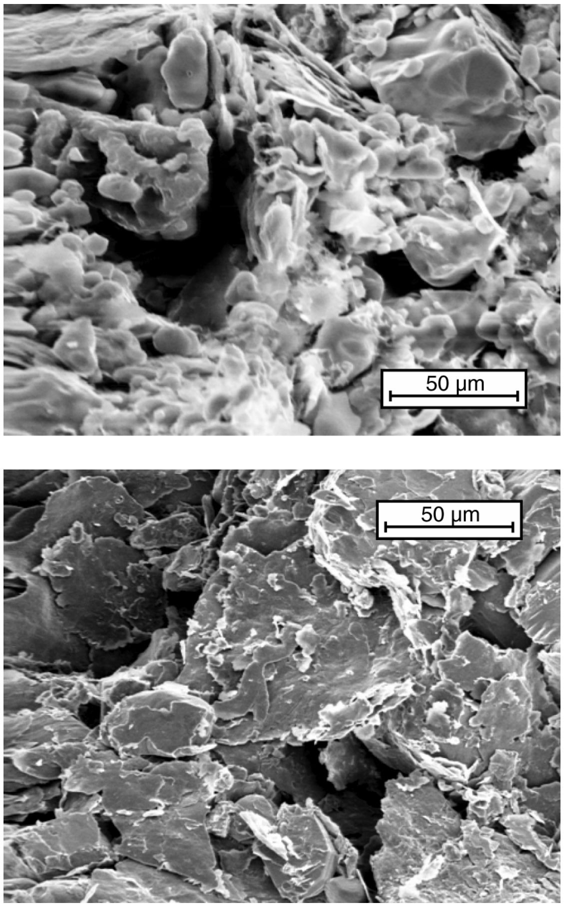


Figure 1. Electron micrograph of the internal structure of two substantially different firework stars. (Upper: rolled color star. Lower: pressed aluminum comet star.)

engine.) If the increase in gas temperature were great enough, it is possible for this high temperature gas (*local hot-spot*) to cause an ignition of at least some of the surrounding pyrotechnic material.[k]

During the collapse of the star, frictional forces (shear) could also contribute to thermal ignition as the grains of composition grind against each other. In addition, the penetration of burning gases from the lift charge, as the star is collapsing under the extreme pressure, must also contribute to the internal ignition of the star composition. In that way, the combination of adiabatic heating of void gas, plus the frictional heating from shear, plus the penetration of burning gas, might reasonably produce nearly simultaneous ignition of composition throughout much of the volume of the star.

When a star shell bursts (explodes) normally in the air, the peak internal pressure reaches a fairly high level before the casing fails and the contents are projected outward. However, based on the observation that most fireworks stars exit a bursting aerial shell in one piece, this peak pressure is obviously one that most well-made stars successfully withstand without being crushed.[l] If, instead, the shell explosion takes place within a mortar, the additional confinement provided by the mortar, must result in significantly greater pressure being produced within the exploding star shell. If this greater pressure is sufficient to cause the collapse of some of the stars in the shell, this might trigger a VIME. (This is the combined effect of the adiabatic heating of the gas in the pore-spaces, the frictional energy of the grains of composition grinding against one another, and the penetration of burning gases from the shell's burst charge into the interior of the stars.) As a result of the essentially simultaneous ignition of the entire mass of a few stars, the total pyrotechnic energy of those stars might then be released in a matter of milliseconds, instead of their normal several-second burn time. As a consequence of the additional, near instantaneous, release of energy from the collapse of a few stars, still greater pressures could result, which might then induce other stars to collapse, increasing the pressures even further, causing still more stars to collapse. In such a manner, essentially all of the stars in the shell might fail in a small fraction of a second, adding substantially to the power of the explosion, thus producing a VIME.

Weak Star Collapse Discussion

As explained above and in the notes, there is at least a theoretical basis to believe that the weak star collapse hypothesis could be one explanation for VIMEs. Further, the star collapse theory is consistent with Brock's observations about "crumbly" stars, along with anecdotal accounts of non-chlorate stars being capable of producing these powerful explosions. In considering the likelihood of an in-mortar star shell explosion producing a VIME, in addition to those things affecting a star's tendency to collapse, all of the other factors affecting pyrotechnic ignition and propagation must be considered. For example, ignition temperature, friction sensitiveness, heat of reaction, and the degree of acceleration of burn rate with pressure,[m] etc., all are expected to play a role in determining whether an in-mortar shell explosion will be a flowerpot or a VIME.

With the weak star collapse theory as background, a couple of related areas deserve a little more attention. One topic relates to voids. The size of voids is critical and is related to the impetus (applied pressure). This is because larger voids contain a greater mass of gas, thus offering the ability to produce and transfer more heat to the surrounding composition and in turn offering a greater potential for the internal hot-spot ignition of the collapsing star.[n] Larger voids also offer greater potential for frictional heating and ignition upon collapse. This is because, for a star with larger void spaces, there will be greater internal movement as the star collapses.

While the size of voids is a prime consideration, attention must also be directed toward the pressure acting to cause the star's collapse. With greater pressure, the amount of adiabatic heating, the shear forces, and the extent of penetration of burning gas from the burst charge will all be greater. Accordingly, smaller voids, under greater pressure, should produce similar results. In much the same way, the number of voids should be relevant, with a large number of voids offering a greater combined ability to produce and transfer heat. Accordingly, with both the size and number of voids as concerns, probably it is porosity (the percent void space) that is most important.

For cut stars, probably the amount of water present in the composition and the degree of consolidation of the *loaf* (block of moistened star composition) collectively play a role in determining the porosity of the stars. In this case excess water and poor consolidation would be expected to produce high porosity stars. For pressed stars, while the amount of moisture added must have an influence on porosity, the loading pressure (compacting force) is expected to have the greatest effect, with low loading pressure producing high porosity stars. For rolled stars, the amount of water used must be kept fairly low, to keep the stars from sticking together during their manufacture. Nonetheless, there is a range of moisture content that is possible and that should also result in a range of porosities. Further, the degree of consolidation of rolled stars seems to depend on the amount of water being used, the amount of star composition added in each layer of the star, and the amount of time the stars tumble between additions of composition.[o]

This star collapse hypothesis is based on the premise that the cause of VIMEs may be the result of sufficiently weak stars with sufficiently great porosity. Accordingly, another topic deserving discussion relates to the structural strength of stars. The crush strength of the star will depend on both the type and amount of binder, as well as the solvent, used. Obviously, when too little binder is used the star will be weak as a result of the individual particles not being well secured to one another. While the strength of the binder is important, and certainly not all binders are equally strong, there is little useful information in the pyrotechnic literature on this subject. Also the nature of the solvent used to activate the binder will affect star strength. For example, for water-soluble binders, sometimes a water and alcohol mixture is used to decrease the star drying time needed. However, while drying times are reduced, it is suspected that using a water and alcohol mixture may result in reduced structural strength of the star because of a reduced effectiveness of the binder.

