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Bonnie Kosanke, Publisher
1775 Blair Road
Whitewater, CO 81527, USA
(970) 245-0692 (Voice and FAX)
email: bonnie@jpyro.com

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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Evaluation of the Hazards Posed by High Energy Bangers

Part 2. Damage to Hand Simulants

R. K. Wharton and A. E. Jeffcock
Health and Safety Laboratory, Harpur Hill, Buxton, Derbyshire, SK17 9JN, United Kingdom

ABSTRACT

This paper reports the development and construction of hand simulant models and their use to evaluate the extent of injury to persons holding, or being near to, high energy bangers when they are initiated.

The test work suggests a risk of severe injury to the hand and wrist from flashbangers containing more than 1 g of composition, with amputation of the hand being possible for the more powerful items examined.

Keywords: potassium perchlorate, barium nitrate, aluminium, flash composition, bangers, damage, firecracker, small salute

Introduction

A previous paper[1] reported details of the noise and overpressure generated when energetic bangers (large firecrackers or small salutes) are initiated, together with estimates of the TNT equivalence of barium nitrate/aluminium and potassium perchlorate/aluminium flash compositions.

In connection with evaluating the hazards associated with the use of such fireworks, a brief qualitative study was undertaken of the effects of powerful fireworks on simulated human hands. This short paper reports the method used to fabricate the model hands and the results obtained when they were used to assess the potential hazards to users posed by high energy bangers.

Experimental

Model Hand Construction

Model hands were constructed around plastic skeletal hands of the type supplied to medical schools.[2] The skeleton was encapsulated in a 25% gelatine/water gel to simulate flesh. Such a mixture has previously been used as a flesh simulant for ballistic wound studies.[3]

Moulds were made from the open palm and closed fist of an adult male, and these were used to cast the gelatine mix around the jointed plastic bones. The metal support wires that connected the plastic bones were left in place to simulate the muscles and tendons in the human hand.

The open palm version of the hand was made to determine the effect of a banger initiating in the open hand or on the fingers, whereas the closed fist hand was constructed to replicate the enclosure of a banger in the fist.

Figures 1 and 2 illustrate the construction of the open-palm and closed-fist model hands, respectively.

To improve the visual presentation of the gelatine, the model hands were sprayed with a flesh coloured paint producing samples with the final appearance of the example shown in the right of Figure 1. Additionally, as the tests were to be video recorded to provide evidence of the potential damage to human hands, the gelatine flesh simulant was dyed red to improve visualisation.

Table 1. Damage to the Model Hands from High Energy Bangers.

Banger Composition	NEC* (g)	Position on / in Hand	Damage
barium nitrate/ aluminium flash	1	open palm	Scorching, no structural damage
		open fingers	
		closed fist	Severe scorching, no structural damage
	10	open palm	Surface damage, damage to wrist due to flexing
		open fingers	Damage to structure of fingers, loss of end bone to one finger, loss of 'flesh' on fingers
		closed fist	Severe damage to structure of hand with multiple loss of fingers and severe 'flesh' loss
potassium perchlorate/ aluminium flash	0.5	open palm	Scorching, no structural damage
		open fingers	
		closed fist	Severe damage to structure of fingers with some 'flesh' loss
	5.0	open palm	Damage to structure of several fingers, loss of end bones on four fingers, loss of 'flesh' on fingers
		open fingers	Severe damage to fingers, loss of digits and flesh on fingers. Some damage to wrist due to flexing
		closed fist	Severe damage to structure of hand with multiple loss of fingers, bones of the palm and severe 'flesh' loss

*NEC = net explosive content

Test Programme

Tests were undertaken using barium nitrate/ aluminium flashbangers with 1 and 10 g loadings and potassium perchlorate/aluminium flashbangers with 0.5 and 5 g loadings.

The bangers were placed in three positions; on the open palm, on the fingers of the open hand and in a closed fist.

In the case of the closed fist, a gelatine sheet was wrapped around the bangers to ensure a close fit in the clenched fist.

Results and Discussion

The results from six tests with each banger type are summarised in Table 1.

To illustrate the differing extents of damage to the model hands produced by fireworks of different strengths, Figures 3 and 4 show the results from barium nitrate/aluminium flash composition and Figures 5 and 6 display the results of tests using potassium perchlorate/aluminium flash.

The range of damage found corresponded well with the findings from the pressure and noise measurements reported in an earlier study,[1] with the potassium perchlorate/aluminium bangers causing the most severe damage.

The damage to the hand simulants also showed a strong visual correlation to the sorts of damage to the human hand produced by fireworks, as reported by Nicolai and Van Twisk.[4] This suggests that the simulants may provide a viable means of assessing damage to the hands caused by the misuse of other small pyrotechnic devices or explosive articles.

Figure 2

Figure 1. Construction of skeletal hand simulant in open-palm version.

Figure 2. Plastic skeletal hand encapsulated in gelatine in closed-fist version.

Figure 3. The effect of a 10 g barium nitrate / aluminium flash composition banger initiated on the open fingers.

Figure 4. The effect of a 10 g barium nitrate / aluminium flash composition banger initiated in a closed fist.

Figure 5. The effect of a 5 g potassium perchlorate / aluminium flash composition banger initiated on the open fingers.

Figure 6. The effect of a 5 g potassium perchlorate / aluminium flash composition banger initiated in a closed fist.

Figure 3

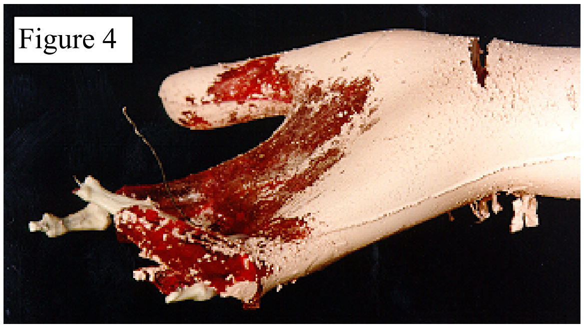

Figure 4

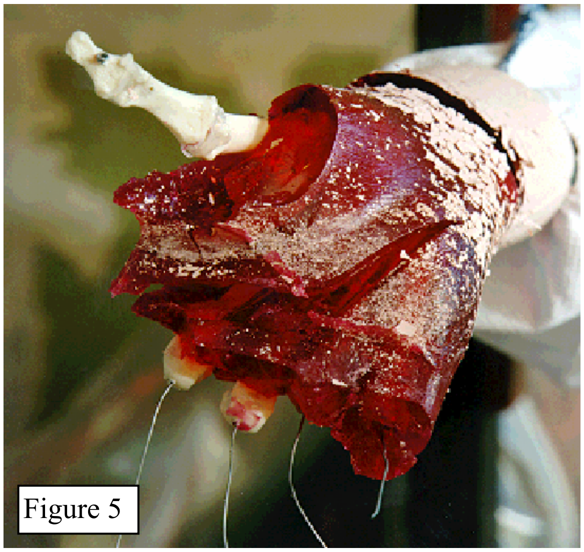

Figure 5

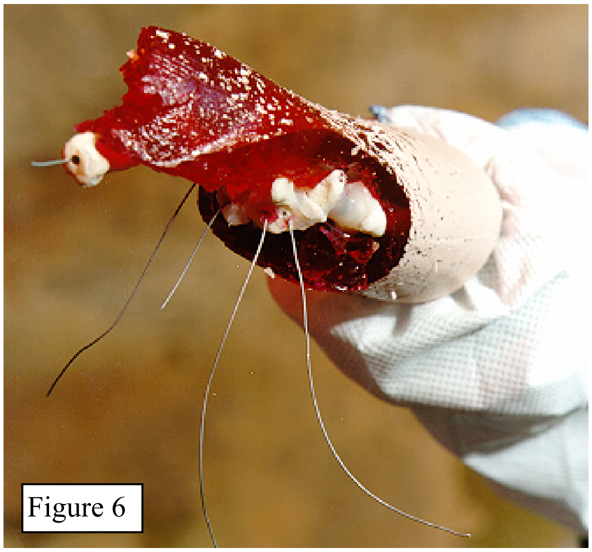

Figure 6

Conclusions

Test work using simulated hands suggests that the damage resulting from the misuse of bangers containing potassium perchlorate/aluminium flash composition is greater than that when the bangers contain barium nitrate/aluminium flash.

The damage found with bangers containing 10 g of the barium nitrate-based composition was approximately equivalent to that obtained with 5 g of the potassium perchlorate-based composition.

The good qualitative correlation between the results reported in this paper and literature data on actual injuries to the hand caused by fireworks suggests that the simulants may have wider application for assessing the effects on the human hand from the misuse of other small pyrotechnics and explosive articles.

Acknowledgement

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Thermodynamic Modeling of High-Temperature Systems

Gleb V. Belov
Glushko Thermocentre, IHED, IVTAN Assoc. of RAS, Izhorskaya 13/19, Moscow, 127412, Russian Federation
gbelov@imail.ru

ABSTRACT

An outline of thermodynamic modeling of high-temperature systems is presented, including a historical introduction. There is no intention to provide a complete history of thermodynamic modeling, so neither vapor-liquid equilibria nor the thermodynamics of non-ideal solutions is discussed. This article reflects the author's personal vision of the state of the art.

Keywords: thermodynamics, modeling, equilibria

Introduction

Methods of computational thermodynamics have been successfully used for the investigation of various processes, and for the development of new technologies for many years. There is no need to prove the practical value of the calculation of equilibrium composition and properties of thermodynamic systems. A number of examples illustrating how thermodynamic calculations may be used as a basic tool in the development and optimization of materials and processes are presented in the excellent book by Hack.[1]

Some fields of science and technology where thermodynamics works best are:

- development of the new high-temperature technological processes,
- the optimization of chemical processes, including synthesis of refractory materials and materials for microelectronics,
- examination of the stability of materials at high temperatures and in various media,
- investigation of the chemical processes occurring in power-generating facilities, including nuclear plants,
- the optimization of the use of raw materials,
- waste management,
- the study of the emissions of burning products and industrial exhaust gases into the atmosphere,
- development of processes to reduce environmental pollution, and
- investigation of the processes of mineral genesis, formation of the atmospheres of planets and of stars, as well as other geo- and astro-chemical processes.

Thermodynamic Modeling

The basic concept of thermodynamics is thermodynamic equilibrium. Thermodynamic equilibrium is some final state of a thermodynamic system isolated from the external medium (i.e., thermal, mechanical and chemical equilibrium exists at each point of the system and there are no flows). In practice, the requirement of isolation means that the processes leading to equilibrium occur faster than any changes on the system's boundaries (local equilibrium hypothesis). Such external changes include changes of pressure, temperature and chemical composition, etc. For example, when the thermodynamics of a combustion process is studied it is common to assume adiabatic conditions (i.e., heat losses are not taken into consideration). When the processes in a chemical reactor are modeled the common assumption is that the rates of chemical reactions are much higher than the velocity of flow, and consequently, that chemical equilibrium is reached while the part of flow is in the reactor. There is much evidence that the equilibrium model is valid for high temperature processes ($T > 1500$ K) or when there is sufficient time to reach equilibrium. Two extreme examples of equilibrium systems are combustion processes in a rocket engine chamber, where equilibrium is reached in approximately 0.00001 s, and some parts of the earth's crust where millions of years are required to reach equilibrium. On occasion, another, less restrictive, hypothesis is used, which assumes partial equilibrium in the system. According to this hypothesis, full chemical equilibrium cannot be reached because of the slow rates of several reactions, nonetheless it can be reached partially because other chemical reactions are sufficiently fast.

The most popular models for the investigation of high-temperature systems and processes are based on the hypothesis of an ideal system. These models assume that the behavior of the gas phase may be described by the ideal gas equation of state and that all mixtures in the system may be treated as ideal. However there are many thermodynamic systems that cannot be adequately described by ideal models. Examples include combustion processes in a closed volume, detonation processes, many metallurgical processes, and so on. To investigate such processes the researcher should use more realistic thermodynamic models that take into account intermolecular forces and other physico-chemical effects in gaseous and condensed phases. Unlike the universal ideal model, most non-ideal models may be applied only for the investigation of specific systems in a narrow range of pressures and temperatures. The main problems are the parameters of the model and the range of application. In some cases it is possible to find relatively universal non-ideal models. An example would be the calculation of equilibrium composition and properties of combustion products at moderately high pressure (up to 600 MPa) using real gas equations of state.[2] A literature review shows that progress in thermodynamic modeling now depends mostly on the development of new, more realistic models that are well-founded theoretically, and ways of obtaining the parameters needed for these models.

The components of a thermodynamic model are:

- two thermodynamic parameters and their values that specify thermodynamic equilibrium;
- a list of chemical elements and their amount in the system;
- a list of the substances that make up the system;
- the thermodynamic properties of those substances;
- equations of state of the phases, and, primarily, the equation of state of the gas phase;
- distribution of substances among possible phases, and the possible existence of condensed phase solutions;
- assumptions concerning the behavior of the condensed solutions if there are any (models of solutions with their parameters); and
- additional constraints that restrict the assumption of equilibrium.

The results of modeling depend on many parameters. Software for thermodynamic modeling is now usually supplied with a database of thermodynamic properties of substances. The list of substances included in the system is determined mostly by the content of the corresponding database. The question of the quality of thermodynamic data is often not taken into account. However, variation of the heat of formation of a substance in the system may have a significant effect on the results of calculations. There is very often some conflict between the number of substances that can be included in the system and the quality of the data available for their thermodynamic properties. One can say that it is equally unreasonable to use either too small a list of substances with reliable thermodynamic properties, or an extensive list of substances with unreliable properties.

Often the question arises—can we believe the results of modeling? There is no definite answer to this question.

The best way to address the question is to compare the results of the calculations with experimental data where possible. The researcher should have answers to the following questions:

- Is there thermodynamic equilibrium in the system under examination?
- Are the components used in the model valid?

Sometimes the specific behavior of the system caused by the *chemical kinetics* of the processes can be taken into account by the exclusion of some substances from the system if one knows from experiment or theory that these substances cannot be formed. Another possibility is the assignment of concentrations for one or several substances, if that can be justified.

One may conclude that thermodynamic modeling is simultaneously a science and an art. The researcher should have a "feel" for the system that he or she is investigating.

Historical

The famous study by Gibbs[3,4] in the 1870s provided the theoretical background for thermodynamic examination of complex chemically reacting systems. Lewis and Randall's remarkable book,[5] published in 1923, provided the bridge from theory to practice, but until the development of digital computers there were no really appropriate instruments for thermodynamic modeling. Brinkley and Kandiner[6,7] developed one of the first algorithms for the calculation of equilibrium composition. The algorithm described by these authors used equilibrium constants. White et al.[8] introduced another algorithm, based on the minimization of the Gibbs free energy, in 1958.

Zeleznik et al.[9] at NASA developed the first "industrial" computer program, supplied with a database of thermodynamic properties of substances. A similar program was also developed in Russia.[10]

The intensive development of thermodynamic modeling was driven by the need to produce better rocket engines. It would have been impossible to create modern rocket engines without preliminary theoretical investigations of the combustion processes and of the expansion of the combustion products, where hundreds of simultaneous chemical reactions occur.

The next stage in the development of thermodynamic modeling is linked with metallurgy. Traditional metallurgical chemistry was based on investigation of the leading (or dominant) reactions. This approach is very unreliable, as variation of parameters such as the temperature, pressure, or composition of the reacting system often changes the dominant reactions. As a result, computational thermodynamics appeared helpful for the examination of metallurgical processes.[11–13]

The book by Siniarev et al.[13] contains FORTRAN source codes of a powerful computer program for the calculation of complex chemical equilibrium, developed by Trusov (Bauman Moscow State Technical University). Today, there are hundreds of algorithms and computer programs intended for the calculation of equilibrium composition of thermodynamic systems. Detailed reviews have been presented in various books.[14–16]

Smith and Missen's book[16] also contains FORTRAN and BASIC source codes for the calculation of complex chemical equilibria.

There are several reasons for the existence of so many algorithms. The most significant is the great variety of thermodynamic systems, ranging from combustion processes to the processes in the earth's crust. Parameters of most thermodynamic models are known only for a small group of substances. The situation is complicated by the fact that the relationship between the equilibrium composition and the parameters of the model is non-linear. The phase composition of the equilibrium system is usually unknown *a priori* and must be found during the calculation. Hence the target function is not continuous but can have disruptions at the phase transition points, which causes some difficulty in solving the problem. One should also take into account the limitations of the computer, which can accomplish calculations only with a limited number of significant digits. Therefore, even if mathematics guarantees the solution for some algorithm, the computer version of that algorithm will fail in some cases. Besides, as noted by McKinnon and Mongeau,[17] the phase and chemical equilibrium problem is atypical of many optimization problems. The aim is not so much to obtain a solution with an objective value that is close enough to the optimal objective value, as is usually the case when the objective function has an economic interpretation. Rather, the aim is to find a solution sufficiently close to the optimal solution that the phase and chemical composition correspond to the equilibria found in nature.

Calculation of the equilibrium composition of the system may be accomplished through the solution of a set of the non-linear equations. The questions of existence and uniqueness of the solution are reviewed in many literature sources.[16] It is shown that if the gas phase behavior is described by the ideal gas equation of state and the condensed mixtures are ideal, the target function is convex and a unique solution usually exists. However, this is not so in the general case when non-ideal models are used in calculations.

Thermodynamic and Thermochemical Properties of Individual Substances

The basis of any serious computer system intended to accomplish thermodynamic modeling is a database of thermodynamic properties of individual substances. The main sources of this information are reference books.[18–20]

Belov et al.[21,22] discuss the problems concerning the quality of thermodynamic data. These references also contain information about other sources of data.

IVTANTHERMO for Windows

Over many years researchers at the Thermocenter of the Russian Academy of Science performed a theoretical study of thermodynamic properties of individual substances and compiled this information in the form of a reference book and a database called IVTANTHERMO. This information is intended for practitioners of various branches of science and engineering, and it must be delivered to them in a practical and easy-to-handle form.