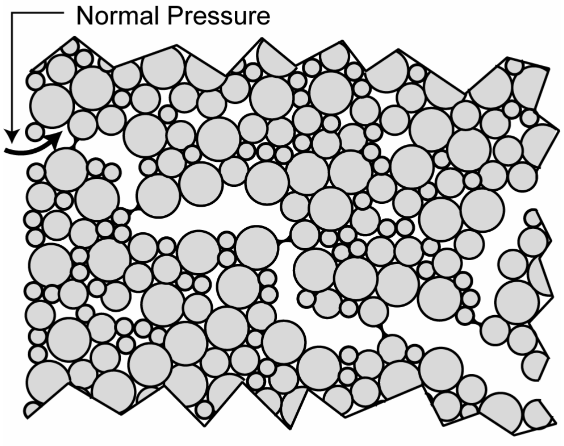
Strong Star Explosion Hypothesis

Imagine a situation where one has a fairly large star that is constructed such that the particles adhere to one another with great strength, producing a star that is quite hard and structurally very strong. In addition, assume that the star has features that under the right circumstances could produce fire paths to its interior. Such features might be the star having marginal permeability, such that its pore spaces are not sufficiently well connected to constitute effective fire paths to its interior when ignited under the pressures[l] experienced within a normally exploding aerial shell (i.e., when the shell is not exploding while still within a mortar). In that case, when the star is ignited on its exterior surface it will burn normally (non-explosively). However, if that same star is ignited during an in-mortar shell explosion, and if the greater pressures are now sufficient to force open the effective connection of the pre-existing void spaces, those void spaces could then become effective fire paths leading to the interior of the star. In that case, very quickly fire will race down the fire paths into the interior of the star producing ever increasing internal star pressure. Given the great structural strength of the star, the resulting internal burning might then be sufficient to cause the explosion of the star. Further the power of the star's explosion will be greater if the star composition is sufficiently fast burning or if it has a sufficiently large pressure exponent,[m] such that the gas pressure inside the star rapidly accelerates to catastrophic (explosive) levels.

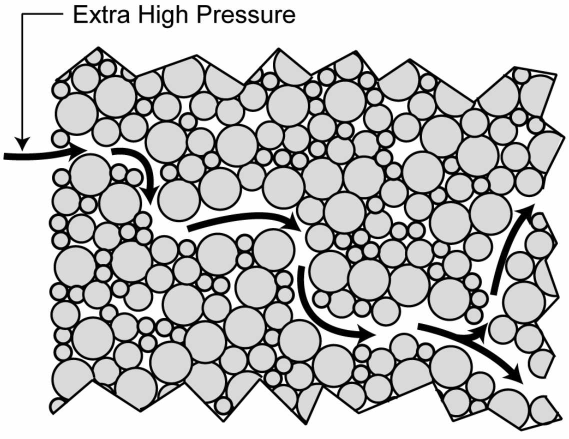
Strong Star Explosion Discussion

As explained above and in the notes, there is at least a theoretical basis to believe that the strong star explosion hypothesis might be another explanation for VIMEs. Further, this theory seems to be supported by some of the testing performed following a recent accident, wherein a number of incredibly violent comet star explosions were observed to occur during their unconfined burning.[10] A close examination of these comet stars revealed a level of porosity perhaps sufficient to be consistent with this strong star explosion theory. In addition, when properly functioning (non-explosive) comets were modified by drilling tiny channels into the center of the star, the star exploded violently upon ignition.

If the fire paths within a star such as described above are sufficiently well developed so as to allow the powerful explosion of the star when burning unconfined at one atmosphere, then it would surely do so under the conditions of a normal (not-in-the-mortar) shell explosion. Thus, it would not require the additional very high pressures that must occur during an in-mortar shell explosion, and it would not seem to be a potential explanation of VIMEs. However, if the degree of permeability is not sufficient under these normal shell explosion pressures but could become sufficient during an in-mortar shell explosion, then it remains a potentially viable explanation. There would seem to be at least two ways this might happen.



[Channel with Blockages]



[Channel Forced Open]

Figure 2. Illustration of a possible star interior that initially (upper) has its pores blocked by thin films of binder, but which are forced to open (lower) upon exposure to the very high pressures during an in-mortar shell explosion.

The first way would be if the connection between the pre-existing pores is marginally blocked, such as might be caused by a relatively thin film of binder at various points along the length of the channel, see Figure 2a. If that were the case, the pores might not function as fire paths under the normal shell functioning pressures. However, under the much higher in-mortar shell explosion pressures, these thin barriers to gas penetration might be breeched to then become connections (fire paths), see Figure 2b. If so, these stars could behave properly during normal shell explosions but might still be the cause of VIMEs. Note that this scenario becomes more likely as the pressure exponent of the composition increases towards unity. This is because there would be a rapid further increase in pressure inside the channels themselves. As a minimum, this could act to force even greater penetration of fire into the star. Further, in general, the higher the pressure exponent, the less pressure is required to initiate explosive burning.

The second way stars might have such a dual mode of functioning has to do with the effectiveness of fire paths as a function of their diameter. Shimizu reports that the effectiveness of fire paths is a maximum for some diameter, but decreases to approach a constant value for large diameter fire paths,[p] and decreases to zero as the diameter of the fire path approaches zero,[14] see Figure 3. Based on general physical principles, a developing pressure gradient accelerates flame propagation down a fire path. Accordingly, consider the case where pores are minimally connected via tiny paths so narrow that they are ineffective as fire paths at the normal shell explosion pressures. However, the same minimally connected pores might serve well as fire paths at the much higher in-mortar explosion pressures. Note that a similar argument might be made for stars that have microscopic cracks in them, perhaps produced during drying or curing.[q]

Conclusion

Fortunately, VIMEs are considerably less common than the substantially less explosive (and thus less dangerous) flowerpot malfunctions. Nonetheless, because they can produce such powerful explosions, apparently rivaling those from salutes and salute containing shells, VIMEs continue to be a serious display crew and public safety concern. It is hoped that this article will provoke further discussion of the causes of VIMEs possibly resulting in research to identify the actual causes of VIMEs.[r] Once the causes are determined, it should be possible for manufacturers to eliminate these most horrific of star shell malfunctions.[s]

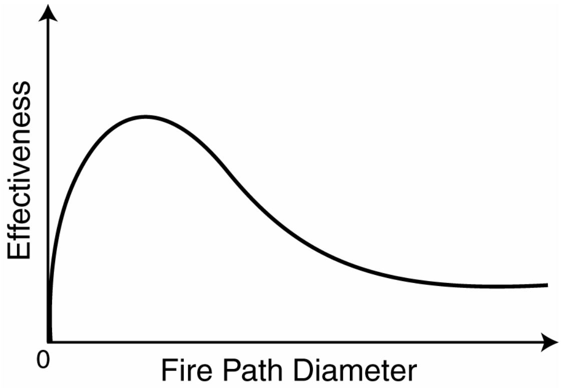


Figure 3. The effectiveness of fire paths as a function of diameter.[14]

Acknowledgments

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Notes

a) The pressure safety margin for many large diameter mortars is less than for small diameter mortars made of the same material. For example, the most commonly used 3-inch high density polyethylene (HDPE) mortars, firing typical spherical shells, have a pressure safety margin estimated to be perhaps as much as a factor of 16, whereas 12-inch (300 mm) HDPE mortars may have a pressure safety margin of no more than 2.[1]

b) Power is equal to the amount of energy produced during a time interval. Thus, if roughly the same energy is produced, but it is produced in a much shorter period of time, this corresponds to much greater power. For a flowerpot, much of the pyrotechnic energy is produced over a number of seconds as the stars continue to burn after the explosion. For a VIME, while the duration of explosion has not been measured, it appears to be on the order of no more than a few tens of milliseconds (and possibly only a very few milliseconds). Accordingly, if the same total amount of pyrotechnic energy is produced by both the flowerpot and the VIME, the power contributed by the stars in the VIME will be on the order of at least 100 times greater than that from the stars in a flowerpot. (Presumably, the power produced by the shell's burst and lift charges will be mostly unchanged.)

c) While it is generally assumed that all of the stars within a shell are consumed during a VIME, it is possible that some (many?) of the stars are not consumed, but rather are "blown blind" (i.e., traveling so fast that they are not capable of remaining ignited as they leave the area of the explosion).[2]

d) Calculations, based on simple physics and the measured pressures during the firing of aerial shells, indicate that the peak acceleration of a shell is approximately 1000 times the acceleration due to gravity.[5] Inertial forces in response to such high acceleration rates, produce large and unbalanced forces on the casings of aerial shells. These forces can produce a more or less complete failure of the shell casing.