The most important characteristic feature of IVTANTHERMO is that the stored information is not borrowed from any other databases or reference books but was obtained by critical analysis and treatment of original data available in the primary literature. Information analysis and all necessary calculations have been performed with the use of original methods, algorithms and software developed for the *Thermodynamic Properties of Individual Substances* handbook[18] and brought up to date by its authors for the IVTANTHERMO database. Presently the database contains information on approximately 2500 substances, formed by 96 chemical elements.

The software package IVTANTHERMO has been developed to enable researchers and engineers to investigate a wide range of thermodynamic systems. Recently a new version of the software appeared, which consists of six programs and the database of thermodynamic properties of individual substances. The software has an intelligent interface, which does not require the user to have special computer knowledge. All six programs with the database represent one software suite—IVTANTHERMO for Windows. These programs are:

THERBASE provides access to all information about substances stored in the database: substance formula and name, heat of dissociation or sublimation for each substance, standard enthalpy of formation, heat capacity, entropy and enthalpy in standard state, nuclear spin, and coefficients of the approximating polynomials for the thermodynamic properties. It allows the user to review the contents of the database, extract information about substances, modify this information, add new information, examine thermodynamic properties of chemical reactions, and to carry out a quick search for a given substance or group of substances. THERBASE can display information as TPIS and JANAF tables, save it into a text file and display it as charts.

EQUICALC allows the calculation of the equilibrium composition and related thermodynamic properties of complex chemically reacting systems. EQUICALC can handle simultaneously up to 700 substances, up to 60 single-component phases and one or two condensed mixtures along with the gas phase. A new algorithm of the calculation of equilibrium parameters has been developed specially for the Windows version. EQUICALC can also display the results of calculations as charts or extract some of them into the table. Not only does the program accomplish the traditional calculations for assigned pressure or volume and temperature values, but it can also handle assigned values of (*p*, *H*), (*p*, *S*), (*U*, *V*), (*S*, *V*), etc. It permits the determination of the composition of combustion products at constant pressure or volume even if the gas phase is absent.

DATANAL is a tool for statistical analysis of the data stored in the database. It may help to elicit correlations among thermodynamic properties of substances stored in the database. It is known that some interdependence exists among chemical and physical properties of substances. However, the laws of this interdependence are not yet well investigated. DATANAL can help to estimate some unknown properties, or verify existing ones, by examination of the information stored in the database.

HB allows the computation of heat, material and temperature balances between given sets of the source components and reaction products, provided that the temperature and quantity of each input and output component is known.

APPROX is intended for the calculation of the coefficients of an approximating polynomial for a given set of heat capacity and temperature values, provided the values of thermodynamic parameters in the reference state and the heats of the phase transitions are known. Results of calculations may be saved into a text (ASCII) file or written into the IVTANTHERMO database. It is possible also to 'construct' a polynomial different from that adopted in IVTANTHERMO and calculate its coefficients. One can say that this program is a complement for THERBASE.

REPORTER is a service tool that allows the user to view the text files and print them.

More detailed information about IVTANTHERMO for Windows may be found in references 23 and 24.

Thermodynamic Data and Thermodynamic Property Calculation Sites on the Web

The growth of the Internet and the World Wide Web marks a new stage in the development of thermodynamic modeling. One can now use remote computers for the calculations. However, stand-alone computers still have their place, and it is more convenient to have one's own software on the table.

Listed below are references to some interesting internet sites where thermodynamic and thermochemical information can be found. Inevitably, the list is incomplete and contains only those references that the author has managed to find. The brief descriptions are borrowed from the original sites.

Chemical WorkBench[25] is a simulation software tool intended for modeling, optimization and design of a wide range of industrially, environmentally or educationally important chemistry loaded processes, reactors and technologies. The software package is a chemistry-centered, desktop simulation environment for detailed, user-friendly, complete-cycle physicochemical modeling of the chemically related processes, reactors and technologies. Chemical WorkBench is a well-furnished suite of software tools that enables researchers and engineers to model the "virtual prototypes" of chemically active systems and to simulate their operation behavior before detailed engineering and physical prototyping. Its most attractive feature is the possibility to simulate a complicated process by means of chains of reactors, each of which models some defined part of the process. There are not only ideal and non-ideal equilibrium thermodynamic reactors available, but also non-equilibrium reactors that take into account chemical kinetics, such as plug-flow reactor, calorimetric bomb, well-stirred reactor, etc. The researcher can combine these reactors on the virtual workbench, define links among them, set input species and parameters, accomplish calculations and visualize the results of modeling.

NIST WebBook provides access to thermochemical data for over 6000 organic and small inorganic compounds,[26] enthalpy of formation, enthalpy of combustion, heat capacity, entropy, phase transition enthalpies and temperatures, and vapor pressure; reaction thermochemistry data for over 9000 reactions: enthalpy of reaction and free energy of reaction. You can search for data on specific compounds in the Chemistry NIST WebBook based on name, chemical formula, CAS registry number, molecular weight or chemical structure.

CEA[27] is the famous NASA program that calculates chemical equilibrium product concentrations from any set of reactants and determines thermodynamic and transport properties for the product mixture. Built-in applications include calculation of theoretical rocket performance, Chapman-Jouguet detonation parameters, shock tube parameters, and combustion properties. Associated with the program are independent databases with transport and thermodynamic properties of individual species. Over 1900 species are contained in the thermodynamic database.

MTDATA[28] is a software / data package for the calculation of phase equilibrium in multicomponent multiphase systems using, as a basis, critically assessed thermodynamic data. It has numerous applications in the fields of metallurgy, chemistry, materials science, and geochemistry depending on the data available. Problems of mixed character can be handled, for example equilibrium involving the interaction between liquid and solid alloys and matte, slag and gas phases. The thermodynamic models necessary to describe the properties of a wide range of phase types are incorporated in the software and database structures.

MALT2[29] is a comprehensive *ma*terials-oriented *l*ittle *t*hermodynamic database for personal computers. The task group of the thermodynamic database was organized in the Japan Society of Calorimetry and Thermal Analysis. MALT2 stores thermodynamic data such as the standard enthalpy change for formation, ΔH_f (298.15 K), the standard Gibbs energy change for formation, ΔG_f (298.15 K), the standard entropy, S(298.15 K), the heat capacity, C_p, and the transition temperature and the enthalpy change for transition, if any, for approximately 5000 species. This covers those compounds important to ceramic materials, semiconductors, inorganic / organic gases for plasma processes in semiconductors, transition metal oxides, nuclear fuels, nuclear reactor materials, etc. From such stored data, the thermodynamic tables and the equilibrium constants at any temperature can be calculated. In addition, molecular mass, coefficient of heat capacity equation, and references for data can be also available.

HSC Chemistry[30] was produced by Outokumpu Research Oy. However, many of the important calculation options are based on code and ideas from other sources. The aim of this software is to simulate chemical reaction equilibrium and processes in the personal computer, to develop new processes, and to improve old ones. HSC Database is a compiled database on thermodynamic properties of individual substances. The number of species in the database is more than 15,000.

These data are not critically evaluated, but the database gives fast access to data and provides references to the literature. The database also has fields for structural formula, chemical name, common name, CAS number, melting point, boiling point, color and solubility in water. The data in these fields are not yet complete but even now they can help, for example, to identify organic substances.

EQS4WIN[31] is a powerful and easy-to-use software package that solves a wide range of problems related to the calculation of the reaction and phase equilibrium composition of complex chemical systems. EQS4WIN incorporates up-to-date technology in numerical analysis, programming, and thermodynamics. It was written under the supervision of Smith, senior author of a classic text in the field (see reference 16). EQS4WIN solves equilibrium problems by minimizing the overall Gibbs free energy of systems involving up to 4 multi-species ideal-solution phases (a gas phase and up to 3 condensed liquid or solid solutions) and any number of pure (condensed) phases. Calculations can be performed for several different types of thermodynamic conditions, either at a single state point, or for up to two simultaneously varying parameters. All versions of EQS4WIN incorporate a thermochemical database based on the species listed in the JANAF Tables.

Thermo-Calc[32] is a software package for equilibrium and phase diagram calculations. It can be applied to any thermodynamic system in the fields of chemistry, metallurgy, material science, alloy development, geochemistry, semiconductors, etc. depending on the kind of database it is connected to. It can also be used as a subroutine package in application programs, for example in phase transformation or process simulations. Thermo-Calc consists of modules for the various tasks the user may wish to perform. There are modules for the selection of database and data, for listing thermodynamic data or interactive manipulation and entering of such data. The most important module for equilibrium calculation together with its post processor makes it possible to calculate and plot diagrams of many different types on all kinds of devices. A useful facility in Thermo-Calc is the module for assessment of experimental data in terms of thermodynamic models. There is also a module for tabulation of data for substances or chemical reactions. The user may also develop and add their own modules by using a documented software interface. With Thermo-Calc one may simulate processes where the time-dependence can be ignored, for example by stepwise calculation of a sequence of equilibria with transfer of heat and matter between the equilibria.

F*A*C*T, which stands for Facility for the Analysis of Chemical Thermodynamics, is a fully integrated thermochemical database that couples software for thermodynamic modeling with critically assessed thermodynamic data. Originally developed as a research tool for chemical metallurgists, F*A*C*T is now employed in many diverse fields of chemical thermodynamics by chemical engineers, corrosion engineers, organic chemists, geochemists, ceramists, electrochemists, etc. Information about F*A*C*T databases as well as many references to similar web sites in inorganic chemical thermodynamics may be found at reference 33.

FactSage is an amalgam of two older programs—ChemSage (GTT Technologies) and FACT-Win (Thermfact). Decades of calculations by hundreds of corporate and academic users have led to a reliable tool that quickly converges to the correct equilibrium state. FactSage includes many non-ideal solution models. These models can be used to describe non-ideal gases, brines, alloys, salts, slags, mattes, alloys, and non-stoichiometric solids. FactSage solution models cover temperatures up to 6,000 K and pressures up to 1 Mbar. FactSage includes pure substance / solution databases from either F*A*C*T or SGTE (Scientific Group Thermodata Europe).[34] Each includes data for over 3,300 pure compounds. The F*A*C*T Solution Database is strong on inorganic oxides, sulfides and salts. The strength of the SGTE Solution Database is metals and alloys. Hundreds of custom databases prepared originally for ChemSage are also available. Custom files to meet specific needs can be supplied. The contents can be searched in detail on the GTT Technologies web site.[35]

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Test Burn of a Temporary Fireworks Stand

David Lynam

Clark County (WA.) Fire Marshal, 505 NW 179th St., Ridgefield, Washington, 98642, USA

This article is based on a report prepared by the Clark County, WA Fire Marshal documenting and discussing the results of a test fire involving a stocked temporary retail fireworks stand. Note that a similar article has been published previously.[1]

ABSTRACT

In 1997, a burn test was performed on a temporary retail fireworks stand stocked with 900 pounds (400 kg) of a range of consumer fireworks. A maximum interior temperature of 1,400 °C was recorded inside the test stand and flashover occurred within approximately one minute of involvement of the fireworks. Ignited fireworks were observed traveling more than 250 feet (75 m) beyond the stand's partially open front side. The greatest heat flux [calculated to be 60 kW/m^2 at a distance of 5 feet (1.5 m)] was also observed on the stand's front side. It was concluded that a setback distance of 20 feet (6 m) was required on sides of the stand without openings, and that a setback distance of 40 feet (12 m) was required where there were large openings in the stand.

Keywords: fireworks stand, consumer fireworks, test burn, flashover, heat flux, setback distance

Summary

In September of 1997 the Clark County, WA Fire Marshal's Office conducted a test with the assistance of the Washington State Association of Fire Marshals, the Oregon State Fire Marshal, the Western Fire Center, fireworks retailers and wholesalers, fire departments and fire districts. Approximately 900 pounds (400 kg) of consumer fireworks legal for possession, sale and use in Washington State were loaded into a wooden structure typical of the type used for the temporary retail sale of fireworks. The purpose of the burn was to document the thermal effects of the fire and to evaluate the sufficiency of proposed code amendments. No attempt was made to quantify the ignitability or extinguishability of either the fireworks or the stand. Stand construction techniques and firework display and storage configurations were established to generally replicate the actual methods and configurations used to sell consumer fireworks. Materials within the stand were ignited, and temperature and heat flux monitoring equipment, and still and video photography documented the test burn. No attempt was made to extinguish the fire once ignited, and the stand and firework packaging materials were allowed to burn completely once ignited.

A maximum interior temperature of 1,400 °C was recorded and flashover occurred in the stand within approximately one minute of confirmed fireworks ignition. Substantially all of the fireworks in the stand ignited within approximately three minutes after confirmed ignition. Once the pyrotechnic materials were consumed, device packaging materials and the stand itself continued to burn. The structure's ¼-inch (6-mm) plywood construction generally contained the firework devices and provided initial thermal protection to exposures except where openings were present. Ignited fireworks were observed traveling more than 250 feet (75 m) beyond the stand's partially open front side. Fireworks exiting the other three sides were minimal. Thermal effects to exposures were greatest along the partially open front side with a maximum peak heat flux of 60 kW/m^2 calculated at a point 5 feet (1.5 m) in front of the stand. Thermal effects on the three sides without openings were considerably less.

Pyrotechnic hazards existed for about the first three minutes of the test. Ignited devices exiting the front of the stand provided ignition sources in high heat flux areas and remote from the test site. Heat flux and temperature recordings outside of the stand peaked at about five minutes into the test—after the firework devices had discharged. By five minutes into the test only the stand construction materials and the firework packaging remained as fuel for the fire.

Test data indicated that on the sides of the structure without openings a 20-foot (6-m) setback provided an adequate level of thermal protection to exposures. Where openings are present, particularly a large open front sales area, 40-foot (12-m) setbacks are required to provide a similar level of thermal protection. Ignited fireworks exiting through structure openings provide ignition sources in high heat flux areas and in locations remote from the site. Setbacks adequate for thermal protection are probably inadequate to protect against the hazards created by the exiting fireworks.

Once the pyrotechnic materials in the fireworks had burned, the fire was reduced to one of a room and contents. The fireworks paper packaging material provided a substantial fuel load to be consumed even after the fireworks discharged. Within three minutes of firework ignition most of the pyrotechnic materials in the test stand had ignited and discharged. Fire departments arriving at fires in similarly constructed and stocked retail fireworks stands will encounter heavy fire conditions in the stand and perhaps involving near and remote exposures but the hazards associated with the fireworks themselves will be substantially absent.

The results of this test were obtained based upon a specifically defined fire load and method of stand construction. Any deviation in the mix of fireworks or stand construction methods or materials could affect the applicability of the results outlined in this report. Additional testing is needed to better understand, document and evaluate fire protection and life safety needs in fires involving consumer fireworks under similar and different configurations and circumstances.

Introduction

In 1995 the Washington State Legislature amended state law to require that the state fire marshal develop and adopt administrative code language controlling the sale of fireworks from temporary structures. The new code, developed with substantial input from fire service providers and the fireworks industry, stipulated among other things, requirements for the type of construction and setbacks for temporary structures used for the retail sale of fireworks. Much of the proposed code language was excerpted from local ordinances in place across Washington State. Little information, literature or test data existed to quantitatively support the code requirements. As a result, the proposed language was a qualitative assessment based upon a collective experience with the Uniform Fire and Uniform Building Code where the sufficiency of a 20-foot (6-m) setback to exposures and combustibles for buildings of non-rated construction without abnormal fire loads or hazards is generally accepted. This 20-foot (6-m) dimension and its code acceptance formed the basis for similar setback requirements to temporary fireworks stands.

A full scale test burn designed to replicate, measure, and document the effects of a fire in a fully stocked temporary fireworks structure constructed consistent with Washington Administrative Code requirements was designed and accomplished as an aid in evaluating the sufficiency of the state's administrative code. The purpose of the test was to evaluate the sufficiency of proposed code language. No attempt was made to evaluate the ignitability or extinguishability of individual or collective firework devices. The Western Fire Center[2] provided technical assistance in the test's design, methodology, instrumentation, documentation, data collection and analysis. A fireworks stand and stand firework loading requirements were provided by Western Fireworks.[3] Fireworks retailers provided technical assistance as to the manner of storage and display of the fireworks within the stand. Fireworks for the test were obtained through enforcement seizures conducted by fire and law enforcement agencies throughout the Portland, Oregon metropolitan area.

Site and Environmental Conditions

The test site was an abandoned eighty-acre, privately owned sand and gravel quarry, graded level and surrounded on its perimeter by berms 20 to 30 feet (6 to 9 m) high. Groundcover vegetation was absent from the site, surface materials being bare rock, sand and gravel. For three

Figure 1. Test structure and site.

days prior to the test temperatures ranged between 55 and 70 °F (13 to 21 °C) with intermittent and sometimes heavy rain and high humidity. Rain fell intermittently throughout the morning of the test and continuously for thirty minutes prior to and during the test burn. Site temperature at test time was approximately 60 °F (16 °C). The ground surrounding the test structure was completely saturated by rainfall with water standing on the ground surface within 10 feet (3 m) of the structure at test time.

Stand Construction

An 8 × 16 foot (2.5 × 5 m) temporary structure (Figure 1) that had previously been used for retail fireworks sales was erected on the site. The structure consisting of ¼-inch (6-mm) plywood over 2 × 2-inch (50 × 50-mm) framing, was pre-assembled in 4-foot (1.2-m) sections. The 4-foot (1.2-m) sections were bolted together at the site such that the fully assembled stand had a solid back with no openings, two sides with 28-inch (710-mm) door openings, a front section open

Figure 2. Fireworks on shelves.

Figure 3. Fireworks on shelves.

its entire 16 foot (5 m) width from a height of approximately 4 feet (1.2 m) to a height of approximately 7 feet (2 m) and a solid roof that sloped from a front end height of 8 feet (2.4 m) to approximately 7 feet (2 m) at the back wall. The roof and sides were not weather tight but the stand was otherwise sturdy. The structure was painted inside and out but was not otherwise protected. The side doors were held closed during the fire test. Three shelves—constructed of 1/4- and 3/8-inch (6- and 9-mm) plywood supported by plywood brackets—were attached across the full width of the back stand interior. A counter top constructed similarly was attached across the full length of the structure's front opening. Having been exposed to the weather for some time prior to the test, the stand materials were wet.

Fire Loading

Approximately 900 pounds (400 kg) of consumer (formerly common or Class C) fireworks of the types that are legal for sale, possession and discharge in Washington state[4] were placed on the shelves and on the ground under the shelves within the structure in a manner consistent with normal retail operations (Figures 2 and 3). The approximately 10,000 individual firework pieces provided a mix of products typically offered for sale and included variety packs, hand held sparklers, novelty items, ground spinners, spinning wheels, cones, whistles, fountains, candles, aerial devices, smoke pieces, shells and mortars and a variety of night time ground pieces. Empty cardboard boxes were placed under the counter along the front of the stand to simulate personal items and bags or boxes provided to the customer upon sale of fireworks. Sufficient fireworks to exactly replicate a typical stand were not available. Table 1 compares the number and type of devices in a typical stand with those provided in the test stand.

Table 1. Product Mix.

Product Description	Typical Stand		Test Stand	
	Quantity	Shots[a]	Quantity	Shots
Package Assortment[b]	84	840	2	20
Wooden Stem Sparklers	570	570	0	0
Novelty Items[c]	1104	1104	909	909
Ground Spinners	1824	1824	1440	1440
Fountains and Whistles	1310	1410	951	951
Cones	38	38	64	64
Spinning Wheels	60	60	6	6
Smoke Devices	792	792	792	792
Metal Stem Sparklers	3168	3168	396	396
Year Round Novelty[d]	444	444	440	440
Helicopters[e]	3624	3624	3528	3528
Parachutes[f]	290	398	290	290
Candles[g]	1008	748	864	8362
Mortars / Shells	120	384	120	384
Large Night Displays[h]	303	7106	303	7106
Total	14,449	29,358	10,105	24,688
Weight of Fireworks	1067[i]		920[j]	
Retail Value	$8,000		$7,500	

a Many devices contain more than one individual discharge of fireworks therefore the actual shot count may exceed that indicated.

b Variety Packs contain assortments of at least ten separate devices.

c Includes small single piece items where fireworks are placed into typically paper carriers - for example a fireworks device that shoots out sparks may be fitted to a small paper vehicle or similar product and other devices that emit smoke or sparks as part of a larger piece.

d Those type of novelty fireworks that are legal for sale, purchase and discharge on a year round basis including "Party Poppers" and "Snap Its". "Snap Its" are packaged 50 per box and were counted as a single item.

e Items with wings that when ignited spin into the air.

f Pyrotechnic devices are shot into the air and float back down under one or more parachutes.

g Roman candles and other devices that fire one or more balls of ignited material.

h Typically "Cake" types of products that hold a number of individual devices that discharge into the air in succession.

i Estimated upon comparison with test stand amounts.

j Actual weight measured includes pyrotechnic material and device tube or container.

Test Procedures

The structure was erected at the test site three days prior to the burn. Prior to the test the fireworks were stored in metal shipping containers remote from the site. Fireworks loading began at 08:00 the morning of the test. As an aid in identifying the location of debris or fireworks that might be propelled from the structure, concentric circles were established on the ground around the stand's exterior perimeter in 10 foot (3 m) intervals. Newspapers placed into wax paper cups were positioned around the structure's exterior to represent ground cover vegetation, which was absent from the site. To record radiant heat flux, radiometers were positioned outside—14 feet (4.3 m) directly in front of the center of the stand, 13 feet (4 m) from the center of one side of the stand and 12 feet 4 inches (3.7 m) directly behind the center of the back side of the stand. To record temperatures developed during the test, thermocouples were located inside the stand—24 inches (610 mm) above the ground, centered on the back wall

Test Chronology[a]

T = 00:00	Ignition device energized.
T = 04:10	Temperature at point of origin 400 °C (Initial ignition of cardboard box).
T = 09:10	Ignition of fireworks (Figure 4). Fireworks burning confirmed audibly and visually outside of stand. Temperature inside of stand rising dramatically ranging between 600 and 800 °C. Fireworks begin to exit stand's open front.
T = 09:27	Visibility in stand near zero (Figure 5). Accelerating ignition of fireworks. Number of fireworks propelled from front of stand increases. Heat flux measured in front of stand at 7 kW/m^2, sides and rear heat flux near ambient.
T = 10:17	Flashover (Figure 6). Temperatures in stand range from 600 °C to almost 1,400 °C. Fireworks continue to exit stand, recorded temperatures and heat flux rising.
T = 14:26	Temperature in stand approx. 1,100 °C. Maximum exterior temperatures and heat flux recorded, 200 °C and 22 kW/m^2 in front of stand, 50 °C and 8 kW/m^2 at the side of the stand. The number of fireworks exiting the stand is negligible. Structure actively burning, collapse begins.
T = 35:00	Temperatures approximately 550 °C. Monitoring of instruments ceases.

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[a] Chronology was prepared from analysis of all data sources.

directly over the point of origin; at 67 inches (1.7 m) above the ground on the side wall approximately 8 feet (2.4 m) horizontally from the point of origin; outside of the stand adjacent to the front radiometer; and 16-feet 4-inches (5 m) from the center of the side of the stand. Exterior devices were located approximately 3-feet (1 m) above the ground.

The fire was ignited with an "electric match" —a section of shorted out heat tape that when energized ignites the combustible tape material. A small trench was dug in the ground at the center of the back interior of the stand. The electric match was placed in the small trench. A cardboard box filled with newspapers and cardboard pieces was placed over the top of the

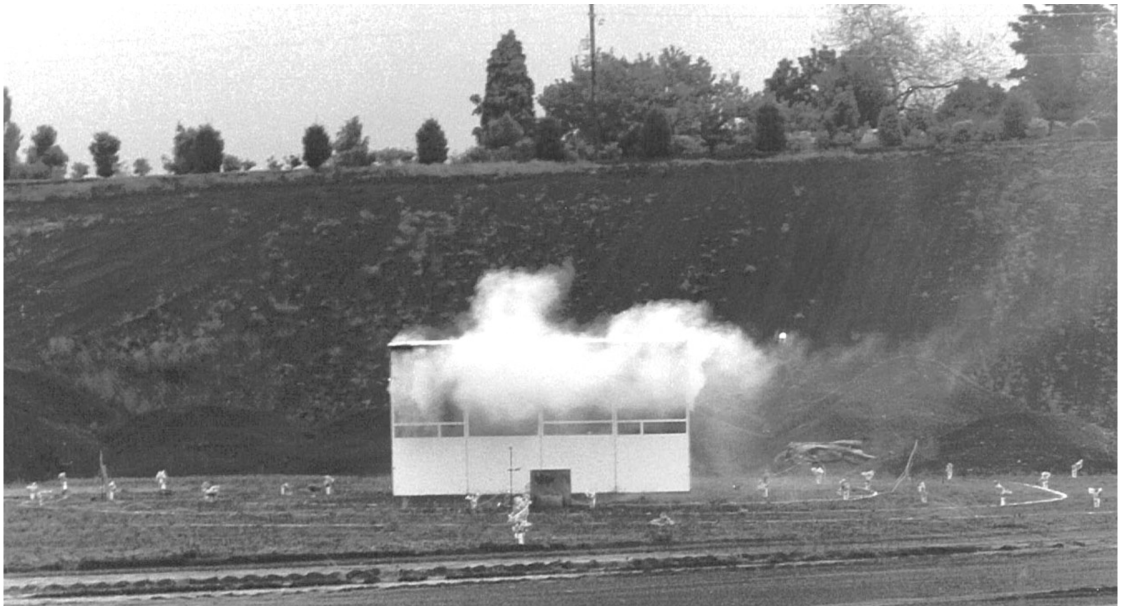

Figure 4. Confirmed fireworks ignition.

Figure 5. Seventeen seconds after confirmed firework ignition.

electric match in the ditch. The cardboard box was directly under a shelf containing firework devices set out for display and in-between cardboard-boxed cases of firework devices. The match was energized and ignited the stand contents.

Test Results

The test was documented with video and still photography. Video cameras recorded the burn continuously—from all sides—from the beginning of the ignition sequence through stand collapse. Still photographers recorded views of all four exterior sides in ten second intervals beginning with the first visible fireworks ignition. Once ignited no attempt was made to extinguish

Figure 6. Flashover.

the fire. At the conclusion of the burn the site was documented and the remains of fireworks or other debris that had exited the stand were identified and their locations recorded. The confirmed firework ignition time was established at the point when device discharge was audibly and visually noticeable.

Actual heat flux recordings graphed against time appear on Chart 1. Temperature recordings are graphed similarly on Chart 2. Chart 3 indicates calculated heat flux intensity at various distances in front of the stand at peak flux as well as the 150-second average intensities. Chart 4 similarly records heat flux intensity at the side of the stand. Chart 5 indicates the site configuration and the location of the identified remains of firework pieces that exited the stand to a distance of 130 feet (40 m).

Paper targets placed within 15 feet (4.6 m) of the front of the stand were ignited during the fire. Targets placed to the side and rear of the stand were not ignited regardless of their placement, however the wax melted out of the paper cups and the newspaper within the cups located within 10 feet (3 m) of the sides and rear of the stand darkened and became brittle. The remains of more than 150 individual fireworks pieces were identified outside the stand at the test's conclusion. The fireworks exiting the stand approximated a normal distribution with a mean of 27 feet (8.2 m) and a standard deviation of 23 feet (7 m) from the stand's partially open front. The number of fireworks that exited other than through the front open sales area was negligible. A number of larger aerial pieces thought to be mortars were observed exiting the stand and landing as far as 250 feet (75 m) from the stand's front during the test. Video recordings confirmed the visual observation however the remains of the larger devices could not be identified at the test's conclusion.

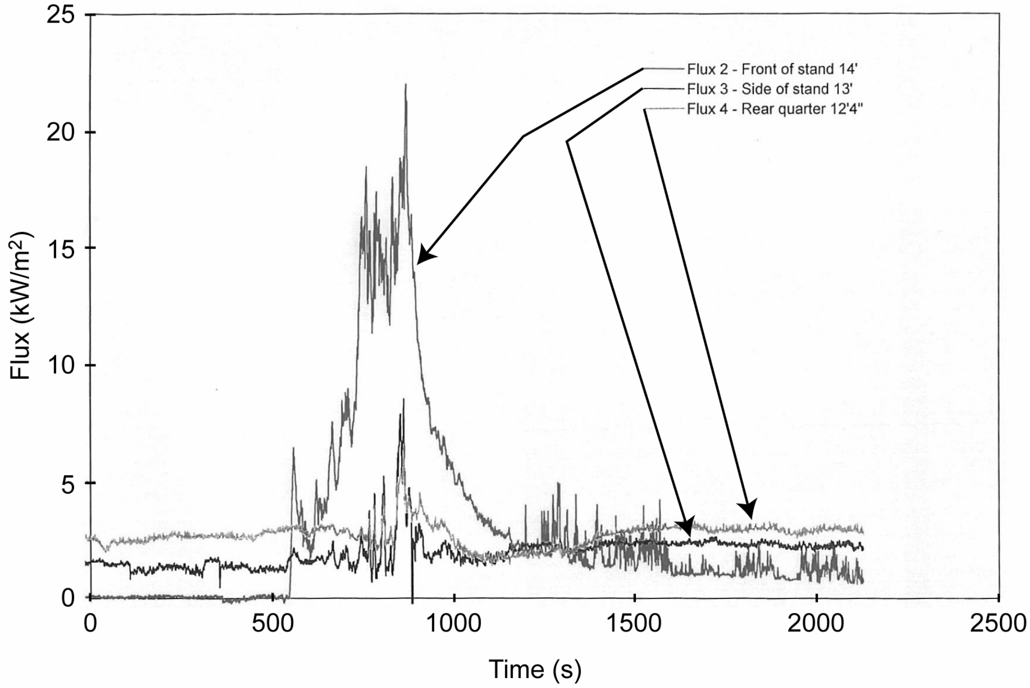

Chart 1. Fireworks stand fire heat flux at different locations.

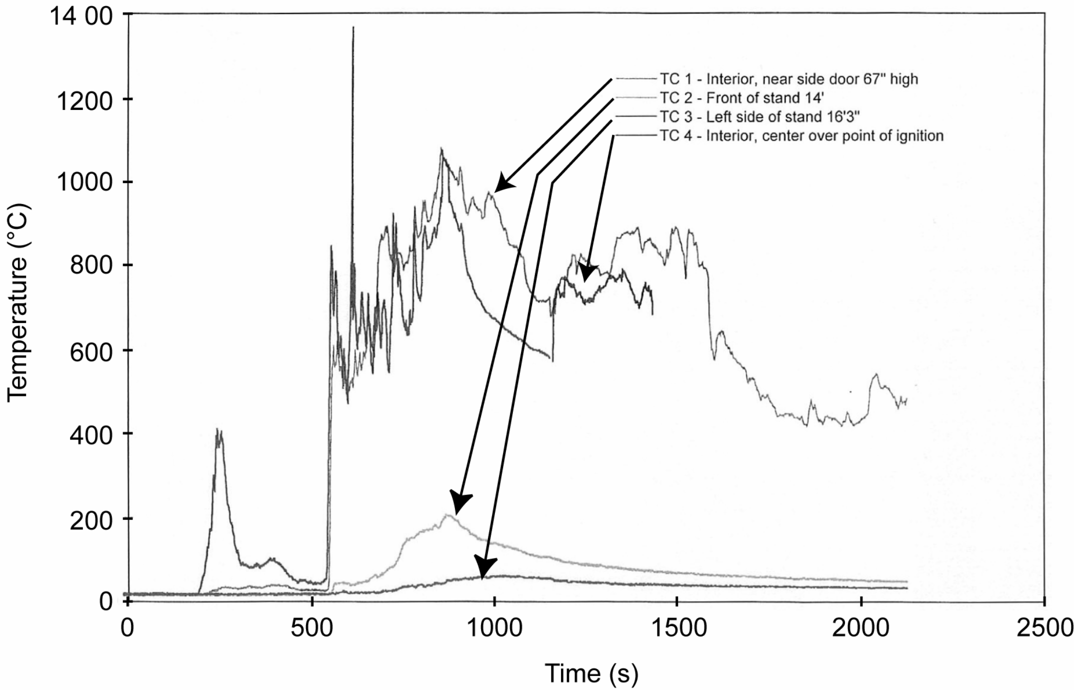

Chart 2. Fireworks stand fire temperatures.

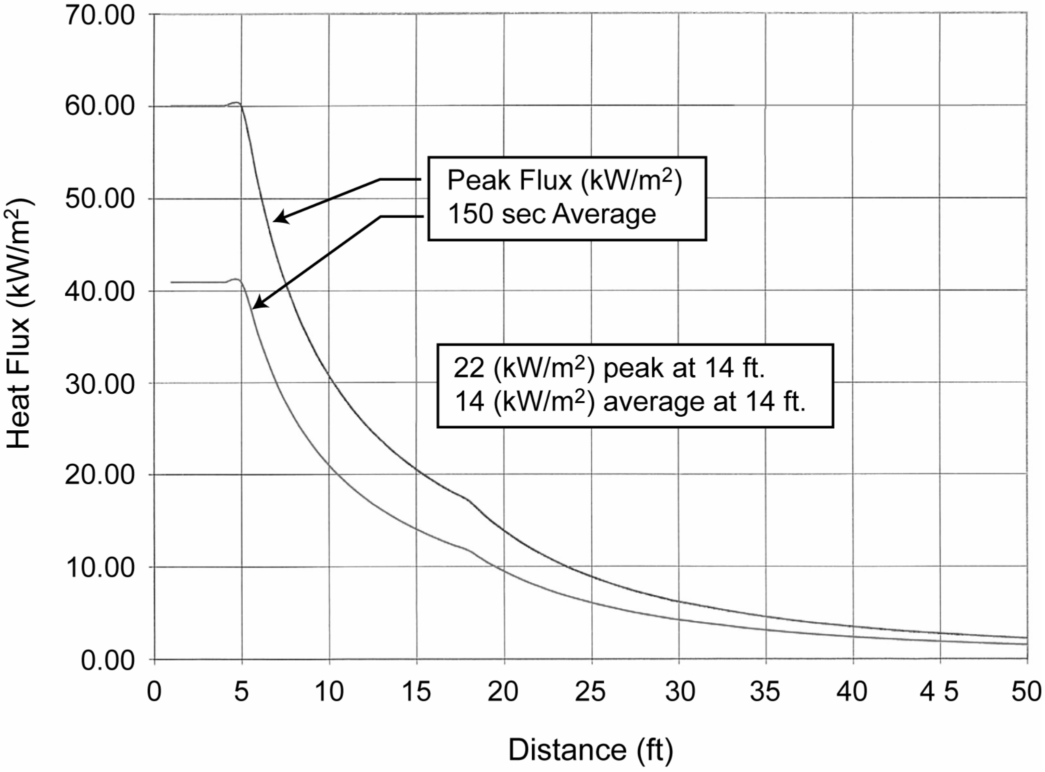

Chart 3. Heat flux at exterior front of stand.