e) The energy produced upon the decomposition of potassium and barium chlorate are 0.34 and 0.38 kJ/g, respectively.[7] The energy produced by the explosive decomposition of tritnitrotoluene (TNT) is 4.4 kJ/g.[8] Thus the decomposition of these chlorate oxidizers, on their own without any fuel, produce roughly 10 percent of the energy that is produced by a common high explosive.

f) The typical formulation of some of these chlorate explosives (called "Cheddites") was approximately 9 parts potassium or sodium chlorate and 1 part hydrocarbon (often paraffin), and they produced detonation velocities of approximately 3000 m/s.[9]

g) The reason for including the word "thought" is that rarely is one completely certain of the actual contents of an aerial shell. For example, often when an aerial shell malfunctions, it is not known with certainty what type of aerial shell was involved. Further, even when it is thought that the type if shell can be identified by recalling the identifying label, there is no guarantee as to the actual contents of the shell. That is to say, it is a common experience of those performing fireworks displays to find that Chinese shells have been incorrectly labeled (e.g., shells labeled as producing one color display are found to actually produce some other color display).

h) The most commonly used binder in the US is dextrin. It is present as approximately 5% of the star composition and is activated by the addition of water. The water dissolves the dextrin, which, upon drying, then holds together the other ingredient particles in the composition. However, the first hypothesis for VIMEs applies equally well to non-aqueous binders and to pressure activated plastic flow binders.

i) Based on measurements of typical fireworks stars, the density of a star may be approximately 1.6 g cm^{-3}, whereas its maximum theoretical density (MTD) might be 2.0 g cm^{-3}. This means that such a star has about 20% void space (porosity). Although not well reported in the literature, the average percent MTD of cut stars is probably the lowest for stars made using common manufacturing methods; while the MTD of rolled stars is somewhat greater. For pressed stars, the percent MTD probably ranges from as low as for cut stars to more than that for rolled stars, depending in how forcefully the stars are compressed.

j) The temperature of a gas heated by adiabatic compression is given by

$$T_2 = T_1 \left({}^{P_2}\!/_{P_1} \right)^{(\gamma-1)/\gamma}$$

where T is absolute temperature, P is pressure, γ is the heat capacity ratio for the gas ($\gamma \sim 1.4$ for air), and subscripts 1 and 2 refer to the initial and final states, respectively.[11] While this equation is most useful, it is only an approximation, in that it assumes the process of compression is thermodynamically reversible and that it is for an ideal gas.[12]

k) Based on the equation in Note j, compression from atmospheric pressure to about 10 atm is sufficient to raise the temperature of air to over 450 °C. While many star compositions would easily be ignited at this temperature, that is not to say that a small mass of gas could transfer sufficient heat to raise the much larger mass of surrounding star composition to this temperature. However, compressions ranging up to 50 to 100 atm should be capable of transferring sufficient heat to a few tiny particles of star composition to cause their ignition.

l) One published value for the peak pressure inside a hard breaking Japanese style spherical aerial shell is approximately 4 MPa[13] (about 600 psi). At this pressure, a fireworks star that was a one-centimeter (about 0.4-inch) cube would experience a force of 400 N (about 100 pounds) on each surface of the cube. Note that this is likely to be somewhat different from just squeezing a star on its two opposing sides with a 400 N force. It seems likely that a star pressed equally on all six sides at once is likely to be able to withstand a somewhat greater force than if that force is only applied to its two opposing sides. Consideration also needs to be given to the rapidity with which the gas pressure is applied and to the permeability of the star. If the pressure is increased somewhat gradually, over a sufficiently long interval, and the permeability of the star is sufficiently high, the externally applied pressure and that within the voids will more nearly have a chance to equalize, and the star is not likely collapse.

m) The burn rate equation (also called the Vieille equation) expresses the relationship between pyrotechnic burn rate and local pressure.

$$R = A\,P^b$$

where R is linear burn rate, P is the pressure in the vicinity of the burning surface, and typically A and b are approximately constant over a moderate range of pressures. (However, these "constants" themselves are commonly pressure dependent when considering a wide range of burning pressures.) Further, if b (the pressure exponent) is sufficiently large, the increase in burn rate with pressure will easily accelerate to catastrophic (explosive) levels, even under conditions of minimal confinement.

n) The volume, and thus the mass, of gas in a void space is proportional to the cube of the effective radius of the void. Whereas the mass of composition immediately surrounding the void is proportional to the square of its effective radius. Thus the ratio of gas to surrounding composition mass increases with increasing void size.

o) While measurements of rolled star porosity were not actually made, the statements about those factors affecting the porosity (density) of rolled stars is based on the authors' significant past experience manufacturing rolled stars.

p) For large diameter fire paths, the rate of flame propagation drops to the rate of propagation across a normally exposed surface.[14]

q) Some binders shrink upon setting. For example, based on recollections of work performed by the authors in the distant past, polyester resins typically shrink by about 6% upon curing. As a result, upon drying or curing some stars could possibly develop microscopic stress cracks. It would seem that the production of such stress cracks may be more likely to occur for large stars, with their larger dimensions and greater aggregate shrinkage. Further, for large stars there is a greater potential for differential drying to occur, wherein the exterior portions of the star dry (and shrink) before the center of the star dries. This too could introduce tiny cracks in those stars.

r) It is not intended to imply that the two hypotheses are necessarily mutually exclusive. It is possible that both could be occurring to some extent at the same time or at different stages of the same VIME. Also, it is certainly possible that there are other explanations of VIMEs that have not occurred to the authors at this time.

s) Experience suggests that fireworks mine effects experience VIMEs at least as frequently as do star shells. There is little reason to think that the mechanisms suggested for star shell VIMEs would not also apply to mines. On the one hand, the in-mortar pressures produced by normally functioning mine effects must certainly be less than the pressure within star shells functioning inside mortars (flowerpots). This potentially makes mine VIMEs less likely. However, all mines function within their mortars, whereas relatively few star shells flowerpot. This makes mine VIMEs more likely. The net result seems to be that mine and star shell VIMEs occur with roughly similar frequency.

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Speculation on the Explosive Decomposition of “Yellow Powder”

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Introduction

Attending a short-course in pyrotechnic chemistry provided the opportunity for the authors to study a little-understood historic explosive currently viewed primarily as a novelty and chemical curiosity. Part of the course was the preparation of a seminar. The instructors proposed the “yellow powder” seminar topic for the authors.

Yellow powder is a combination of potassium nitrate, potassium carbonate and sulfur. Alone, the combination of potassium nitrate (KNO_3) and sulfur (S) burns with difficulty. Potassium carbonate (K_2CO_3) is used as the main component in some dry chemical fire extinguishers. However, a melted and slightly cooked mixture of three parts KNO_3, two parts K_2CO_3 and one part S (sometimes called “yellow powder”) can react with great violence. The purpose of the following communication is to relate the authors’ experiences with “yellow powder”. An extensive on-line search was performed to supplement some information supplied by the instructors. Some (very limited) experimentation and additional research followed the initial literature research. Nonetheless, the course instructors suggested that the results of this brief study should be shared by preparing this article.