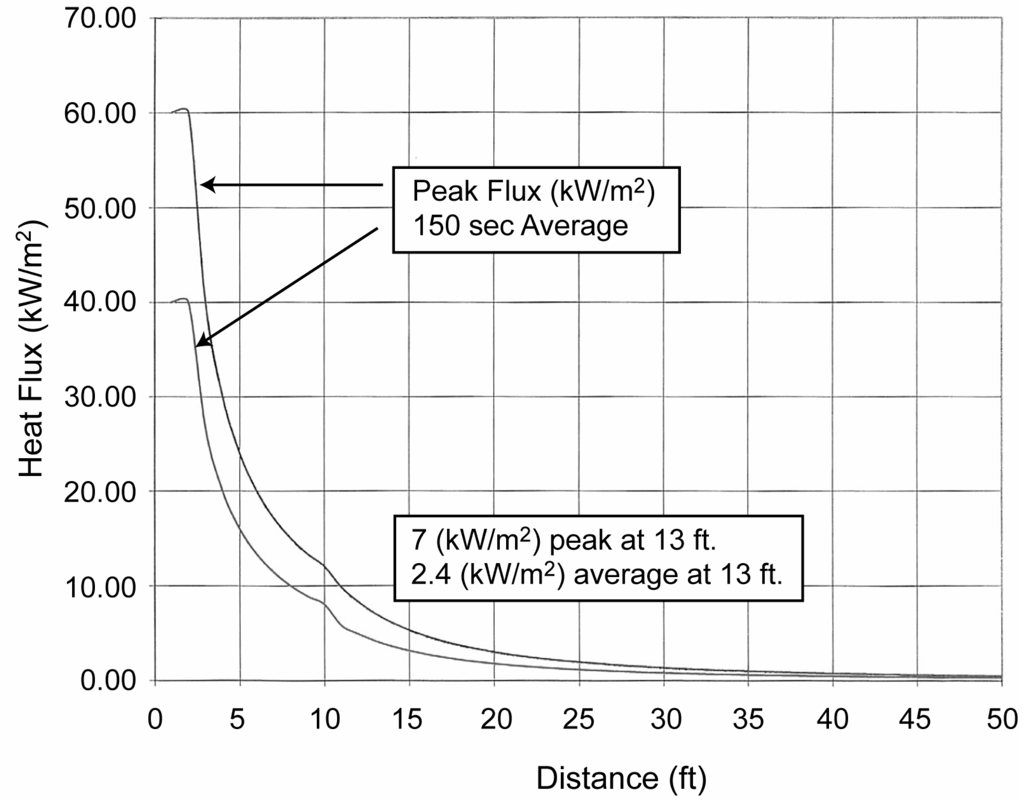

Chart 4. Heat flux at exterior side of stand.

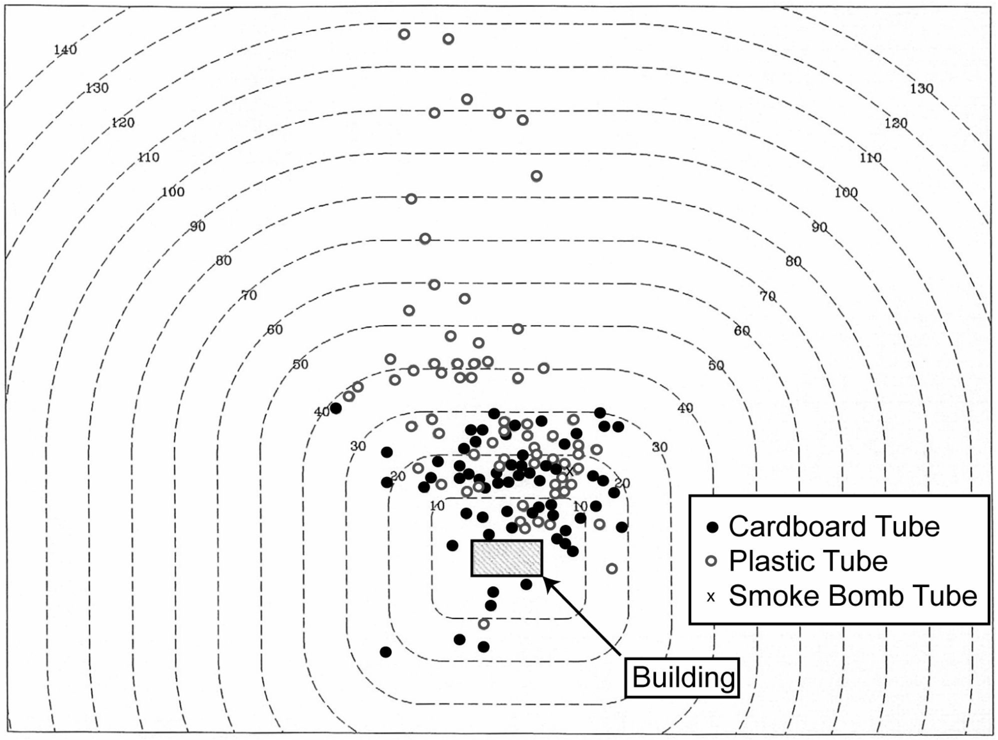

Chart 5. Site configuration and the location of the identified remains of firework pieces that exited the stand to a distance of 130 feet (40m).

Discussion / Analysis

The following tables are provided as an aid in evaluating and interpreting the information in this report and are intended to be general in nature for illustrative purposes.

Effects of Heat Flux[5]

Heat Flux (kW/m^2)	Effect
1.0	Noonday sun on the beach in Florida.
6.0	Cardboard will propagate flame.
7–8.0	Solid wood will propagate flame.
10.0	Exposure to skin will cause unbearable pain within five seconds.
10–11.0	Critical flux to self-ignite cardboard.
20.0	Exposure to floor of room at flashover.
20.0	Solid pine will ignite in 70 seconds.
40.0	Exposure to wall (mid-height) of room at flashover.
50.0	Solid Douglas Fir will self-ignite in 6–10 seconds.
60.0	Exposure near ceiling of room at flashover.
120–140	Exposure from E199 furnace at one hour.

Effects of Temperature on Wood

Temp. (°C)	Effect[6a,7]
180	Piloted ignition in 14–40 minutes
200	Piloted ignition in 12–25 minutes
225	Piloted ignition in 7–17 minutes
250	Piloted ignition in 4–9 minutes
300	Piloted ignition in 1.6–3.5 minutes
400	Piloted ignition in 20–30 seconds
600	Spontaneous ignition of solid wood

Firework devices in the stand discharged for approximately three minutes after confirmed fireworks ignition. Although actively burning, the stand remained intact during this three-minute period. Collapse of the stand began about five minutes after confirmed firework ignition. By the time the stand began to collapse firework ignition and discharge had virtually ceased. Prior to its collapse the ¼-inch (6-mm) plywood construction generally contained aerial and other devices within the stand and provided thermal protection to exposures on the sides and rear. Once collapse began and the stand materials were heavily involved in fire, the thermal effects emitted from the sides and rear increased.

Calculated at 20 feet (6 m) from the sides and rear of the stand, radiant heat flux was insufficient throughout the test to propagate flame across cardboard. Few devices capable of providing a piloted ignition source exited or landed to the sides or rear of the stand. After the stand became involved in fire, the conditions within 20 feet (6 m) were sufficient to ignite common combustible materials. The wax paper cups and newspaper located within 10 feet (3 m) of the sides and rear of the stand turned brown and became brittle during the fire. The conditions surrounding these materials were probably capable of propagating combustion had an ignition source been introduced. At 20 feet (6 m) from either the back or the sides of the stand, peak and 150 second average flux rates were insufficient to propagate flame across cardboard.

Conditions extending from the stands partially open front side were markedly different than those experienced to the sides and the rear. Almost immediately after confirmed firework ignition, devices began exiting through the open front sales area. As the contents of the stand became more involved during the initial minutes, the number of devices exiting the stand increased. Fireworks exiting from the front were generally finished three minutes after confirmed ignition. During this three-minute period measured flux at 14 feet (4.3 m) in front of the stand exceeded 18 kW/m^2 approaching that experienced at the floor level in rooms during flashover (20 kW/m^2). Ignited fireworks fell within 14 feet (4.3 m) of the front of the stand while these conditions persisted. The maximum radiant energy recording, 22 kW/m^2 occurred 14 feet (4.3 m) in front of the stand at approximately five minutes after confirmed firework ignition after firework discharge was substantially complete.

The calculated radiant energy conditions within 5 feet (1.5 m) of the front of the stand were consistent with those obtained at the ceiling level of rooms at flashover. At 20 feet (6 m) in front of the stand calculated radiant energy was sufficient to self-ignite cardboard and propagate fire across solid wood. At a distance of

40 feet (12 m) in front of the stand both the peak and 150 second average flux rates were below that required to propagate flame across cardboard. The heat flux emitted from the back or the sides of the stand was approximately one half that observed at the front at similar distances. Except for the fireworks exiting the stand, conditions 40 feet (12 m) in front of the stand were similar to those experienced 20 feet (6 m) to the sides or rear of the stand.

Most of the pyrotechnic materials were consumed within three minutes of confirmed fireworks ignition. Heat flux rates and temperature readings peaked at approximately five minutes after fireworks ignition indicating the greatest heat release rate due to the combustion of the structure and the combustible remains of firework devices rather than the pyrotechnic material itself. Identifiable firework devices propelled from the stand during the test were almost exclusively aerial devices that fell approximately in a 45° arc beginning at the stand's front and extending out 250+ feet (75+ m). Half of the device remains landed within 27 feet (8.2 m) of the stand's open front, two-thirds within 60 feet (18 m). The devices continued to burn in varying degrees upon hitting the ground providing ignition sources in areas where the heat flux was sufficient to either ignite or propagate flame across light combustibles and wood. The hazards created by aerial devices exiting the stand were unquantified, however their effect on nearby pedestrian or vehicles access points and routes could be significant.

The fireworks in the stand did not ignite immediately upon energizing the "electric match" ignition device. The cardboard and paper initially surrounding the electric match did however ignite and were at least partially consumed prior to igniting fireworks or stand materials. Personnel were prohibited from entering the structure after the ignition sequence began, preventing adjustment of the materials to aid ignition. The extremely wet conditions at the site undoubtedly had an overall mitigating effect on the fire conditions, slowed the ignition of the cardboard and paper within the stand and delayed fireworks ignition. Once fireworks were ignited the fire built rapidly. The atmosphere within the stand became lethal (thermally toxic[6b]—exceeding 140 °C) within seconds after confirmed fireworks ignition. Within one minute after confirmed fireworks ignition upper gas layer temperatures exceeded 1,100 °C consistent with flashover conditions.[6c] Had the ignition device been situated to achieve immediate fireworks ignition upon being energized neither the pyrotechnic nor the thermal effects would have varied.

Environmental conditions have an effect on the rates of combustion of common combustibles. Ambient temperature, humidity, preheating and moisture content are generally accepted as factors having an effect on the ignitability, burning characteristics and the rates of combustion of commonly combustible materials. These factors can affect pyrotechnic materials similarly.[8] Lower ambient temperatures, high humidity and high moisture content generally slows the rate of burning of pyrotechnic material while the phenomenon of "heat cycling" where materials are subjected to alternating high and low temperatures can increase pyrotechnic burn rates. The fireworks used for the test came from multiple manufacturers with unknown manufacture dates, had not been stored in environmentally controlled conditions prior to their use and were subject to the damp, cool environmental conditions present at the site the day of the test. The environmental effects on the burning rates of the fireworks used were not quantified. However, it is reasonable to speculate that fireworks sold at retail may be subjected to similar conditions.

The environmental conditions and their effect on the burn rate of the test structure were not quantified. The wooden stand and the ground underneath the structure were thoroughly soaked with water by the time the test was initiated. Neither the amount of heat absorbed drying the ground under the stand nor the amount absorbed by the structure prior to reaching its ignition temperature is known. Visual observations captured on video and still photography show that the walls and roof of the structure produced clouds of steam prior to their ignition. Although environmental conditions similar to those experienced on the day of the test could occur at other times, the cool temperatures, heavy rain and high humidity are thought to be atypical of the weather during a fourth of July selling period. For this reason it is believed that the environmental conditions had an unquantified mitigating effect on the test fire conditions and the subsequent thermal effects recorded.

Conclusions

This test documented and recorded the effects of a fire in a structure typical of the type often used for the temporary retail sale of fireworks. To evaluate the adequacy of fire protection for this or any other type of fire hazard requires an examination of multiple factors including: type and materials of construction; the type and configuration of the fire load; physical location and setbacks from combustibles, buildings, property lines, roads and pedestrian access points and hazards; nearby hazards and exposures; environmental conditions, and the availability of fire suppression forces. Any modification of a single factor without consideration of its affect on the others can render the complete fire protection "package" inadequate. State and local laws differ as to the types of firework devices that are legal for sale and discharge. Different mixes of fireworks, particularly the presence of firecrackers or similar devices or display fireworks could create fire conditions much different than those encountered during this test. The information provided in this report, although specific to a given set of criteria, has general implications useful for similar applications.

Once the pyrotechnic materials in the fireworks are consumed—in this case within about three minutes after ignition—the fire involves essentially a room and contents. The presence of the pyrotechnic materials accelerates the fire leaving little time for occupants to react once fireworks are ignited. In this test even light construction materials such as ¼-inch (6-mm) plywood were sufficient to contain the fireworks within the structure and provide a degree of thermal protection while the fireworks discharged. Where openings are present, typically along the front side to facilitate sales, thermal protection and firework device containment is compromised creating exposure hazards remote from the stand itself.

The radiant heat flux data supports the adequacy of a 20-foot (6-m) setback to combustibles from temporary stands constructed and loaded with fireworks similar to that described in this report—except where openings are present. Where openings are present, particularly a large front sales opening, a 40-foot (12-m) setback is required to provide a level of thermal exposure protection similar to that provided on sides without openings. A 20-foot (6-m) setback may also be appropriate where openings are provided with automatic closing mechanisms.

Fireworks exiting the structure create a different and perhaps compounding set of hazards. While the fire is actively burning, fireworks exiting through openings place ignition sources in high heat flux areas close to the stand. Ignited devices were also observed traveling more than 250 feet (75 m) from the stand, spreading ignition sources a considerable distance. Where a setback may be sufficient to provide thermal protection, it may be insufficient to provide protection from firework ignition sources. The absence of aerial devices or the presence of automatic closing devices on openings could mitigate this hazard such that setback requirements established for thermal exposure protection may be appropriate.

Test data indicates that lightweight temporary construction of at least ¼-inch (6-mm) plywood over light wood framing can contain certain common fireworks within a structure upon ignition and provide limited thermal protection for exposures. Other construction techniques and materials that provide at least an equivalent level of protection should be similarly adequate. A different or more concentrated mix of fireworks may require more substantial construction methods and different setback requirements to provide similar levels of protection.

The presence of openings in the construction has a dramatic effect on a structure's ability to protect exposures and contain ignited fireworks. Test data documented a much higher level of thermal and pyrotechnic device exposure to surrounding materials on the side of the stand with the large sales opening. Had the number or dimensions of openings from the stand been greater or had construction materials been less substantial or had they failed sooner, the thermal and pyrotechnic exposures would have been greater around the stand's perimeter.

This test was conducted outside of a controlled environment yet similar to conditions that may be encountered in real life applications. No attempt was made to evaluate the ignitability of the devices or the ease at which they may have been extinguished if ignited. Similarly, the test made no attempt to evaluate the configuration of the fireworks but again, the arrangement was intended to reflect those conditions actually encountered in the field. There is little publicly available literature documenting similar large or small-scale tests. The fire service and the pyrotechnic industry would both benefit from additional testing designed to evaluate protection needs under different fuel loads and configurations where consumer fireworks are sold and stored.

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4) Washington Administrative Code Section 212-17 limits consumer fireworks to:
   (1) Ground and hand-held sparkling devices that include dipped stick sparklers, cylindrical fountains, cone fountains, illuminating torches, spinning wheels, ground spinners, and flitter sparklers;
   (2) Aerial devices including helicopters and aerial spinners, roman candles, mines and shells (mortars);
   (3) Combination items containing two or more of the listed devices; and,
   (4) Smoke devices. Those items specifically prohibited and excluded from the product mix used in this test include firecrackers, salutes, chasers, skyrockets, or missile-type rockets.

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Accidents and their Role in Aiding the Management of Health and Safety in Pyrotechnics Manufacture

Allen Webb
Health and Safety Executive, Merton House, Bootle, L20 3DL, United Kingdom
allen.webb@hse.gsi.gov.uk

The opinions expressed in this article are those of the author and do not necessarily reflect the position or policies of the Health and Safety Executive. Information about accidents in this article without specific references is based on the author's personal knowledge or information contained in the Explosives Accident Database Advisory Service (EIDAS).

ABSTRACT

The investigation and analysis of the causes and circumstances of accidents can be an invaluable tool in assessing the effectiveness of systems for the management of health and safety. This article considers and draws on the lessons learned from a number of accidents to suggest a general framework to aid the development of management systems for the manufacture of explosives. While the emphasis is on firework and pyrotechnic manufacture, the issues have wider application.

Keywords: safety management, pyrotechnics, health and safety, manufacture

Introduction

The dangers associated with the manufacture of explosives have long been well recognised as has the need to control the consequences arising from accidents. Historically the intuitive response has been to minimise the risk of communication of any explosion between process and storage buildings and to ensure that the public is not put at risk. The question of the safety of employees did not feature strongly in the minds of early regulators.

In the UK, the first attempt to provide control of explosives manufacture came with the gunpowder Act of 1772. This Act set out limitations to the amounts of explosive that may be involved in any manufacturing process and set out minimum distances between process buildings and places outside the factory. This concept was extended in the Gunpowder Act of 1860, which implemented more detailed provisions and introduced a requirement for a licence to manufacture gunpowder, mercury fulminate, percussion caps, fireworks and other preparations or compositions of an explosive nature. The Explosives Act, 1875 (EA 1875)[1] developed the licensing requirements further and ensured that its provisions covered all explosives. This most recent act also made a real effort to provide some reduction of risk to employees through general and special rules.

In spite of the efforts of EA 1875, there was still a tacit acceptance that those working in a factory would, from time to time, be involved in an explosion. When such an accident occurred, the response was "well they knew the risks". This "laissez faire" attitude was exemplified by an article in the Strand Magazine in 1895 describing a visit to the government gunpowder factory at Waltham Abbey.[2] The article commented on the thoughtful provision by the factory operator of a water filled pond outside a process building to enable any worker involved in a fire or explosion to jump in and extinguish their burning clothes. The fact that workers were likely to be involved in an explosion didn't warrant comment.