Historical Overview

Following are the principal historical developments of this seventeenth-century novelty labeled “yellow powder”:

1) “Yellow powder” behaves very similar to *aurum fulminans* (fulminating gold) and *aurum tonitruans* (thundering gold), well-known explosive substances. [1]
2) In at least two historical accounts of experiences with “yellow powder”, reference was made to placing the reactants on an iron surface (plate, bowl, shovel). [2,3] We were quite curious about the possible role of the iron surface on the chemistry. This curiosity will be elaborated in this paper.
3) The formation of “yellow powder” and its subsequent explosive nature was stated to be dependent upon proper heating. Rapid heating tended to result in the combustion of sulfur—forming SO_2—and the melting and eventual decomposition of potassium nitrate. Under-heating results in the slow sublimation and dissipation of the reactants eliminating the potential of any explosive reaction. Johann Rudolf Glauber,[4] a seventeenth century chemist, designed an apparatus for properly heating the reactants needed to make “yellow powder”. He also elaborated on the need for proper heating to produce the characteristic explosion.
4) In the eighteenth century Antoine Baumé proposed and showed that potassium polysulfide is an intermediate in the reaction by first reacting sulfur with potassium carbonate to produce potassium polysulfide. He also proposed that the precursor to the explosion was “nitrous sulfur”.[5]

Guiding Questions

Upon considering the historical development of this seventeenth century novelty, five important questions were formulated to help guide our efforts. Prior to addressing the questions, a sample of “yellow powder” was prepared by mixing 0.30 g of potassium nitrate, 0.20 g of anhydrous potassium carbonate, and 0.10 g of powdered sulfur together with a wooden stir-stick. Approximately 0.1 g of this mixture was placed on a metal spatula and heated gently with a propane torch. After several minutes, the evolution of a gas was noted, and the powder began to acquire a golden-brown color. Shortly after the gas evolution ceased, there was a rapid (1–2 seconds) change in color to a deeper shade of brown/gold. The mixture then exploded leaving virtually no residue.

Guiding Questions for this Study

1) Do polysulfides really form as intermediates?
2) Would the reasonably stable polysulfide intermediate explode when mixed with potassium nitrate and then properly heated?
3) Does an iron heating surface play a significant role in the chemistry?
4) Is "nitrous sulfur" the precursor to the explosion?
5) Can a sequence of equations be formulated to describe the process?

Experimental Results and Discussion

Do the Polysulfides Really Form as Intermediates?

In an attempt to produce one or more polysulfides, a mixture of potassium carbonate and sulfur were reacted; 0.10 g of sulfur and 0.20 g of anhydrous potassium carbonate were mixed together. Approximately 0.1 g of this mixture was placed on a metal spatula and heated gently with a propane torch. During the heating process, the melted mixture bubbled (probably CO_2 and trace amounts of other side reaction gases were produced) then the material turned reddish brown and crumbly when cooled. Upon referencing the *Merck Index*[6] and the *CRC Handbook of Chemistry and Physics*,[7] it seems most likely that the reddish brown solids were a mixture of K_2S_4 and K_2S_5. Thus, it was concluded that polysulfides form when potassium carbonate is heated with sulfur.

Would the Reasonably Stable Polysulfide Intermediates Explode When Mixed with Potassium Nitrate and Then Heated?

To 0.30 g of the previously prepared potassium polysulfide powder, 0.30 g of potassium nitrate was added and mixed. Approximately 0.1 g of this "yellow powder" mixture was placed on a metal spatula and heated gently with a propane torch. After melting and a brief period of continued heating of the polysulfide-potassium nitrate product, an explosion occurred. This further gives credence to the speculation that polysulfide intermediates were produced and that they are quite capable of producing an explosion when reacted with potassium nitrate. Subsequent literature research[8,9] supported the conclusion regarding the production of potassium polysulfide intermediates from the reaction of potassium carbonate with sulfur.

Does an Iron Heating Surface Play a Significant Role in the Chemistry?

A properly proportioned mixture of potassium carbonate, sulfur, and potassium nitrate was heated in a porcelain crucible behind a protective shield to determine if iron played a role. Upon heating, the reactants exploded. Thus it was concluded that iron does not play a significant role in the reaction chemistry.

Is "Nitrous Sulfur" the Precursor to the Explosion?

In responding to this question the following was also considered. Is the original reaction between potassium carbonate, sulfur, and potassium nitrate a combustion reaction using potassium nitrate as an oxidizer, or is the explosive reaction occurring via an alternate reaction? To answer this question it was proposed that potassium perchlorate be used as a potential oxidizer rather than potassium nitrate. (Note that in pyrotechnics potassium perchlorate is generally considered to be a more vigorous and powerful oxidizer than potassium nitrate.) When potassium perchlorate was substituted for potassium nitrate in a similar stoichiometric amount, a rapid combustion ensued, but there was no explosion. Accordingly, it was concluded that the nitrogen in the potassium nitrate probably does play an important role in the reaction.

Based on Baumé's suggestion of "nitrous sulfur" as an intermediate,[5] a preliminary search was conducted to identify sulfur nitride compounds that may be explosive and bear similar physical properties to the observed reaction intermediate. Initial descriptions found in the *Merck Index*[6] and the *CRC Handbook of Chemistry and Physics*[7] led us to conclude that the reaction most likely produced tetrasulfur tetranitride (S_4N_4) and disulfur dinitride (S_2N_2). This suspicion was further confirmed when more detailed descriptions of these compounds were located in several sources described below.

The first formally published synthesis and characterization of tetrasulfur tetranitride was done by Becke-Goehring[10] in 1960 utilizing sulfur(II) chloride and ammonia. Follow-up work by Villena-Blanco and Jolly[11] in 1967 provided additional information and observations regarding the properties of tetrasulfur tetranitride. Villena-Blanco and Jolly report that tetrasulfur tetranitride, which is "golden poppy" colored, is explosive and that the "sensitivity of S_4N_4 toward both shock and temperature increases with its purity".

Cotton and Wilkinson[12] describe tetrasulfur tetranitride as forming thermochromic crystals that range from orange-yellow at 25 °C to red above 100 °C. Tetrasulfur tetranitride has a square-planar molecular geometry containing alternating sulfur and nitrogen atoms. This highly stressed geometry could help account for its shock sensitivity and explosive nature. Cotton and Wilkinson caution that the compound must be handled with care since "grinding, percussion, friction, or rapid heating can cause it to explode". These statements are consistent with our observations during the induction period immediately preceding the explosion of "yellow powder".

Disulfur dinitride is also reported[12] to be stable in air, but is potentially explosive in response to shock, friction or heat, especially. Disulfur dinitride has a square-planar molecular geometry containing alternating sulfur and nitrogen atoms. Similar to tetrasulfur tetranitride, this highly stressed geometry helps account for its shock sensitivity and explosive nature.[13,14] Recent Raman and X-ray studies of tetrasulfur tetranitride and disulfur dinitride confirm the square-planar geometries, as well as the physical and chemical properties noted in the sources mentioned earlier.[8,14]

Can a Sequence of Equations Be Formulated To Describe the Process?

The **unbalanced** proposed equations are as follows:

1. Production of potassium polysulfides

$$K_2CO_3 + S \rightarrow K_2S_n + K_2O + CO_2$$

2. Production of nitrous sulfides

$$K_2S_n + KNO_3 \rightarrow S_4N_4 + S_2N_2 + K_2O + SO_2$$

3. Explosion

$$S_2N_2 + S_4N_4 + NO_3^- \rightarrow SO_2 + N_2$$

The above sequence was the consensus view of the authors; however, the following sequence was also considered as a possible alternative:

1. Production of potassium polysulfides

$$K_2CO_3 + S \rightarrow K_2S_n + SO_2 + CO_2$$

2. Production of carbon disulfide

$$K_2S_n + CO_2 \rightarrow CS_2 + SO_2$$

3. Production of nitrous sulfides

$$CS_2 + NO_3^- \rightarrow S_4N_4 + S_2N_2 + CO_2$$

4. Explosion

$$S_2N_2 + S_4N_4 + NO_3^- \rightarrow N_2 + SO_2$$

The above progression indicates a somewhat different involvement of the carbonate ion.