This system of control is simply not acceptable by modern standards. It is no longer reasonable that workers in explosives factories, just because they are prepared to work with explosives, should accept lesser standards of protection than workers in other industries. Of course there will be risks but it is incumbent on the operators of any factory to ensure that the safety of their employees is adequately managed through the reduction of risks to an acceptable level and the provision of adequate protection from the effects of any accident that might nevertheless occur.

The current approach in the UK to controlling the dangers arising from explosives manufacture and storage therefore relies on a two-layered approach:

1) The licensing of explosives factories and magazines, limiting the processes that may take place in any building, setting amounts and types of explosive in each building, and defining the separation distances between buildings and from places outside the site. This follows the concepts described above and has its origins in EA 1875. Provisions in EA 1875 also require the occupier of a licensed factory or magazine to draw up and implement general and special rules. These set out restrictions on how activities may be carried out thus seeking to limit the risks of an ignition. The rules are required to be endorsed by an explosives inspector, a process that limits the ability to modify or adapt the rules on a day to day basis to address new safety issues that might arise.
2) The assessment and management of risks and hazards by the operators of the site to minimise the danger to those working in the factory or magazine. This draws on wide duties placed on employers and employees stemming from the Health and Safety at Work Act, 1974 and the Management of Health and Safety Regulations, 1999. These controls require employers to operate safe systems of work and to conduct and implement risk assessments aimed at reducing risks to health and safety to "As Low as Reasonably Practicable" (ALARP). Factories and magazines handling large quantities of explosives are additionally subject to the Control of Major Accident Hazards Regulations, 1999 (COMAH). Top tier sites under these regulations are required to prepare a major accident prevention policy, a safety report and an on-site emergency plan.

The inspection of explosives factories and magazines by the Health and Safety Executive routinely examines levels of compliance with both of these areas.

Management of Health and Safety

Much has been done to set out an environment in which factory operators can develop and implement systems for the management of health and safety. A significant amount of work has taken place in the UK over the last 20 years producing guidance on the general aspects of safety management, risk assessment and human factors.[3–5] Additionally, specific guidance on the safe management on specific high risk operations has been produced.[6] Tools and guidance have been developed to enable manufacturers of explosives to estimate the potential effects of their activities and to provide suitable protection.[7,8] Where poor safety performance has been identified, auditing techniques have been applied at senior company levels with good effect identifying failings in management.

Under the broad title of "Loss Prevention", the analysis of accidents and the lessons they offer to the development and refining of safety management has become a common tool. Accidents are, in effect, a demonstration of the ineffectiveness of management and control systems. Accidents and their root causes can shed a great deal of light onto the failures of safety management systems and teach lessons on how these may be improved. Trevor Kletz has shown this in his work relating to safety in the general chemical industry, and I have found his books to be a valuable source of common sense advice on plant design and operation. The application of root cause analysis techniques to the investigation of accidents can pay dividends in the development of safety management and control systems.

In this article I want to examine a number of accidents that have occurred in the pyrotechnics industry in the UK and draw out the lessons learned and what they tell us about key issues in the effective management of safety.

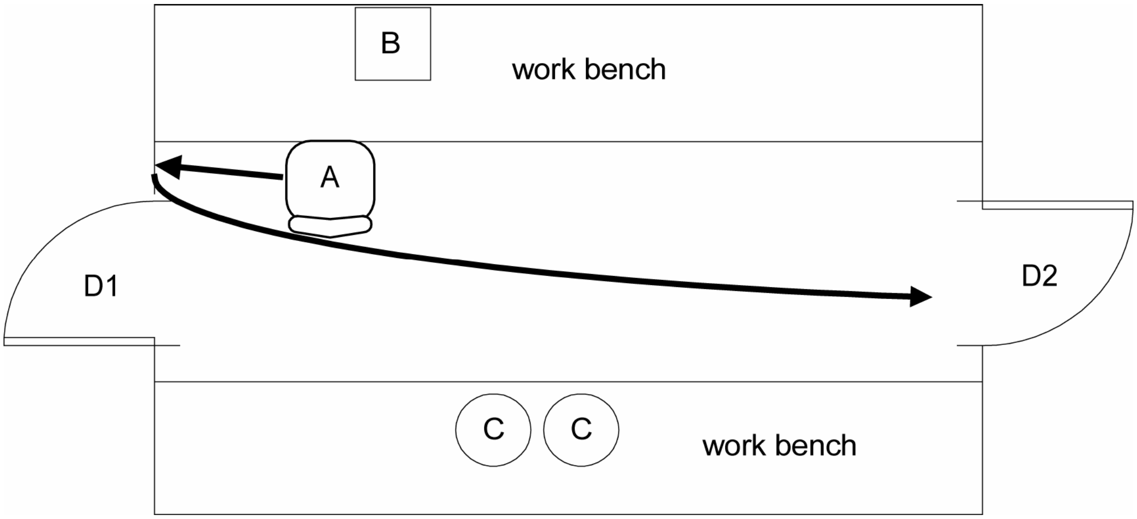

Figure 1. Process building floor plan.

Accident 1

A company was involved in filling gerbs with a blackpowder/titanium mixture. The process involved incremental filling using a drift and mallet. The building involved was of normal construction with a door at each end and was licensed for 50 lb (23 kg) of composition. The general building layout is shown in Figure 1. The workman sat at point A, next to one exit door and had a stock of composition in a work box on the bench at location (B). Two stock containers, C, were located on the bench behind the workman. An ignition occurred during the filling of a gerb, and the fire spread rapidly to the composition in the workbox and in turn ignited one of the stock containers of composition.

The workman turned to his left and moved to leave through the door D1 but in the confusion and smoke he ran into the wall instead of the door. He assumed that he had turned the wrong way. He therefore turned back into the building and crawled on his hands and knees past the burning stock container. He escaped through door D2 but was severely burned on his back. The bold arrows show his overall route.

The building contained 50 lb (23 kg) of stock composition but did not exceed the licensed building limit at the time of the accident. Although 50 lb (23 kg) of composition was not required in the building, the runner who delivered fresh composition during the day had delivered a double amount to save a journey.

The issues arising from the accident are simple:

1) Although they did not exceed the licensed limit for the building, the company had not kept the amount of composition to a level consistent with safe operation. A safe system of work would require only the amount of composition necessary for the work in hand to be present at any time.
2) The work boxes used in the building were not self closing, meaning that the initial ignition spread rapidly. Had the boxes been well sealed and self closing, the initial ignition might not have escalated. It is interesting that one of the two plastic stock containers did not ignite proving the benefit of well fitting lids.
3) The company did not have an assessment of the sensitivity of the composition to impact or friction and was not able to demonstrate that the method of filling was appropriate.
4) The accident demonstrated how easy it is to get confused in a fire and how careful design of building layout might help assist escape.

Accident 2

Joseph Green, a safe maker, ran a "small firework factory" in his spare time. The concept of the "small firework factory" is peculiar to the EA 1875 and perhaps requires some explanation. Provision was made under the Explosives Act for local authorities to licence "small firework factories". The law prescribed in some detail what was permissible in terms of buildings, safety distances, allowable activities and quantities of explosives.

The factory in this case was comprised of two process sheds and a magazine. Mr. Green was involved in making "Five Pointed Stars". The report quoted from a pyrotechnist's textbook that was current at the time:

Five Pointed Stars: These are cases about 2 1/2 inches long and 1 inch diameter. Make a bottom to the case with 1/4 inch thickness of plaster of Paris, so that it looks like a large pill-box. Charge it solid and at 3/8 inch from the extremity, that is, 1/8 inch beyond the plaster bottom; round the circumference make five holes as for Saxons; run a bit of match round connecting the holes. These, when fired, stand out at right angles, the plaster towards the spectator, so that the fire resembles a gas fire, with five points.

The cases described were normally made from paper.

The composition usually was comprised of meal powder, sulfur, potassium nitrate and antimony sulphide and when filled in the method described was generally considered by the firework industry to produce a relatively mild firework.

Mr. Green had decided to "improve" on the design by using a tube made from brazed iron or steel sheet. He also decided to fill them with red and green fire composition. Subsequent analysis of the residues suggested that the composition used probably contained barium nitrate, potassium chlorate, sulfur and possibly some carbon.

A five pointed star exploded as Mr. Green was filling it, killing him. His injuries were clearly a result of blast and shrapnel, his hand being amputated and his femoral artery cut.

The lessons are fairly clear:

1) Any attempt to change a design must be analysed carefully and any resulting change in risk or hazard assessed. In this case, the use of a steel or iron container introduced a frictional hazard that Mr. Green did not appreciate. This hazard was increased by the use of a much more sensitive composition.
2) Mr. Green had been holding the firework as he was filling it. He had no protection at all from the effects of the explosion.
3) Mr. Green was no more than a hobbyist with little understanding of the science of pyrotechnics. He simply wasn't competent to judge the suitability of his actions.

Accident 3[9]

Work commenced at 8 am one morning on the filling of 4-1/2 inch (115 mm) rockets in building B6. This was a new product, a trial filling having been carried out the day before. Three women were carrying out this work. The process involved filling tubes with a rocket composition (70% potassium nitrate, 20% charcoal and 10% sulfur). Once filled, the choked ends of the tubes were drilled using a hand drill fitted with a steel drill bit. Drilling was usually done once all filling was complete and then only by one person in the building.

Because the women had little experience in rocket production, they asked the foreman to carry out performance tests on the rockets. The test proved unsuccessful and a further quantity were bored and tested. These tests were successful. It was decided that some further tests would be performed on rockets filled in B6 that day. The layout of the building at the time of the accident is shown in Figure 2.

Filling continued in building B6 during the morning. At approximately 12:30 pm Mr. L., the person tasked with carrying out the further tests, went into the building. He took a tray of filled rockets and placed them on the left of table B. He was located at point 3. At that time there were 5 lb (2.3 kg) of FFF grade gunpowder in a box on table A; on table C there was a partly completed rack of rockets and 1 lb (0.5 kg) of composition; on table B, there were two filled frames and 5 lb of composition; and there was one filled frame of motors and 5 lb of composi-

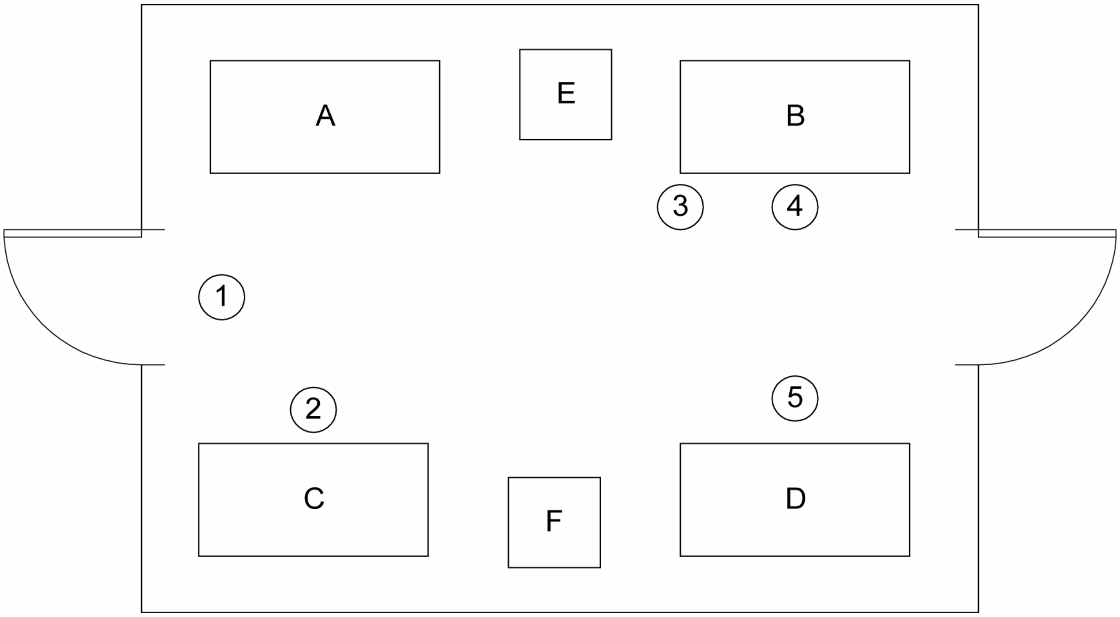

Figure 2. Process building floor plan

tion and on table D. Overall it was estimated that there were 76 lb (35 kg) of composition in the building, well in excess of the 50 lb (23 kg) licensed limit.

Mr. L. had bored two motors and was in the process of boring a third when it ignited. The ignition communicated almost immediately to the gunpowder on table A. The accident resulted in the death of Mr. L. and the women at work positions 2 and 5 with injuries to two other people. The foreman, who was present just inside the building when the ignition occurred, made no comment on Mr. L.'s activity in the building.

The causes and contributory factors are easy to see:

1) The building was overstocked and held explosives not required for the job in hand. The gunpowder on table A was for banger production. This material significantly increased the severity of the accident.
2) The use of a hand drill was not a suitable method of boring rockets. The usual method was to use a cone-shaped bronze needle operated by a lever or a foot treadle. The composition was found to be sensitive to steel on steel, and the suspected cause of the accident was ignition by the drill breaking.
3) The boring should have taken place in a separate building where filling was not being done.
4) The technical knowledge of the supervisory staff was found to be inadequate. The foreman had a total of 12 weeks experience in fireworks manufacture. There were significant failures in supervision.

Accident 4[10]

The building involved in this accident comprised of a series of 4 compartments in a row (A to D). The licence for the building was slightly unusual in that it allowed the use of both chlorate and perchlorate based compositions and compositions not containing these substances, provided that only one type was in use in all the compartments at any time.

At the time of the accident, compartment A was not occupied but contained 25 to 30 lb (11 to 14 kg) of explosive. Compartment B was not in use for manufacture but was being used to help with the transfer of fireworks. It contained between 236 and 300 lb (107–136 kg) of fireworks. Compartments C and D were being used for the filling of bangers. Compartment C was occupied by one woman and held between 100 and 115 lb (45–52 kg) of fireworks. Compartment D was occupied by two women and held between 135 and 160 lb (61–73 kg) of fireworks.

A supervisor of the building was working in another building but walked over to the building concerned to ask the time. He went into compartment B to check whether more tea chests were needed. As he entered the compartment, he saw a flash under a bench behind the steam pipe. He fled the building seeking help. There were two explosions destroying the building and spreading fire to other buildings. All three women were killed. The official investigation and report concluded that the most likely cause of the ignition was grit on the shoes of the supervisor. The key issues were damning:

1) The building was hugely overstocked. The official report estimated that the total inventory of explosives in the building was between 430 and 650 lb (195–295 kg) whereas the licensed limit was 145 lb (66 kg). The report also concluded that the three women would have had a better chance of escape if the inventory had been within the licensed limits. The amount of explosive was such that communication between the compartments was rapid.
2) Many of the operatives did not use protective overshoes. The supervisor who probably caused the ignition admitted that he never wore overshoes. It was suggested that workers were only required to wear overshoes when the government inspector visited. Management claimed that they found it difficult to make workers wear overshoes.
3) There was no effective system to prevent prohibited items such smoking materials from being brought into the factory.
4) Workers were allowed to wear their own clothes, which were often made from man-made fibres and had pockets.
5) A lack of effective control was observed with a tendency by management to disclaim personal responsibility for compliance with the licence and other legal duties. The investigating inspector was satisfied that the conditions applying on the day of the accident were typical for the factory. The accident was inevitable.

Accident 5

A fire occurred in the early hours of the morning burning out a compartment in a process building. The building was unoccupied and no one was hurt. The cause of the fire was a smoke formulation that had spontaneously ignited. The composition contained potassium chlorate, ammonium chloride, kaolin and a resin. Previously the mixture had been wetted with an alcohol and had not presented any problems. The company had changed the process electing to use a solution of gum in water.

The likely cause of the ignition was a chemical reaction between the potassium chlorate and ammonium chloride producing unstable ammonium chlorate—a reaction that required an aqueous environment in order to take place.

This accident demonstrates that it is crucial to understand the chemistry of your compositions. The arbitrary switch from an alcoholic to an aqueous wetting agent had led to a dangerous chemical reaction, which caused the fire. The control and recording of change is particularly important in areas such as research and development and plant design, typical issues being effects of new sources of ingredients, change in processing sequence or conditions and the effects on change in plant behaviour.

Accident 6

A factory had been temporarily closed and was being completely cleared of explosives. A worker had been assigned the task of collecting materials, tools and equipment and moving them off site. The worker was asked to help move rubbish to the burning ground. Paper and other non-explosive waste were being burnt on a bonfire. Nearby was a stack of match frames that were contaminated with blackpowder residues. The worker decided, on his own initiative, to burn these frames off by placing two at a time on the edge of the bonfire and then retrieving them once they had burnt off. He dealt with six frames this way and was carrying another two frames towards the bonfire when they ignited. The ignition spread to the stack of frames (60 frames in all). The worker received burns to his hands, face, neck and midriff (where his jumper and jeans did not meet).

It is not difficult to envisage that the ignition was almost inevitable. The sad fact is that the worker had received no instructions on how to dispose of the frames and, indeed, no instructions to dispose of them.

Accident 7

A fireworks company was asked by another company to dispose of some waste pyrotechnic articles. A test burn showed that the articles burned slowly and agreement was given to burn the main consignment. This work proceeded all day without incident. A second consignment arrived by lorry the following month and its contents were unloaded into a building. This time there seemed to be a mixture of the pyrotechnic articles with containers of composition. Half the load was burned without incident.

Some months later the weather was considered suitable to deal with the remaining half of the second load. The material was laid out and the company director attempted to light the fire with a hand flare. This failed and he took three port fires, lit them and threw them onto the waste. As he turned away the waste ignited with a large fireball, which set his clothes on fire and burned his legs, arms, shoulders and face.

Although a test firing of the original load had been carried out, the company didn't carry out a similar check on the second load, even though it contained composition in addition to the waste articles. The director clearly underestimated the hazard from the second load and stood too close to the waste when he ignited it.

The Lessons from these Accidents

It doesn't take profound analysis to identify the key issues arising from these accidents and their importance to adequate control and management of the manufacture of pyrotechnics—the messages are there for all to see. The question is how do they fit into a wider management structure? It is useful to gather the issues from these accidents into a structured form. These can be listed under a number of key themes, which can be used as a framework for the development of a suitable safety management regime. These themes are listed below.

To those readers whose job includes the management of workers and their safety, "Do you recognise these issues? Do your procedures encompass them? How well does your company address them?"

Competence

- Are workers trained? Not only in terms of the nuts and bolts of the process but also the basic safety issues relating to handling and manipulating explosives and energetic materials in general?
    - Do they understand basic safety procedures?
    - Do they know how to use personal protective equipment correctly?
    - Do they understand the limitations imposed on any given process building?
    - Do they understand why things are done the way they are?
- Are supervisors competent? Not only the issues outlined in the previous paragraph but are they experienced? Have they done the work prior to being promoted?
- Do senior managers have technical competence? Do they understand the basis and rationale behind the safety systems in use? Do they recognise and respect the role of the lower managers or is there a tendency to interfere or over-rule when the occasion or company demands suit them?
- Does your company have a framework of competences identified for each post with a training regime to ensure that employees gain the necessary skills and knowledge? Do you use succession planning to ensure that, when employees leave, trained staff is available to fill the posts if they are vacated?
- How do senior managers ensure that they keep abreast of technical developments, new standards, legislative requirements and industry good practice? Is this information cascaded effectively to staff?

Technical Understanding

- Is the chemistry of the formulations and processes well understood?
- Have the hazards of materials been assessed [e.g., explosive properties, flammability, toxicity, sensitization (e.g., dermatitis, asthma)]?
- Have the properties of the materials (such as sensitiveness, stability, flash points, and other key properties) been assessed?
- Are there procedures in place for monitoring and controlling change in process or materials? How are changes to processes, materials or plant assessed prior to implementation? Is there a system of control and peer review to prevent unauthorised change? Are changes recorded along with the reasons for the change?

Management of the Processing Environment

- Based on the known hazards of the materials are the processing conditions appropriate (e.g., clean areas, overshoes, electrostatic protection, specially made tools)?
- Are hazards controlled to minimise danger to operators? The usual hierarchy of controls in order of priority are:
    - Prevent exposure—options include enclosing the hazardous material, using a less hazardous alternative, remote operation, etc.
    - Use adequate control—minimise the amount of material in process, use Local Exhaust Ventilation (LEV), self closing work boxes, etc.
    - If adequate control cannot be achieved, use Personal Protective Equipment (PPE)—including screens, fire proof clothing, masks, gloves, leather wrist protectors, respirators, machinery guarding, etc.
- Have noise level surveys been carried out (e.g., at proving and test areas)?
- Have all hazardous substances been assessed and control measures identified?
- Are the systems of protection and control based on risk assessments?
- What systems of supervision and control are in place to ensure that the needs of the processing environment are met? For example, appropriate issued clothing and footwear are worn, contraband is excluded, and operating rules and controls are met.
- How are controls implemented? Constant presence of supervisor or spot checks. What inspection regime is in place? Posting of manufacturing and operating instructions. Training of operators. Tool box talks. Is the reporting of "near misses" encouraged (or even mandatory)?
- Manual handling training.
- Routine health monitoring (e.g., blood lead monitoring).
- Maintenance. Provision of suitable tools and equipment. Use lists. Permit to work systems.
- Cleaning. Decontamination. Procedures when changing formulations. Exclusion of incompatible systems (e.g., chlorate with sulphur).

Risk Assessments

- Have risk assessments been prepared for each of the processes taking place?
- Do the assessments include the following elements:
    - Identification of hazards. Are recognised hazard identification tools such as Hazard and Operability (HAZOP) and Hazard Analysis (HAZAN) used?
    - Some method of scoring and ranking hazards.
    - The identification of controlling or mitigating actions.
    - The assessment of the residual risks once controls are applied and comparison to established standards for tolerable risks (in the UK the concept of ALARP is used to assess the acceptability of risks).

    - The application of additional controls until the residual risks are acceptable.

- Is there a robust system for reviewing risk assessments to accommodate change such as in process or formulation?

Burning Grounds

Burning ground activity can be a particular problem area and statistics show that accidents due to lack of control are a major issue. Disposal and burning are frequently seen as being activities not requiring the same level of control and rigor as manufacture. It is somehow perceived as being less hazardous. The reality is that disposal presents a range of issues that are unique and potentially very severe. Frequently the explosives will be in a form not usually encountered in processing. They may be in bulk, under confinement or mixed with other explosives, which can cause a synergistic enhancement of hazards. Assessment of hazards and effective systems of work are crucial.

The disposal of explosives and waste ingredients will inevitably require consideration with regard to long term effects. For example, an accident occurred in the UK where waste ingredients from a firework factory had been buried and the site capped with concrete. After a lengthy period of time there was an explosion. Water seeping through the soil had reacted with metal powders in the waste leading to the evolution of heat and hydrogen.

Finally

A number of incidents are given below with a little detail; I leave the reader to ponder this question:

If you were the manager of a factory and you had had any of these accidents, what actions would you take to prevent them in the future?

- Two lb (0.9 kg) of an experimental mix for stars was sent for destruction. The trial ground staff added a further 4 lb (1.8 kg) and attempted to destroy the lot. On ignition, a detonation occurred. There was no injury to plant or personnel other than 16 factory windows being broken.
- An attempt to extinguish a magnesium fire with a water extinguisher resulted in an explosion that removed the roof of the laboratory and an adjacent wall.
- Pressed stars of a composition including barium nitrate, potassium perchlorate and aluminium ignited spontaneously in an expense magazine during warm weather. A strong smell of ammonia had been noticed in the magazine some minutes previously.
- A tray of 96 formed stars was set to dry with one end resting on the heating system. A spontaneous ignition subsequently occurred—fortunately nobody was injured.
- An ignition occurred as a process worker was using a brass scraper to remove a deposit of blackpowder and nitrocellulose that had built up on the floor of a building used for drying igniter cord. The ignition spread to the contents of the drying compartment.
- A quantity of match composition, which had been mixed by hand, ignited as it was passed through a sieve. The fire spread to other explosives in the compartment and thence to an adjacent compartment. One man died from burns.

Conclusions

Usually the reaction when reading accident reports is “How could they let that happen?” or “It’s obvious you don’t do that.” The simple fact is that accidents do happen whether through carelessness, poor management, slack controls or simply inexplicable behaviour. It’s easy to spot the issues when reading reports on accidents that have happened. It’s not always so simple to spot them before the accident occurs.

Hopefully the lessons from these incidents will strike a chord and, whether you are a manager or actually involved in manufacture, they will raise questions in your minds and prompt you to challenge and possibly change how you do things.

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Contact Addresses

Confederation of British Industry
Explosives Industry Group
Centre Point
103 New Oxford Street
London WC1A 1DU
UK

http://www.eig.org.uk

HSE Books
PO Box 1999
Sudbury, Suffolk CO10 2WA
UK

http://www.hse.gov.uk

Thermodynamics of Black Powder and Aerodynamics of Propelled Aerial Shells

John E. Mercer
18906 107th St. Ct. KPN, Gig Harbor, WA, 98329, USA

ABSTRACT

This paper describes the theoretical basis of a computer code that numerically models firework mortars. The code analyzes both the Black Powder propelling and flight segments of a shell. Equations for the gas dynamics of Black Powder combustion, leakage flow around the shell and aerodynamics of flight are included. Representations for commonly used Black Powder grain sizes allow for simple modeling of test cases. The numerical equation solver in the code uses standard parameters for specifying any mortar test condition. This solver computes every model parameter of the gas and shell dynamics in 2 μs time steps while in the mortar and in 1 ms time steps in flight. The modeling demonstrates that the release of energy from Black Powder is a multi-step process, first from the burning of the grains, next from the latent heat release from condensation, and finally from the latent heat release from fusion. The shell flight dynamics are based on aerodynamic theory employing conventional parameters. Uses of this code include design of mortars, and parametric and safety analyses. The code even includes a crosswind drift analysis for predicting expected dud fallout location. The analytic models were verified on a multitude of test cases, taken from both firework mortars and muzzle loading firearms data. Agreement with the experimental data is within the experimental measurement variation.

Keywords: mortar, latent heat, Black Powder, thermodynamics, aerodynamics, leakage flow, shell drift, muzzle velocity, drag

Introduction

Most people have a fascination with fireworks. In 2001 after viewing a 4th of July display, the author wondered if the dynamics of the mortar firing and shell flight could be modeled to provide an accurate prediction of flight performance. Accurate height predictions and velocity profiles could be used to improve display design, while accurate predictions of mortar pressures and dud fallout location could make fireworks performances safer.

In an effort to address these issues, the author conceived a simple model based on adiabatic, isentropic expansion. The model was programmed in a short time, but the results did not match the available data. This quick, analytical model evolved into more than a 6-month effort that was a major technical challenge.

The initial, simple model assumed that the burning produced packets of compressed gas that would expand isentropically, producing a pressure that would propel the shell from the mortar. Efforts to find any papers or texts on the burning of Black Powder produced references by Conkling,[1] Davis,[2] Shimizu,[3–5] Shidlovskiy,[6] von Maltitz,[7] Sassé,[8] Jones[9] and Freedman.[10] Davis presents extensive information on the products of combustion of Black Powder, including the heat of explosion and combustion temperature. Shidlovskiy presents a model for the burning rate, specific heats as a function of temperature, and approximations for the heats of vaporization and fusion. A burning model and a representative model for the Black Powder grains were developed based on these references. From these models a code was produced for generating the packets of compressed gas. The effort then turned to finding experimental data that could verify the modeling. This search led to articles in the *Journal of Pyrotechnics*[11] and to Shimizu's[12] *Fireworks from* *a Physical Standpoint*. Recently the work of Contestabile[13,14] was brought to the authors' attention. Although the extensive experimental parametric study by Contestabile was not included in the comparisons presented here, it should be key to further refinements of the model.

Shimizu' work[12] contains both experimental data and a parametric model for the mortar firing dynamics. Using the parametric model, Kosanke[11] performed a study of the sensitivity of mortar dynamics to parameter variations. Shimizu's model was based on equations developed for smokeless powder. However, smokeless powder produces entirely gaseous products while Black Powder has substantial nongaseous products. As will be shown, these nongaseous products play a major role in the gas expansion process. The Shimizu model, therefore, can only account for small perturbations from the basic model. Regardless of the model, the experimental data were excellent.

In an effort to verify any proposed universal model, data from the other end of the spectrum from firework mortars was sought. This search led to Black Powder muzzle loading data sources.[15] These data extremes were used to validate the isentropic model. The test validations revealed that the isentropic expansion model was not accurate and did not follow the data trends. Several patches and "fudge factors" were added to the model, but they did not produce the correlation expected of a good model. The simple model was abandoned.

The revised analysis was based on the fundamentals of thermodynamics. The fundamental model revealed, as mentioned above, that the particulate matter, which had been ignored in the earlier analysis, was critical to the modeling. In fact it was discovered that the delayed release of heat from the phase transitions of condensing and solidifying products of combustion were key elements to the propelling characteristics of Black Powder.

This paper describes the analytical model that accurately predicts the burning and gas dynamics of Black Powder as a propellant including leakage effects during shell launch. It also describes the aerodynamic model that predicts the flight characteristics of shells including drift due to crosswinds. A description of the numerical code that solves the equations for these models presents the input and output parameters currently used.

Models Used in the Program

Black Powder Thermodynamics

The first law of thermodynamics provides the fundamental concept for modeling the forces acting on the shell to accelerate it while in the mortar. The first law is expressed in differential form as:

$$\frac{dU}{dt} = \frac{dQ}{dt} - \frac{d\int PdV}{dt}$$

where U is the internal energy, Q is the heat, P is the gas pressure and dV is the change in volume of gases. The integral

$$\int PdV$$

represents the work done.

The internal energy, U, is generally expressed as:

$$U = C_v T$$

where C_v is the specific heat at constant volume and T is the temperature of the gas. The left side of the first law equation becomes:

$$\frac{dU}{dt} = C_v \frac{dT}{dt} + T\frac{dC_v}{dt}$$

The second term reflects the change in specific heat, C_v, with temperature. Specific heat for a gas depends on whether the gas molecule is monatomic, diatomic or polyatomic. The variation is due to the different degrees of freedom of motion for the different molecular structures. The value of C_v is relatively constant at near ambient temperatures, but at higher temperatures the value increases because of additional degrees of freedom associated with intramolecular vibrational modes.

The heat term, Q, has two components. The first component is the immediate heat released at the instant of combustion, and a second component is associated with the delayed release of heat due to phase changes of the combustion products.

Table 1. Black Powder Data Based on Davis.[2]

Heat of explosion = 718.1 cal/g
Explosion temperature = 2770 °C

Mass of gases/mass of Black Powder = 0.4298
Mass of solids/mass of Black Powder = 0.5591
Mass of water/mass of Black Powder = 0.0111
Moles of gas/kilogram of Black Powder= 12.14
Average gram molecular mass of gases = 35.41

Gases		Solids			Temperature (°C)		Vapor Phase		
Volume (%)		Mass (%)		Mol Mass	Fusion	Vapor.	Particles	(%)	Mol Mass
CO_2	49.29	K_2CO_3	61.03	138.21	891	d	K_2O	41.59	94.19
CO	12.47	K_2SO_4	15.10	174.27	588	1689	CO_2	19.44	44.01
N_2	32.91	K_2S	14.45	110.27	840		K_2SO_4	15.10	174.27
H_2S	2.65	KNCS	0.22	97.18	173.2	d 500	K_2S	14.45	110.27
CH_4	0.43	KNO_3	0.27	101.11	334	d 400	KNCS	0.22	97.18
H_2	2.19	$(NH_4)_2CO_3{\cdot}H_2O$	0.08	114.1	d 58		KNO_3	0.27	101.11
54.56% polyatomic		S_8	8.74	256.5	112.8	444.7	$(NH_4)_2CO_3{\cdot}H_2O$	0.08	114.1
		C	0.08	12.01	4827	4827	S_8	8.74	256.5
45.38% diatomic							C	0.08	12.01
		Average gram molecular mass of solids = 149.6 Average atoms/molecule = 5.27			Average Fusion Temperature = 1042 K		Average gram molecular mass of vapor = 113.0		

Notes: K_2O will also dissociate according to Reference 16. This effect was found to have a negligible impact on the results.
Mass and temperature data provided by Reference 16.

Table 1, taken mainly from data provided by Davis,[2] provides the characteristics of Black Powder used in the model. The heat of explosion, Q_{exp}, and the weights and volumes of the products of combustion were used directly with one modification. Potassium carbonate, K_2CO_3, the main component of the condensed products, does not exist as a vapor. The model treats K_2CO_3 the same as the other nongaseous components, below the vaporization temperature, to calculate the mean fusion temperature but assumes that it dissociates above the fusion temperature.

Rather than having individual vaporization and fusion temperatures associated with each of the phase changing products* of combustion, the model was simplified by having only one representative vaporization and one representative fusion temperature. A mean value is used for the fusion temperature based on published data.[16] No comprehensive data could be found for the vaporization and dissociation temperatures so a single vaporization-dissociation temperature was determined by adjusting the temperature to give the best comparison of the model's predictions to the available experimental data.

Shidlovskiy[6] provides average values for C_v over a temperature range for the different molecular structures (i.e., monatomic, diatomic and polyatomic). These values were used to compute a segmented-linearized approximation to the temperature variation of specific heat for each of the molecular structures. Scaling, corresponding to the instantaneous mix of constituents, is used to calculate instantaneous values of C_v. The constituents of air are diatomic (excluding the trace components) so the diatomic C_v value is used for it. Derivatives of C_v are calculated from the linearized approximation.

Numerical experimentation, using the complete code to minimize the error between computed and experimental results, provided the following temperatures and heat parameters for Black Powder:

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* The term "phase changing products" refers to those products of combustion that eventually become solid but are formed initially as gases.

$$T_{vap} = 2400 \text{ K}$$

$$T_{fus} = 1042 \text{ K}$$

$$Q_{vap} = 4.44 \times 10^6 \text{ J/kg}$$

$$Q_{fus} = 6.85 \times 10^5 \text{ J/kg}$$

where T_{vap} is the vaporization temperature, T_{fus} is the fusion temperature, Q_{vap} is the latent heat of vaporization, and Q_{fus} is the latent heat of fusion.

These heat values, determined by the model, indicate that only 5% of the total heat is released at the instant of combustion while the other 95% is released subsequently. These model heat values indicate that 82% of the heat of explosion is associated with the latent heat of vaporization and ionization energy while 13% of the heat of explosion is associated with the latent heat of fusion. The author believes that much of the heat of combustion goes into ionizing the products of combustion. Davis[2] provides an experimental measurement for the combustion temperature of Black Powder as 3043 K. This temperature is well above the temperatures for fusion and vaporization and most likely produces most or all of the combustion products in an ionized state. The current model does not include ionizing energy effects, and as a consequence, the numerical experimentation results presented above produced values that did not comply with the approximate formulas specified by Shidlovskiy.[6] The heat of vaporization was 60% of the formula value while the heat of fusion value was twice the formula value, yet the overall match to the experimental data is good. By not specifically providing a model for the ionic energy release mechanism, the model accommodates this phenomenon by altering the available modeling parameters, including the apparent vaporization temperature, drawing it closer to the combustion temperature and reducing the apparent heat of vaporization as compared to Shidlovskiy's approximation. The computed heat of fusion is also affected, producing a greater heat release at the mean fusion temperature. The numerical error minimization procedure produced these values so that the heat release model would closely approximate the actual physical heat release. The next generation model should include a separate model for the latent ionic energy release to provide a better overall heat release model.