Conclusion

Due to the limited duration of the short course and very limited lab facilities, questions and instrumental confirmation of these proposed reactions remain speculations. The capture and analysis of the exit gases during the gentle heating, as well as after the explosion, may confirm the proposed reactions. Mass spectrometry, Raman spectroscopy, and ^{15}N NMR spectroscopy could help in distinguishing the components. An exhaustive search of the Chemical Abstracts Services database for articles pertaining to the explosive decomposition of the sulfur nitrides may also provide an insight to the reaction pathways suggested here.

It is hoped that this brief communication may spur additional interest in this phenomenon and potential clarification of the events that take place during the gentle heating of “yellow powder”.

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Bridgewire Temperature Estimation Using a Constant Current Supply

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Owens Crossroads, AL, 35763, USA

A brief description is presented of a means of measuring the *average* temperature of a bridgewire during firing using a constant current source.

Many functional tests of electroexplosive devices, such as electric matches, utilize a constant current power supply as part of the firing circuit, as this is the only way to comply with many specifications that call for functional testing to be done at a specified current. Frequently, if a constant voltage source is used, the change in resistance of the bridgewire during heating will put the current out of the specification tolerance. This is often the case when producing electroexplosive devices for the military and aerospace customers.

A simple constant current supply is shown in Figure 1. The operation of this circuit is as follows: When some reference voltage is supplied to the “+”, non-inverting, input of the operational amplifier, A1, a voltage is produced at A1-Eout; this voltage produces a current in fixed resistor R1. This produces a voltage, referenced to ground that is fed back to the “–”,

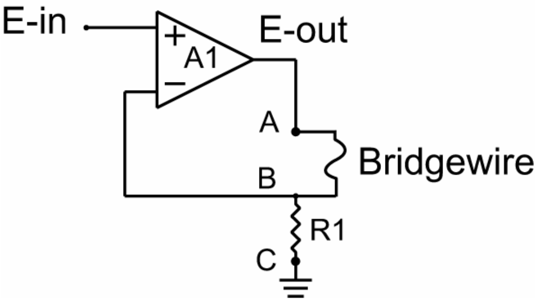

Figure 1. Basic constant current circuit.

inverting, input of A1. This "–" feedback input acts to maintain the output voltage, and thus current through R1, at a constant value. If the circuit and components are correct, the supply will accommodate a wide range of resistance in the bridgewire and still maintain a constant current through R1, and thus through the bridgewire. If the resistance of the bridgewire is not fixed but varies with temperature, the constant current supply must vary its output voltage to accommodate the total resistance of the load by maintaining a constant current through R1.

Figure 2 shows a more realistic circuit for bridgewire temperature measurements. Transistor Q1 serves to supply more current than would most operational amplifiers. Amplifiers A2 and A3 and their associated components will allow the nulling out of most of the testing voltage and then amplification of the portion of the voltage above the level that has been nulled out. Note that this circuit serves only to illustrate how these sorts of operations are performed. In the data presented, the author used a 12-bit digital oscilloscope, and a "simple" constant current supply. If, as an example, the voltage across the bridgwire had first been 1V, and then risen 6%, the range of the instrument would have to have accommodated approximately 1.06 volts. If some circuitry were to have been utilized that allowed nulling-out/subtracting the original 1 volt starting value, then the oscilloscope could have been set to accommodate only, perhaps, 0.1 volt. This would have allowed greater precision in the measurements taken.

Most materials used as resistors have some temperature coefficient associated with them. If they are made of the common "resistance" bridgewire alloys, such as the various platinum or Ni/Fe alloys, the resistance coefficient is positive. This results in the resistance of the bridgewire increasing as its temperature increases. Because the constant current supply depends on the resistance of R1, it is important that the resistance of R1 remain constant during testing. This may usually be accomplished by having the thermal mass of R1 be "large", or the temperature coefficient of resistance be very small. In practice, typically a 1 ohm, 10–20 watt power resistor will remain sufficiently constant during the occasional short and moderate amperage pulse used to function the typical hot bridgewire electroexplosive device, and it will provide a suitably stable feedback for the operational amplifier.

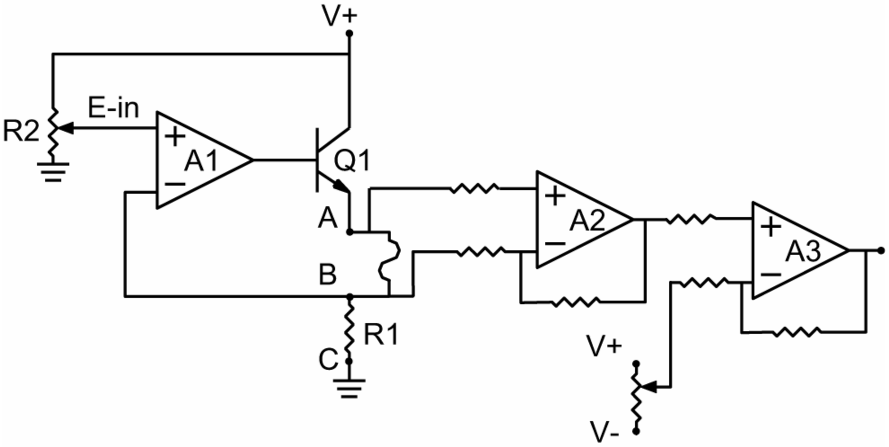

Figure 2. Example circuit showing high current, amplification, and nulling, capabilities

Because the resistance of R1 is constant and known, a voltage measurement from point B to point C can be used to calculate the current flowing in both R1 and the bridgewire. Similarly, a measurement of the voltage from point A to point B along with the known current allows one to calculate the resistance of the bridgewire. However, for the present purpose, using only the voltage will do, as it is proportional to the resistance of the bridgewire and therefore to the temperature of the bridgewire.

For most bridgewire materials, the resistance of the bridgewire is some reasonably smooth function of its temperature. Based on that fact, one can calculate the temperature of the bridgewire assuming the temperature prior to heating is known. The temperature will be determined from the ratio of the starting resistance (voltage) to the "final" resistance (voltage) plus the starting temperature.

Note that there are some potentially important factors that are extremely difficult to determine. There are, among others, thermal end effects, where the bridgewire loses heat to its contacts, and a possibly non-homogenous thermal environment caused by "bubbles" or non-uniform pressing, which may make the temperature change of any particular portion of the bridgewire difficult to determine with accuracy, since all that can actually be measured is the *total resistance change.*

Table 1 presents data for five electric matches taken near the beginning of the firing pulse and showing the voltage across the bridgewire. The first column shows the time, including some points prior to the onset of the firing pulse (shown as time 0.0000). The next five columns are voltages across the bridgewire for each of the matches. Then an average of these voltages is given, followed by the calculated temperature based on the average. The last column is the temperature smoothed using a Savitsky-Golay method. The temperature for each data point V_x is calculated by selecting the first low stable voltage reading (V_o) after the beginning of the firing pulse and before the bridgewire has heated significantly, then

$$T_x = T_0 + \left(\frac{V_x}{V_0} - 1 \right) \alpha$$

where, α is the temperature coefficient of the bridgewire material.

To avoid extreme artificial excursions caused by the smoothing algorithm, the values prior to V_o were set to ramp up to T_0 from zero. In data in Table 1, the time selected for V_o = 0.00006 (*), or 60 microseconds after the leading edge of the firing pulse which triggered the

Table 1. Data for Five Electric Matches Showing the Voltage across the Bridgewire.