The modeling revealed that approximately 3 to 15% of the available latent heat of vaporization/ionization is released as the projectile moves through the barrel or mortar. The model also revealed that there was negligible heat released from the fusion process since the muzzle temperatures of the test cases were at or above the fusion temperature. For the particular cases modeled, the time from combustion initiation to projectile exit ranged from 1.1 to 13 ms. This means that the time scale for latent heat release is of the order of milliseconds. As will be shown later in this paper, the rate of heat release depends on both time and the gas expansion profile that determines the instantaneous gas temperature. The latent heat release is therefore a critical factor in the thermodynamics of the process since the energy released from latent heat is of the same order of magnitude as the energy released at the instant of combustion.

Black Powder Particle Model

Table 2 provides the screen sizes for various industry standard grain sizes.[11,12,17] Shimizu,[4] Sassé,[8] and Jones[9] considered various modeling of the Black Powder grains. Some of the authors used ellipsoidal shapes while others used a combination of spheres and cubes. Although the particles have irregular shapes, the author decided to represent the particles as spheres with an equal radius probability distribution over the range from minimum to maximum screen size. Since the burning rate is related to the surface area, a weighted average based on surface area is used to model the particle. The equations describing the model are:

$$\frac{dN}{dr} = K$$

$$N = \int_{r_{min}}^{r_{max}} K \, dr = K\left(r_{max} - r_{min}\right)$$

$$r^2_{mean} = \frac{1}{N}\int_{N_{min}}^{N_{max}} r^2 dN = \frac{1}{N}\int_{r_{min}}^{r_{max}} r^2 K \, dr$$

$$r_{rms} = \sqrt{\frac{\left(r^3_{max} - r^3_{min}\right)}{3\left(r_{max} - r_{min}\right)}}$$

where N is the number of particles and K is the probability distribution constant. The mean radius, r_{rms}, represents the particle with the root mean square area. The number of particles of Black Powder in the powder charge is:

Table 2. Black Powder Screen Sizes.

Designation	Radius Values (cm)		Ref.
	Min. Size	Max. Size	
FA	0.20	0.40	12
2FA	0.084	0.24	12
3FA	0.060	0.10	12
4FA	0.042	0.084	12
5FA	0.015	0.042	12
6FA	0.015	0.030	12
7FA	0.0075	0.021	12
Meal D	0.0	0.021	12
Fg	0.060	0.084	12
2Fg	0.030	0.060	12
3Fg	0.015	0.042	12
4Fg	0.0075	0.021	12
0	0.020	0.060	6
1	0.010	0.020	6
2	0.020	0.060	6
3	0.060	0.085	6
4	0.12	0.17	6

$$N_{BP} = \frac{M_{BP}}{\frac{4}{3}\pi r_{rms}^{3}\rho_{BP}}$$

where ρ_{BP} is the density of Black Powder particles, assumed to be 1750 kg/m^3.

There are some differences between the shapes of powders of different granulation. For example, the Fg powders are glazed while the FA powders are not. Glazing tends to eliminate sharp edges and to make the grains closer to spherical. These differences can be handled in the model by adjusting the apparent particle burn rate based on the changing geometry as the particle burns. The author did not have sufficient experimental data to resolve this effect, so the spherical model was used for all granulations.

Ignition Propagation Rate Model

The propagation of flame through the particles is modeled as an exponential function. The underlying assumption is that the rate of increase of ignition is proportional to the number of ignited particles.

$$N = N_0 e^{P_r t}$$

where N_0 is the initial number of particles ignited by the fuse or percussion cap and P_r is the propagation rate. Numerical experimentation yielded a propagation rate of 5000 particles per second for a good match to the available data. The value of N_0 for fuse ignition is set to $0.1\,N_{BP}$ while that for percussion cap ignition is set to $0.5\,N_{BP}$. Numerical experimentation did not show a strong dependence on this initial value since the propagation rate is very fast compared to the total burn time.

Burn Rate Model

The burn rate model is taken from a combination of models presented in Shidlovskiy[6] and Conkling.[1] The burn rate is given by,

$$\frac{dr_{BP}}{dt} = B e^{\alpha T_{BP}} P_{atm}^{\eta}$$

where r_{BP} is the radius of the Black Powder particle, T_{BP} is the temperature of the Black Powder in °C, P_{atm} is the pressure of the gases in atmospheres, α is the exponential temperature dependence coefficient, B is the linear burn rate at standard conditions and η is the exponential dependence of burn rate on pressure. An optimized fit of the models to the experimental data taken from references 12 and 15, showed that the value of B is 0.0115 m/s, slightly less than the value given by Conkling and Shidlovskiy. The optimized value of η was found to be 0.30, slightly greater than that given by Conkling and Shidlovskiy. Since the available experimental data were recorded at near standard temperatures, the value for α was set to 1.5×10^{-3}/°C, the average value specified in Shidlovskiy.

The burning of the Black Powder produces an immediate heat release equal to the change in mass times the heat of explosion less the latent heats of vaporization and fusion.

$$\frac{dQ}{dt} = 4\pi r^2 \rho_{BP} \frac{dr_{BP}}{dt}\left(Q_{exp} - Q_{vap} - Q_{fus}\right)$$

where ρ_{BP} is the density of the Black Powder particle as defined above, Q_{exp} is the heat of explosion per unit mass and Q_{vap} and Q_{fus} are the latent heats per unit mass of the burning products that participate in the phase change model described below. The value of Q_{exp} used in this study is 3.014×10^6 J/kg as specified in Davis.[2]

Latent Heat Release Model

The phase changing components of combustion, which eventually become solid particles, are assumed to be produced as gases that cool by radiation and convection heat transfer at a rate based on the surrounding gas temperature. To simplify the modeling, the delayed release of sensible heat from these components is ignored since it is much less than their latent heats of vaporization and fusion. As the combustion process progresses, a portion of the gases cool and condense into liquids releasing their heat of vaporization. Further cooling releases their heat of fusion.

The cooling of these phase changing components consists of two mechanisms, as stated above: radiation and convection. The rate of mass phase conversion per unit mass due to radiation is dependent on the fourth power of the temperature and is modeled as:

$$R_v = k_R\left(T_{vap}^4 - T^4\right)$$

where R_v is the rate of mass phase conversion per unit mass kg/kg-s due to condensation of vapor, k_R is the coefficient of the conversion rate, T_{vap} is the vaporization temperature and T is the gas temperature.

For transition through the fusion regime the relation becomes:

$$R_f = k_R\left(T_{fus}^4 - T^4\right)$$

The variables are defined as above except that the fusion temperature, T_{fus}, replaces T_{vap}. The rate coefficient k_R is assumed to be the same for both phases. Numerical experimentation provided a value of 5.0×10^{-14}/s-$(K)^4$ for k_R.

The rate of mass phase conversion per unit mass due to convection was assumed to be proportional to the temperature difference and the rate of molecular collisions. This rate is a function of the molecular density of the gaseous constituents, ρ_{mole}, and the speed of the molecules, which is proportional to $\sqrt{T}$. The rate of mass phase conversion per unit mass kg/kg-s due to convection is:

$$C_{vap} = k_C\rho_{mole}\sqrt{T}\left(T_{vap} - T\right)$$

where k_C is the proportionality constant found to be 2.5×10^{-6} m^3/s-mol-(K)$^{3/2}$ by an optimization study.

For the fusion regime the formula remains the same except for substitution of T_{fus} for $T_{vap.}$

$$C_{fus} = k_C\rho_{mole}\sqrt{T}\left(T_{fus} - T\right)$$

The rate of conversion of the total mass from one regime to another is the rate of mass conversion per unit mass times the mass undergoing conversion:

$$\frac{dM_{(gas\leftrightarrow liquid,\,liquid\leftrightarrow solid)}}{dt} = \left(R_{(vap,fus)} + C_{(vap,fus)}\right)M_{(gas,liquid,solid)}$$

where $M_{(gas\leftrightarrow liquid)}$ is the mass of condensing vapor or vaporizing liquid (in the vapor transition regime) and $M_{(liquid\leftrightarrow solid)}$ is the mass of solidifying liquid or fusing solid (in the fusion transition regime). The choice of the mass value on the right hand side of the equation depends on the temperature of the gas relative to the phase transition temperature. For example, for a temperature above the fusion temperature, the appropriate mass to use is the solid mass and for a temperature below the fusion temperature the appropriate mass is the liquid mass. The calculation of these masses is described in detail later in this section. The heat release is then:

$$\frac{dQ}{dt} = \frac{dM_{(gas\to liquid)}}{dt}Q_{vap} + \frac{dM_{(liquid\to solid)}}{dt}Q_{fus}$$

where Q_{vap} and Q_{fus} are the latent heat values per unit mass (vaporization or fusion).

The mass conversion calculation is part of the latent heat model. The basic scenario for mass conversion modeling is that the burning powder creates gases that will eventually become particles, first liquid then solid particles. This gaseous mass is M_{gas}. The net rate of change of the mass of gas is:

$$\frac{dM_{gas}}{dt} = \kappa\frac{dM_{BP}}{dt} - \frac{dM_{(gas\to liquid)}}{dt}$$

where dM_{BP}/dt is the mass burn rate of the Black Powder, κ is the fraction of the Black Powder mass that is converted to gaseous components that participate in the latent heat release, and dM_{gas}/dt is the net rate of increase in the mass of gas. If the temperature of the gases is below the vaporization temperature then $dM_{(gas\rightarrow liquid)}/dt$ will be positive and will remove mass from the gas phase. If it is negative, it will add mass to the gas phase by converting liquid.

The net rate of change of the liquid particle mass is:

$$\frac{dM_{liquid}}{dt}=\frac{dM_{(gas\rightarrow liquid)}}{dt}-\frac{dM_{(liquid\rightarrow solid)}}{dt}$$

where dM_{liquid}/dt is the rate of increase of the liquid mass.

The net rate of change of solid particle mass is:

$$\frac{dM_{solid}}{dt}=\frac{dM_{(liquid\rightarrow solid)}}{dt}$$

If the temperature is above the fusion temperature, any solid mass will be converted to liquid mass and dM_{solid}/dt will be negative.

The mass of matter residing in each phase is tracked using the above equations. This mass in each phase is represented as $M_{(gas,liquid,solid)}$ in the prior equations for computing the latent heat release.

Pressure Model

Freedman[10] and Belov[18] address the non-ideal effect of extreme pressure. Although the pressures in the mortar barrel are high, the author felt that they were not extreme enough to significantly influence the results for fireworks mortars; therefore these non-ideal effects are not included in the present model. The pressure model uses the perfect gas relationship for computing the combustion pressure:

$$P_{comb}=\frac{nR_{const}T}{V}$$

where R_{const} is the universal gas constant, n is the instantaneous total number of moles of gaseous constituents present and V is the volume of the combustion chamber less the volumes of the unburned Black Powder, the condensed matter and the volume of the shell that extends below the reference plane (below the equator for a spherical shell and the bottom of a cylindrical shell). The temperature, T, is calculated from the internal energy term in the first law equation. The volume, V, comes from the dynamic equations for the shell movement.

Leakage Model

The last element of the combustion dynamics model is the calculation of gas and particulate matter leakage around the shell. The model assumes that the gases and condensed particulates are a homogeneous blend and are therefore proportionately ejected through the gap. It ignores any unburnt particles of Black Powder that might be ejected from the combustion volume. The basis for the last assumption is the density and initial size of the Black Powder particles. Inertial and gravitational forces more heavily influence the large particles and tend to keep them in place. When the unburnt particles become smaller and more easily transported by the flowing gases, their persistence becomes very short and therefore less likely to transport significant mass through the gap.

Several different model possibilities were examined. The one chosen that most closely matches the data is based on compressible isentropic flow with the momentum equation altered to accommodate the nongaseous particulate matter. The derivation of the isentropic flow equations can be found in gas dynamics texts such as Shapiro.[19] The compressible flow model limits the Mach number through the narrowest portion of the gap between the shell and the barrel to ≤ 1. Increasing the chamber pressure beyond a critical pressure will cause the flow to "choke" and the Mach number will remain at 1. The critical ratio of the pressure ahead of the shell to the combustion pressure is:

$$r_{crit}=\left(1+\varepsilon\frac{\bar{\gamma}-1}{2}\right)^{-\frac{\bar{\gamma}}{\bar{\gamma}-1}}$$

where $\bar{\gamma}$ is the average ratio of specific heats (C_p/C_v) and ε is the ratio of total mass (gas + particulate) to the mass of the gas alone. C_p is the specific heat at constant pressure and is equivalent to $C_v + R_{const}$. The density of the gas as it passes through the gap between the shell and the barrel is then:

$$\rho_{gap}=\bar{\rho}\,r^{\frac{1}{\bar{\gamma}}} \qquad r\geq r_{crit}$$

where $\overline{\rho}$ is the bulk density of the gas components in the combustion volume and r is the ratio of the pressure ahead of the shell to the combustion pressure. If r is $< r_{crit}$ then r is set to r_{crit} to model the choking effect.

The speed of sound in the gap, a, is given by:

$$a = \sqrt{\frac{\overline{\gamma}\, P_{comb} r}{\rho_{gap}}} \qquad r \geq r_{crit}$$

The Mach number, M, of the gas flow through the gap is given by:

$$M = \sqrt{\frac{r^{-\left(1-\frac{1}{\overline{\gamma}}\right)} - 1}{\varepsilon \frac{\overline{\gamma} - 1}{2}}} \qquad r \geq r_{crit}$$

The velocity through the gap, v_{gap}, is then:

$$v_{gap} = aM$$

The leakage fraction rate, dL/dt, is defined as the rate of gas mass loss divided by the total gas mass in the combustion chamber:

$$\frac{dL}{dt} = C_f v_{gap} \left(A_{gun} - A_{shell} \right) \frac{\rho_{gap}}{\overline{\rho}\, V}$$

C_f is a flow coefficient to account for viscous and non-uniform flow effects. Viscosity will reduce the flow velocity on the wall of the barrel and on the surface of the shell, causing a reduction of the overall flow rate. C_f was numerically determined from an optimization study to be 1.0 for round shells, in other words the viscous effects were negligible. For cylindrical shells the viscous effect is expected to be much greater since the length of the gap is much greater. The greater gap length will cause a thicker boundary layer that will reduce the effective gap flow area. There may also be other effects that influence cylindrical shell leakage such as deformations or non-concentric motion in the mortar. The terms in parentheses in the above equation represents the gap area. A_{gun} is the mortar cross-sectional area based on the internal diameter of the mortar and A_{shell} is the shell cross-sectional area based on the outside diameter of the shell. Assuming a homogeneous mix of all the constituents, this leakage fraction term also represents the rate of loss of each of the constituents at any instant. As this factor accounts for the loss of constituents, the burning of the powder adds to the constituents causing the mix to change with time.

Shell Dynamics in Barrel Model

The shell dynamics model assumes that the pressure is uniform on both the combustion chamber side of the shell and the opposite side of the shell. The pressure on the opposite side is calculated by assuming that, as the shell leaves the mortar, the air ahead of it must be pushed out as a slug moving at the speed of the shell. Correspondingly, the pressure acting on the shell is the total pressure:

$$P_{total} = \frac{1}{2} \rho_{air} v_{shell}^2 + P_{air}$$

where P_{air} is the ambient air pressure.

Having defined the equations for the pressure acting on the shell, the complete dynamic equation for the shell movement is:

$$\frac{d^2 x_{shell}}{dt^2} = \frac{\left(P_{comb} - P_{total}\right) A_{shell}}{m_{shell}} - g$$

where x_{shell} is the shell position along the barrel axis, m_{shell} is the mass of the shell and g is the gravitation acceleration constant. This assumes the mortar is fired vertically, if not, then the vector component of the gravitational acceleration along the barrel must be substituted for g. This equation is integrated to calculate the velocity and integrated again to compute the position within the barrel.

Shell Flight Model

Once the shell leaves the barrel more complex aerodynamic forces will act on it. These forces will depend on air density, air viscosity, shape and surface roughness of the shell, etc. The current model has been verified only for spherical shells and the experimental comparisons will only focus on this configuration. The classical source of data on the aerodynamics of spheres is from Hoerner.[20] There have also been studies on the aerodynamics of baseballs.[21] All these studies show similar results for the drag characteristics. The drag on a body moving through the air has a basic dependence that is represented by:

$$D_{shell} = \frac{1}{2} \rho_{air} v^2 C_D \left(R_N \right) A_{shell}$$

where C_D (R_N) is the drag coefficient and is a function of the Reynolds number, R_N. $1/2\rho_{air}v^2$ is the dynamic pressure. The Reynolds number is defined as:

$$R_N = \frac{\rho_{air} v d_{shell}}{\mu_{air}}$$

Here, ρ_{air} is the air density, v is the shell velocity, d_{shell} is the diameter of the shell and μ_{air} is the viscosity of air. All the data show that at low speed (low R_N), C_D (R_N) is higher than at high speeds as shown in Figure 1. This is caused by a laminar boundary layer that separates from the shell near the maximum diameter at slow speed (low Reynolds number). At higher speeds the boundary layer becomes turbulent and remains attached past the maximum diameter. The increased extent of attached flow lowers the drag coefficient.

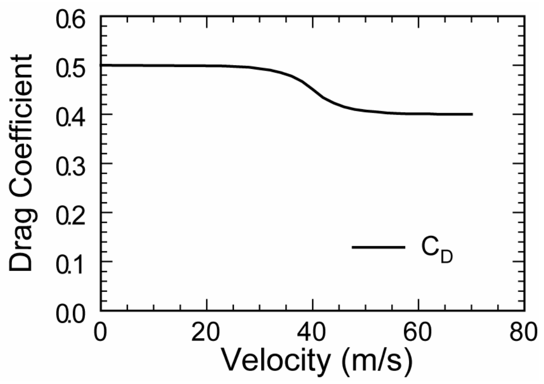

Figure 1. Drag coefficient of a sphere as a function of velocity

A simple model for the drag on a shell is to have one drag coefficient below a transition Reynolds number and another above that transition number. All the experimental data[20,21] show that the transition Reynolds number, R_T, is approximately 400,000. These data also show that the magnitude of the two drag coefficients varies with the surface roughness of the sphere and that the coefficient transitions smoothly from one drag coefficient to the other over a range of Reynolds numbers.