Time s	Match 1 V	Match 2 V	Match 3 V	Match 4 V	Match 5 V	Average V	Temp. °C	Smoothed °C
–0.00004	–0.0002	–0.0000	–0.0000	–0.0001	–0.0000	–0.0001	0	1
–0.00002	–0.0002	–0.0000	–0.0000	–0.0001	–0.0000	–0.0001	0	3
0.00000	0.9773	0.0004	–0.0005	0.7679	0.6260	0.4742	5	6
0.00002	0.7618	0.8335	0.7659	0.7759	0.8085	0.7891	10	10
0.00004	0.7913	0.7859	0.7779	0.7959	0.8325	0.7967	15	14
0.00006*	0.7888	0.8074	0.7874	0.7919	0.8200	0.7991	20	19
0.00008	0.7868	0.8054	0.8014	0.7874	0.8145	0.7991	20	25
0.00010	0.7938	0.8019	0.7975	0.7914	0.8180	0.8005	32	28
0.00012	0.7968	0.7984	0.7919	0.7959	0.8225	0.8011	37	32
0.00014	0.7928	0.8035	0.7934	0.7939	0.8200	0.8007	33	35
0.00016	0.7913	0.8049	0.7984	0.7929	0.8200	0.8015	40	35
0.00018	0.7943	0.8014	0.7954	0.7924	0.8195	0.8006	33	37
0.00020	0.7928	0.8014	0.7944	0.7939	0.8200	0.8005	32	38
0.00022	0.7923	0.8059	0.7984	0.7949	0.8200	0.8023	47	39
0.00024	0.7958	0.8014	0.7954	0.7919	0.8215	0.8012	38	41

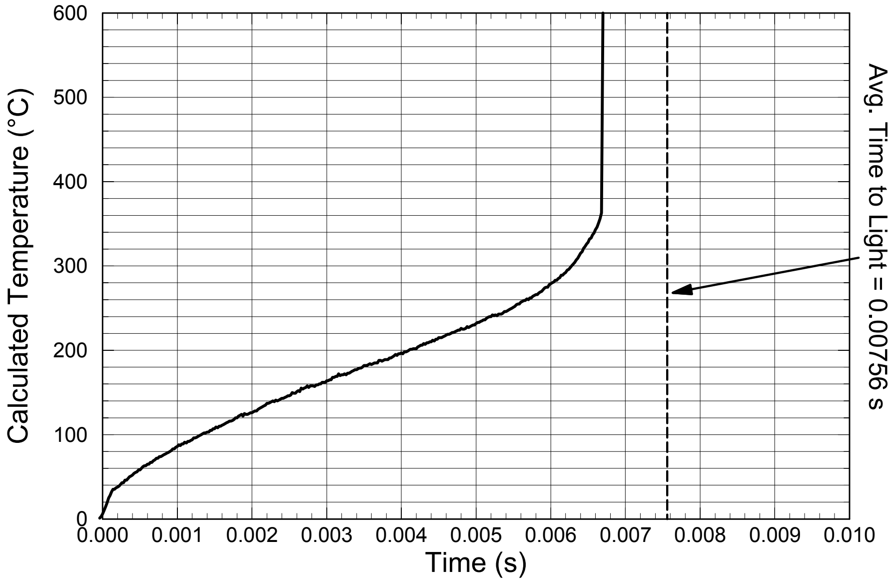

Figure 3. Test data for average of 5 electric matches.

oscilloscope to begin storing data (s = 0.0). T_o was selected by inspection of the unsmoothed average data prior to smoothing.

Tests 1 and 2 show the graphed results of tests using two different production lots of a potassium chlorate-based bridgewire composition. These lots differed, only slightly, in the method of application to the bridgewire.

In Test 1 (Figure 3), it appears that the thermal environment of the bridgewire was quite uniform and the composition adhered well to the wire. Notice that there is almost linear heating until about 275 °C when a change in slope occurs. This slope change may indicate either a decomposition of the nitrocellulose binder used or a thermal decoupling of the composition from the wire. At about 350 °C there is a very abrupt change in slope, which may indicate either a severe decoupling, or (fortuitously) the chlorate decomposition/reaction onset.

In Test 2 (Figure 4), the binder decomposition, or thermal decoupling, seems to begin at a somewhat lower temperature. There is a longer period of more rapid heating until about 425 °C and then another abrupt slope up.

Of course, in both cases, these are the present interpretations of the author and may not be necessarily correct.

The vertical dotted lines, in both figures, show the average time to light output indicating "function time" average for the electric matches as determined by a signal produced by a Schottky diode reacting to the light output from the match.

This general technique has also been used to determine the "goodness" of bridgewire attachment welds and to look for defects in the bridgewire, and is mandatory for some military and aerospace devices. In these cases, the stimulus is usually supplied in a short high current pulse, insufficient to cause firing, and the resultant heating causes an elongation and movement in the bridgewire which results in a "ragged" trace that may then be compared to known good traces.

One should not, at least under the test conditions used by the author, rely very much on the calculated temperature values being accurate. However, this general technique may prove useful in finding differences between items, and it adds another tool to the pyrotechnist investigators' armentarium.

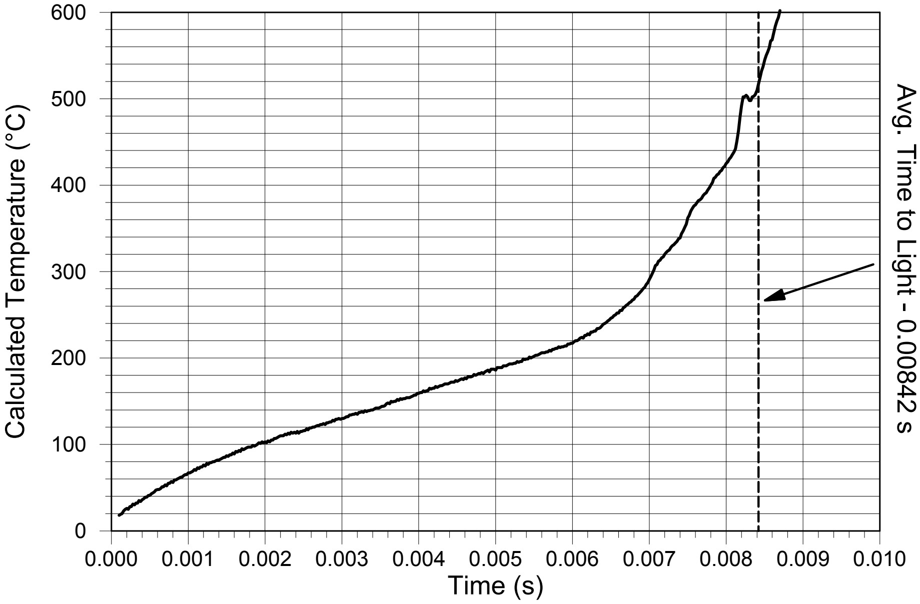

Figure 4. Test data for average of 10 electric matches.

An Observation Regarding: "Fireworks Shell Drift due to Shell-to-Bore Clearance"

K. L. Kosanke

ABSTRACT

Some empirical evidence is presented in support of a recent suggestion by R. K. Norton that a significant portion of aerial shell drift may simply be the result of shell-to-bore clearance. The support for this stems from the observation that aerial shells, during the very earliest portion of their free flight, were occasionally found to deviate from approximately 2.5 to 4 degrees from the axis of the mortar that fired them. At such an early stage in their flight, other possible mechanisms sometimes cited in an attempt to account for aerial shell drift (the magnus effect and other aerodynamic effects) cannot provide the explanation. However, Norton's suggestion regarding shell-to-bore clearance does provide a ready explanation for this observation. If the effect of shell-to-bore clearance operates during this early portion of a shell's flight, then certainly it will continue to play a major role in producing deviations from a shell's trajectory from the mortar's axis.

Keywords: aerial shell drift, shell clearance

Observation and Comment

Recently R. K. Norton suggested[1] that a significant fraction of aerial shell drift is probably due to simple bore balloting as a result of the clearance between the aerial shell and the inside mortar wall. This is quite consistent with an observation the author has occasionally made during testing to measure aerial shell muzzle velocities. In these tests, mortars were used that were specially configured with a pair of eight foot (2.44 m) rails extending upward from the mouth of the mortar and having a wide circular steel band at the top to stabilize the rails. Additionally, a series of trip wires were run between the rails at four locations along the length of the rails. (See Reference 2 for a photograph of one test mortar.) In these measurements, the shells' velocities were determined using timing circuits started by the ignition of the lift charge and stopped by the breaking of each of the series of the electrically conducting trip wires.

Occasionally during the course of testing, an aerial shell would fail to break the trip wire at the top, and on rare occasion, an aerial shell would strike the wide circular steel band at the very top. For this to happen requires a deflection of the aerial shell of at least 2.5 to 4 degrees, depending on the orientation of the cylindrical shell. That an aerial shell would deviate so far from the axis of the mortar tube, so early in its course, clearly seemed not to be attributable to magnus forces[3] or other aerodynamic forces.[4] There are two reasons for this. First, during this portion of the flight of the shell, it is still traveling upward in an escaping column of lift gases moving at approximately the same velocity as the shell. Accordingly, any aerodynamic forces on the shell at this time will be minimal, and these forces do not substantially increase until the rising aerial shell leaves the column of lift gases behind. Second, even if fully developed aerodynamic forces were operating at this time, the approximately 25 ms that it takes the shell to travel the first eight feet (2.44 m) is not sufficient to produce the necessary amount of lateral displacement. [To further demonstrate this point, assume aerodynamic forces could somehow produce the observed displacement during the first short portion of the shell's flight. If that were the case, then the total shell drift (displacement) manifested over the total flight time of aerial shells would be on the order of 100 times greater than observed experimentally.]

It is of interest to note that, under the conditions stated in his article,[1] Norton suggests maximum shell deflections in the range of approximately 2.5 to 5 degrees for aerial shells experiencing zero and one ballot (shell to mortar wall contact), respectively. Accordingly, the empirical observations made during the author's measurements of aerial shell muzzle velocity are quite consistent with Norton's shell-to-bore clearance explanation for at least a major portion of shell drift observed over the total flight path of an aerial shell.

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Review of

The Big Bang

A History of Explosives

George I. Brown

Sutton Publishing (1998, paperback 1999)
ISBN 0-7509-1878-0

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George Brown's *The Big Bang*, subtitled A History of Explosives is a good popular treatment of explosives from the ninth century AD to modern times. The first third of the book is taken up with gunpowder, starting with its obscure origins in China. In a section on rockets, Brown mentions the use of metallic colored-flame agents. Most of what he says is right, but calcium gives an orange and not a red color, and antimony sulphide (sic) is not the agent of choice for white. He ends this part of the book with a brief (one paragraph) treatment of modern firearms. Unfortunately, the importance of two major advances—recoil-operated machine guns and fixed ammunition (projectile, propellant, and primer in a single cartridge)—is not mentioned.

Brown goes on to discuss the use of gunpowder in mining and civil engineering, and tells the story of Davy's invention of the miner's safety lamp, usable even in explosive concentrations of 'fire-damp' (methane). He then talks about some early explosives based on chlorates, but with no mention of Sir William Armstrong and his deadly chlorate-phosphorus-sulfur mixtures. Another omission is flash powder, a material widely used to produce big bangs in fireworks. There is an account of other explosives based on liquid oxygen, as well as various mixes and slurries using ammonium nitrate.

The next sections of the book are on modern explosive materials and their development—nitroglycerin, dynamite, nitrocellulose, and similar nitration-based technologies. Brown discusses the two giants in the field, Alfred Nobel and Fritz Haber, both really tragic figures. Nobel hated guns and all things connected with war but developed the basic technology widely used in WWI and subsequent wars. He had much tragedy in his own life, including the death of his younger brother in the explosion of a Nobel nitroglycerin factory.

Haber invented the process for making ammonia from atmospheric nitrogen, for which he got the Nobel Prize in Chemistry in 1918. This 1909 work freed Germany from dependence on imported nitrates; without the Haber-Bosch process providing nitrate-based explosives and propellants Germany could not have continued with WWI, a great many lives would have been saved, and the course of history changed. Haber also provided the technology for Germany's WWI use of poison gas. He was forced to leave the country in 1933 when the Nazis rated hatred of Jews above his earlier services to Germany.

Brown then turns to guncotton, invented by Schonbein, and its major use in smokeless powder. Since smokeless powder had more energy than Black Powder, it permitted lighter ammunition and smaller-bore, lighter firearms. Nobel appears again with the invention of blasting gelatine in 1875.

The next chapter discusses Lyddite (trinitrophenol) and TNT. Brown tells the story of the naval battle at Jutland in which British shells filled with Lyddite exploded from shock on contact with steel plate, while German shells filled with TNT could be fused to explode after penetrating armor, and thus do more damage.

Brown's "Setting It Off" chapter discusses how explosives are successfully initiated. Here too Nobel leads the field. His invention of the multiple-explosive initiating device was probably more important than his invention of dynamite; blasting caps and military detonators using a multiple-explosive sequence are now widely and routinely used. There is discussion of the development of percussion caps, safety fuse, and detonating cord.

The last quarter of the book is devoted to nuclear explosives. Brown quotes Oppenheimer, the leader of the Manhattan Project to develop the fission bomb, who said of physicists, "We have blood on our hands". Alas, too true. The first use of this horrific technology was to kill and maim 280,000 men, women, and children at Hiroshima and Nagasaki; their only crime was to be in the wrong place at the wrong time

During most of the cold war the US and the USSR had many thousands thermonuclear weapons, and were prepared on a few minute's notice to kill tens of millions of civilians on 'the other side'. Brown tells the story of the extraordinarily talented scientists who brought these devices into existence, including Einstein, Fermi, Feynman, Oppenheimer, Sakharov, Szilard, and Teller. Some like Einstein, Szilard, and Sakharov came to understand the terrible implications of nuclear weapons and sought to mitigate the horrors; others, most notably Edward Teller and his protégé Lowell Wood, thought that thermonuclear devices could solve almost any military problem.

Brown's description of nuclear weapons technology is quite good. However, he omits what I believe are two significant matters. The first is the great importance of absolutely-simultaneous detonation of all the chemical explosive sections of an implosion-triggered fission device. This and other exacting technical requirements have made it (fortunately) quite difficult for nuclear wanna-be's to achieve a successful fission explosion.

The second of these matters is the Fission-Fusion-Fission bomb, in which the tamper that concentrates X-ray radiation from the fission device toward the fusion fuel is made of an inexpensive fissionable material like U238 or thorium. This technique can be used to build bombs of unlimited size rather cheaply. Unfortunately, these bombs also produce a large amount of fallout.

At the end of the book there are two appendices dealing with chemical and energetic details. The first is on Names and Formulae, and the second is on Energy and Power.

There is a two-page bibliography. It includes Urbanski's *Chemistry and Technology of Explosives*, but not Davis's *The Chemistry of Powder and Explosives*. Davis's work is older than Urbanski's, but it is still a useful reference.

Pyrotechnic aficionados may be disappointed that the only fireworks reference is to Plimpton's *Fireworks, a History and Celebration*. It might have been a good idea to include more practical and detailed works like Shimizu's *Fireworks, the Art, Science, and Technique*, Lancaster's *Fireworks Principles & Practice* and Perigrine's *Introductory Practical Pyrotechnics*.

There are numerous footnotes, and a complete index (always a blessing).

I think Brown has done an excellent job; the material is readily available to the non-technical reader, all the important facts and history are covered, more sophisticated readers will still learn something, and it is a good 'read' with many fascinating and often tragic stories.

Review of *Incendiary Art: The Representation of Fireworks in Early Modern Europe*

Kevin Salatino

Bibliographies & Dossiers, Getty Research Institute
for the History of Art and the Humanities (1999)
ISBN (0-8923-6417-3)

Jim Malek
3701 Westbrier Ter, Midland, MI, 48642, USA

This is a richly documented paperback book, one of the series called Bibliographies & Dossiers from the Getty Research Institute for the History of Art and the Humanities, documenting an exhibit held at the Institute in 1999. It contains 53 black and white engravings and 23 color plates, and the time period covered is from the late 1500s to the early 1800s, although the text itself is not chronological. This work is more concerned with the objects as pieces of art and their use as historical records, rather than using them to describe the fireworks themselves. Each of the figures is described in detail, with heavy emphasis on the political, social, and cultural meanings that are represented in the scene. Historical facts are presented, explaining why the displays were originally staged. Many of the details of the displays were obtained from written programs that were distributed to the audience so that they could fully appreciate both the significance of the production and the work involved.

The book consists of two sections; The Culture of Fireworks, and Fireworks and the Sublime. Unfortunately, these titles are as abstract as many of the descriptions themselves. The writing style is academic in the extreme. An example from the first few pages will illustrate the point:

> *The narrative and iconic strategies adopted by artists to illustrate fireworks constitute a kind of pictorial lexicon consisting of a highly heterogeneous vocabulary of idioms and dialects diverging morphologically according to time and place.*

The artists use a variety of techniques in an attempt to portray the event. In some cases, the entire display, which may have lasted for hours, is condensed into a single frame. Due to limitations of the time, most works were black and white engravings, with only a few color reproductions included. Not all of the referenced figures were produced by artists actually in attendance, as some were done for promotional purposes prior to the event. Others were reproduced long afterwards as “historical” records.

Thorough reading brings up some interesting points, some of which are as relevant today as they were in the 16th century. Expenses were a concern, even to the royalty that usually staged the shows, as several months of effort could be involved in constructing machines—the structure and stage of the display. Some pyrotechnicians put on demonstrations to perfect their techniques, but most of the displays were used to celebrate victories in war, using the obvious similarity of fireworks with warfare. Weddings, coronations, and royal birthdays were also occasions for celebration, where representations of volcanoes were common.

This is definitely not a casual read, but the enthusiasm of the author for his subject is evident, as in these statements near the end of the book:

> *We are left, in the end, with the images themselves, ironically static emblems of the perpetually disintegrating. And the visual records are, inevitably, no more than pale reflections of their subjects.*

Events Calendar

Pyrotechnics and Fireworks

4th Int'l Autumn Seminar on Propellants, Explosives and Pyrotechnics

Oct. 25–28 2001, Shaoxing, China

Contact: Dr. Chen Lang
Mechanics & Engineering Department
Beijing Institute of Technology
P O Box 327
Beijing 100081, China
FAX: +86-10-6891-1849
email: webmaster@iaspep.com.cn
web: www.iaspep.com.cn

28th Int'l Pyrotechnics Seminar

Nov. 4–9 2001, Adelaide, Australia

Contact: Ken Smit, 28th IPS Coordinator
DSTO, Bldg 307 EOP
PO Box 1500
Salisbury, SA 5108, Australia
Phone: +61-8-8259-6737
FAX: +61-8-8259-6585
e-mail: Adelaide.ips@dsto.defence.gov.au
web: www.intlpyro.org/IPS28/

6th Int'l Symposium on Fireworks

Dec. 3–7 2001, Orlando, FL, USA

Dawn Stewart
Canadian Explosives Research Laboratory
555 Booth St.
Ottawa, ON K1A 0G1, Canada
Phone: +1-613-995-1026
Fax +1-613-995-1230
email: dstewart@nrcan.gc.ca
web: fireworksfx.com/symposium.html

Western Winter Blast – 2002

Feb. 15–18, 2002, Lake Havasu, AZ, USA
Contact: Beckie Timohovich
Box 10116
Canoga Park, CA 91309, USA
Phone: +1-818-662-9721
FAX +1-818-662-9723
email: Beckie@pyro.org
web: www.wpa.pyrotechnics.org
Must be member to attend.

The Application of Pyrotechnic Principles

June 9–14 2 2002, Chestertown, MD, USA
Contact: John Conkling
PO Box 213
Chestertown, MD 21620, USA
Phone: +1-410-778-6825
FAX: +1-410-778-5013
email: John.Conkling@washcoll.edu
web: www.John.Conkling.washcoll.edu

29th Int'l Pyrotechnics Seminar
in conjunction with
6th Conference on Life Cycles of Energetic Material

July 14–19 2002, Westminster, CO, USA

Contact: Alita Roach, Coordinator
Los Alamos National Laboratory
MS P915
Los Alamos, NM 87545 USA
Phone: +1-505-665-6277
FAX: +1-505-665-3407
e-mail: alita@lanl.gov
web: www.intlpyro.org/IPS29.htm

Chemistry of Pyrotechnics & Explosives

July 28–Aug. 2 2002, Chestertown, MD, USA
Contact: John Conkling
PO Box 213
Chestertown, MD 21620, USA
Phone: +1-410-778-6825
FAX: +1-410-778-5013
email: John.Conkling@washcoll.edu
web: www.John.Conkling.washcoll.edu

Pyrotechnics Guild Int'l Convention

Aug. 3–9 2002, Fargo, ND, USA

Contact:, Ed Vanasek, Sec. Treas.
18021 Baseline Avenue
Jordan, MN 55352, USA
Phone: +1-952-492-2061
e-mail: edvanasek@aol.com
web: www.pgi.org
Must be member to attend.

Energetic Materials

Computational Mech. Assoc. Courses–2002

Contact: Computational Mechanics Associates
PO Box 11314,
Baltimore, MD 21239-0314, USA
Phone: +1-410-532-3260
FAX: +1-410-532-3261
web: www.compmechanics.com

1st Int'l High Energy Materials Society of India (HEMSI) Workshop

Nov. 27–29 2001, Birla Inst. Tech., Ranchi, India

Contact: Mohan Varma
Department of Space Engineering & Rocketry
Birla Institute of Technology
Mesra: 835 215, Ranchi, India
Phone: +91-651-275-983
FAX: +91-651-275-401
email: varma_mohan@hotmail.com
web: 1st International HEMSI Workshop/cnet.com

ISEE's 28th Annual Conference on Explosives and Blasting Technique

February 10-13, 2002

Contact: Lynn Mangol
Las Vegas, NV, USA
Phone: +1-440-349-4004

3rd Int'l Symp. on Heat Flow Calorimetry for Energetic Materials

9–11 April 2002, French Lick, IN, USA

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1st Int'l Symp. on Energetic Materials and their Application (ISEM 2002)

May 15–17 2002, Tokyo, Japan

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33rd Int'l Annual Conf. ICT "Energetic Materials – Synthesis, Production & Application"

June 25–28 2002, Karlsruhe, Germany

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20th Int'l Symp. on Ballistics

Sep. 23–27, 2002, Orlando, FL, USA

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13th Int'l Symp. on Chemical Problems Connected with the Stability of Explosives

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