The drag model used in the current study uses two exponential functions to provide this smooth transition:

$$C_D \left(R_N \right) = C_{D_{min}} + \left(C_{D_{max}} - C_{D_{min}} \right) e^{\frac{R_T - R_N}{\Delta R_N}} \qquad R_N \geq R_T$$

$$C_D \left(R_N \right) = C_{D_{max}} - \left(C_{D_{max}} - C_{D_{min}} \right) e^{\frac{R_N - R_T}{\Delta R_N}} \qquad R_N < R_T$$

ΔR_N was set to 50,000 to match experimental data. Comparisons were made with the experimental data. The results set $C_{D_{min}}$ at 0.4 and $C_{D_{max}}$ at 0.5. These values compare favorably with Shimizu[4] who used a single value of 0.472 in his model without any Reynolds number variation.

The above discussion pertained to spherical shells; however the basic drag model can be used for cylindrical shells as well. Cylindrical aerial shells generally do not have longitudinal stabilization so they tumble through the air. This affects both the reference cross-sectional area and the drag coefficient. A proposed model for cylindrical shells assumes the area for the reference in the drag equation is the average area exposed to the flow:

$$A_{ref} = 0.5 \left(\frac{\pi d_{shell}^2}{4} + d_{shell} \; l_{shell} \right)$$

where d_{shell} and l_{shell} are the diameter and length of the cylindrical shell, respectively. The drag coefficient and the dependence on Reynolds number remains to be determined from experimental data but is expected to be between 0.5 and 1.0.

One limitation of this model is that the flow velocity over the shell must not approach the speed of sound where compressible effects would impact the drag. For spheres, the shell velocity that produces sonic flow over the shell is about half the speed of sound. Most fireworks shells should not encounter sonic flow effects, but firearm projectiles would generally operate at and beyond the sonic regime.

One last consideration is the force of gravity on the shell. As the shell exits the barrel, the dominant force is the aerodynamic drag, but as the shell approaches apogee and the velocity is greatly diminished, gravity becomes the dominant force.

The equation of motion for a shell fired from a vertically oriented mortar, accounting for both aerodynamic drag and gravitational force, is:

$$\frac{d^2 x_{shell}}{dt^2} = -\frac{D_{shell}}{m_{shell}} - g$$

Solving this equation for vertical position, x, and velocity, $\frac{dx}{dt}$, provides the apogee, the impact velocity, if the shell remains intact and returns to $x = 0$, and the elapsed times associated with theses locations.

As discussed above, if the shell is not fired vertically, the forces are divided into the vector components and integrated to compute the velocities and displacements along the additional coordinates.

The numerical code for the flight analysis also incorporates the effects of side winds. The side wind is added vectorially to the shell velocity to produce a new dynamic pressure, and the drag vector is aligned with the total velocity vector. This results in the drag having two components: one aligned with the initial direction of flight and the other transverse to that direction. This produces two differential equations, one for each direction, which must be solved. The side wind model is used to calculate drift for both the apogee position and dud fallout location.

Numerical Equation Solver

All the above equations were incorporated in a numerical solver. The solver is a simple time step routine that updates the variables every 2 μs for the combustion model (shell in mortar) and every 1 ms for the free-air model (shell in flight). The solving process starts with an initial set of conditions computed from the input parameters. The void in the combustion chamber is assumed to be filled with air at ambient conditions (also specified). The dynamic equation solver calculates the amount of Black Powder burned over a time step. This calculation is based on the ignition propagation model and the burn rate model previously discussed. Ignited particles will have a burn rate that depends on how much time has elapsed from the ignition time. Eventually particles will burn away and no longer contribute to the process. The sum of the individual burn rates from all the ignited particles provides the total burn rate for a time step. The numerical process is a discretized convolution integral with the burn rate model being the kernel function. Then, using the burn rate result, the code calculates the new constituent mix and heat added. The heat added from the burned Black Powder and the latent heat released from phase changes cause a change in the internal energy, altering the temperature. The new temperature and moles of gas produce a new pressure. In the same time step, the leakage is computed and used to update the mass of the constituents including those involved in the phase changes. The combustion pressure and total pressure act on the shell to accelerate it. The acceleration is integrated with a second order accurate algorithm to calculate a new velocity. That same algorithm is used to calculate the new position of the shell in the mortar and in turn, the change in the volume, density, etc. The variables are all updated and the process is repeated for the next time interval.

Once the shell leaves the barrel, the calculation switches to the aerodynamic model. The aerodynamic force and the gravitational force decelerate the shell. These forces are integrated, again using a second order accurate algorithm, to produce a new velocity. The new velocity is used to calculate a new Reynolds number and the dependent drag coefficient. The velocity is integrated with the same second order algorithm to calculate the new shell position.

The input variables to the solver are commonly used to define a mortar set-up. These input specification variables provide a great deal of freedom in modeling various arrangements. Analyses such as the effect of shell standoff in the mortar, mortar length or the effects of shell diameter changes can be readily performed. The ambient temperature and elevation are input parameters that are used to correct for density, viscosity, pressure and temperature effects.

The atmospheric pressure model is based on a standard atmosphere so that the input parameter is elevation. With these input variables it is possible to examine the difference between a cold day on an ocean beach versus a hot day, high in the mountains.

The wind speed input is used to calculate the drift on the shell based on the drag model and a rotation of the drag vector based on the angle of attack of the shell. The drift calculation predicts the displacement of a vertically fired shell for the given wind speed and the impact velocity and total time to impact from firing if it falls to the ground unexploded.

Since the solver calculates every detail of the firing and flight process, it can provide a detailed analysis of temperature and pressure or any other calculated parameter as a function of time, mortar position or any other independent variable. Also peak values or mean values can be calculated.

The code variables for input and output that have been selected are shown below; starting with the input parameters:

- Units (Imperial or metric; output values are given in the same units as specified for the input parameters)
- Mortar inside diameter
- Mortar length
- Shell type (spherical or cylindrical). The program was written to handle both types, but only the spherical shell portion was verified with experimental data.)
- Shell diameter (also length for cylindrical shells)
- Shell mass
- Standoff in mortar (program calculates dead volume). The standoff is defined as the distance from the equator of a spherical shell to the top of the end plug. For cylindrical shells it is the distance from the bottom of the shell to the top of the end plug. The program calculates the volume of the lift charge based on a bulk density of about ½ the particle density and makes certain that there is enough volume to accommodate the charge. If not, the shell is displaced upward to allow for the lift charge. For calculating position of the shell, a convenient reference is the bottom of cylindrical shells and equator of spherical shells.
- Black Powder mass
- Black Powder grain size (e.g., 2FA, 3Fg, “0”, etc.)
- Ambient temperature
- Elevation
- Wind speed
- Ignition source (percussion cap vs. electric match or fuse)

Output calculated values are:

- Dead volume (due to standoff and Black Powder volume)
- Time to end of ignition
- Time to exit muzzle
- Unburned Black Powder at muzzle exit or powder burn time
- Barrel pressure at muzzle exit
- Maximum barrel pressure (MBP)
- Shell position at MBP
- Maximum gas temperature
- Percentage of total gas generated lost as leakage through gap
- Maximum acceleration
- Muzzle velocity
- Apogee height
- Drift at apogee due to side wind
- Time to apogee
- Terminal velocity
- Drift at impact with ground
- Side velocity at impact
- Total time

Model Verification

Two sources of empirical data were obtained. One was from Shimizu[12] for mortar internal diameters ranging from 7.6 to 30.5 cm, shown in Table 3. These data are for numerous test firings. A few parameters are missing from some test cases while other parameters are presented with statistical variations. The second set of data shown in Table 4 is from Kirkland.[15] The catalog has many tables of muzzle velocity versus powder load for muzzle loading Black Powder firearms. Only two sets of data were selected for comparison because they were specifically documented as chronographic meas-

Table 3. Shimizu's Data for Shooting Spherical Shells under "Normal Conditions".

Mortar ID (cm)	7.6	9.2	9.2	12.3	15.5	15.5	18.8	21.9	24.9	30.5
Length (cm)	44.6	81	81	89.5	103	103	119	134.4	148	142
Shell Dia. (cm)	7	8.4	8.4	11.5	14.2	14.2	17.4	20.4	23.5	29
Mass Sh. (kg)	0.208	0.22	0.115	0.53	1.25	0.61	2.115	3.17	4.83	8.27
Mass BP (kg)	0.013	0.02	0.02	0.038	0.075	0.075	0.131	0.17	0.28	0.45
Muz. Vel. (m/s)		103.9	122.2	104.9	119.6	151.9	118.7		150.5	114.8
Std. Dev.					6.5	10				
Height (m)	108	149	132	191	263	208	284	353	406	340
Std. Dev.		13.1	11.8		18.2	9.1				
Rise Time (s)	3.9	4.8	3.8		6.9	5.4	6.6	8.3	8.4	8.2
Std. Dev.		0.38	0.29		0.34	0.56				
No. of Samples	2	15	15	2	15	15	2	2	3	3
	Computed Values									
Muz. Vel. (m/s)	84.6	106.8	130.7	112.4	107.5	139.5	123.5	120.3	144.2	146.7
Height (m)	161	170.5	130.2	205.9	248.4	205.8	302.9	308.5	395	426
Rise Time (s)	5.04	4.91	3.94	5.47	6.24	5.18	6.81	6.94	7.74	8.09

Notes: The Black Powder grain size used was "0".

All computed standard deviations for data in this table are computed using the difference between the computed and measured values divided by the measured value expressed in percent. The measured standard deviations are in the parameters' units.

urements provided with configuration and powder charge specifications. One set of data is for a pistol and the other is for a rifle. The set of data for the pistol was presented with a maximum variation.

The data used covers a wide range of parameters including: barrel exit times from 1.1 to 15 ms, muzzle velocities from 282 to 2227 ft/s (86 to 679 m/s), maximum barrel pressures from 13 to 570 atm and gas leakage from 0 to 45%. These data were used in an optimization study to refine: time constants, latent heat values, leakage flow coefficient, Black Powder burn rate dependence and drag coefficients. The refined parameters were then fixed and remained unchanged for all the test cases.

Figure 2 shows the results for the flight model verification. The experimentally measured muzzle velocity from the Shimizu[12] data along with the shell diameter and mass were used for input. The figure shows the comparison of the calculated results with the measured

Table 4. Raw Data from the Dixie Gun Works, Inc.[15]

Pistol Muzzle Velocity Data for .40 cal., 9-inch Barrel Ball Size = 0.395 in.				
Charge (gr)	Velocity (fps)	Variation (± fps)	Variation (%)	Comp. Vel. (fps)
20	816	49	6	823.3
30	872	86	9.9	985
35	1145	110	9.6	1049.6
40	1178	50	4.2	1104.6

Note: All tests were performed with 3Fg Black Powder. Standard Deviation = 0.0641 for the computed results.

Rifle Muzzle Velocity Data for .45 cal., 44-inch Barrel		
Charge (gr)	Velocity (fps)	Comp. Vel. (fps)
30	1180	1222.1
40	1560	1418.1
50	1700	1589.1
60	1800	1741
70	1940	1877.5
90	2100	2117.4
100	2140	2223.7

results. The agreement has a standard deviation, weighted by the number of test firings for each case, of 6.9%. The experimental data from Shimizu[12] show standard deviations ranging from 4.4 to 8.8%. Those data with muzzle velocity measurements had shell sizes ranging from 9.2 to 30.5 cm (3.6 to 12 in.). Some of the variation can be attributed to slight changes in surface roughness of the paper shells that could change the drag coefficients or alter the transition Reynolds number. Even so, the data cover a wide range of Reynolds numbers with agreement within the documented experimental error.

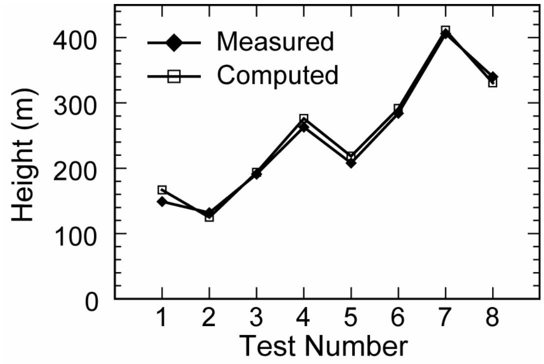

Figure 2. Drag model comparison using C_D = .4/.5 with empirical velocity as input and height as comparison.

Figure 3 shows a comparison of the computed and measured muzzle velocities using the complete firing analysis. The agreement has a weighted standard deviation of 9.5%. The experimental data only presented measurement standard deviation values for two test conditions: one value is 5.4% and the other is 6.6%. One possible reason for the slightly larger error match is the number of parameters that are sensitive to small changes. For instance, the standoff distance was not specified for the experimental data so the modeling assumption was that the distance was the amount necessary to accommodate a shell resting on a level layer of the mass of the powder specified. Another possible source of variance is the sensitivity to small changes in the diameter of the mortar or shell. Table 5 summarizes the results of a 5 mm variation in shell diameter. Almost all the velocity variations can be explained by approximately a 3% variation in shell to mortar diameter. The shell with an outside diameter of 29 cm (11.4 in.) had the greatest variation, and it can be entirely explained by a 5.2% reduction in shell diameter or increase in mortar diameter or a combination. Finally the quality of the Black Powder used can have a major effect on the results. The modeling assumed that all the Black Powder used for the experiments was of equal quality.

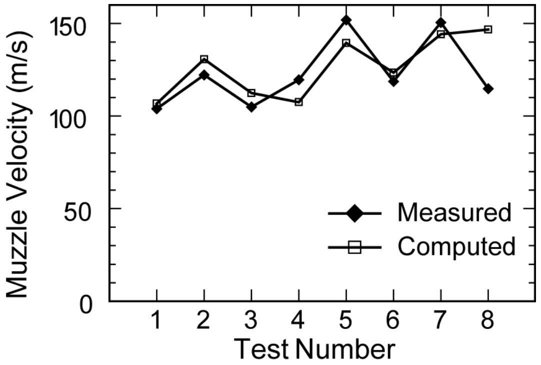

Figure 3. Comparison of computed and measured muzzle velocities.

Table 5. Analysis of Shimizu Data for Shell Diameter Variation.

Test No.[a]	2 of 8	4 of 8	8 of 8
+5 mm	160.6	127.9	161.3
0 mm	133.9	110.1	149.8
–5 mm	111.7	94.6	139
Meas. Vel. (m/s)	122.2	119.6	114.8
Shell Dia. (cm)[b]	8.4	14.2	29
Calc. Ch. (mm)[c]	–2.9	+2.7	–16.2
% Change[d]	–3.1	1.9	–5.6

Notes: The program was run with a ±5 mm variation in diameter to test the effect on muzzle velocity.

[a] The numbers represent the text number for the velocity data (8 tests).

[b] The variation in shell diameter to match velocity seems to be within experimental error (2–3%) except for the 29 cm shell that seems to be noticeably more than the others.

[c] This is the calculated change in diameter needed to match the measured velocity.

[d] This is the percent change in shell diameter.

Figure 4 shows a comparison of the computed heights. The calculations employ the complete model (both the firing and flight models). The standard deviation of the comparison, weighted by the number of measurements for each test point, is 12.1%. If the first and last points are omitted, the standard deviation drops to 7.8%. The first point was for a 7.6-cm (3-in.) mortar and did not have muzzle velocity data that would reveal sources of the disagreement. The last point was for the 30.5-cm (12-in.) mortar, where the disagreement is attributed to the difference between the computed and experimental muzzle velocities. Shimizu's data only have measurement standard deviations for 4 test conditions. For these tests, the average measurement error is 6.2%. The computed standard deviation for the same set of data is 7.8%.

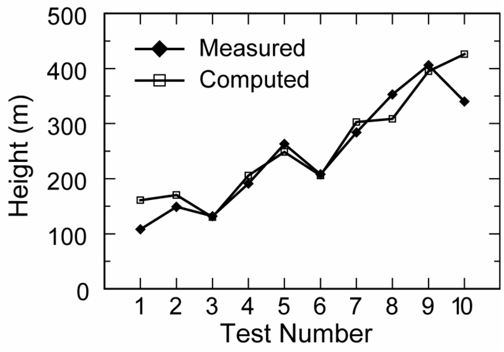

Figure 4. Computed height vs. measured height.

Figure 5 is a composite plot showing both the flight model calculations and the total model (firing and flight) calculations along with the experimental results. Except for the 30.5-cm (12-in.) result from the total (firing + flight) model, the data are in close agreement.

Figure 6 is a comparison of the rise times (time to apogee) using the full model. The comparison agreement has a standard deviation of 7.4% while the experimental data measurements have a standard deviation range from 4.9 to 10.4%. The notable result in this plot is the good agreement between computed and experimental values for the 30.5-cm (12-in.) shell. That agreement does not seem to be consistent with the previously noted agreements for muzzle velocity and height. Currently this remains a conundrum.

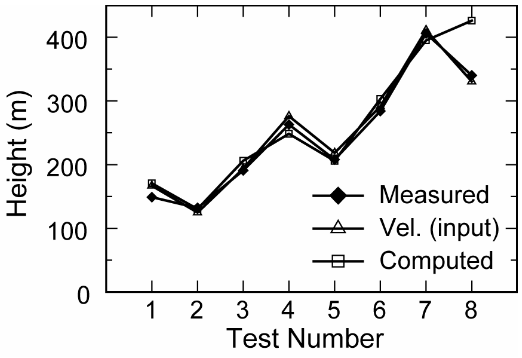

Figure 5. Height comparisons.

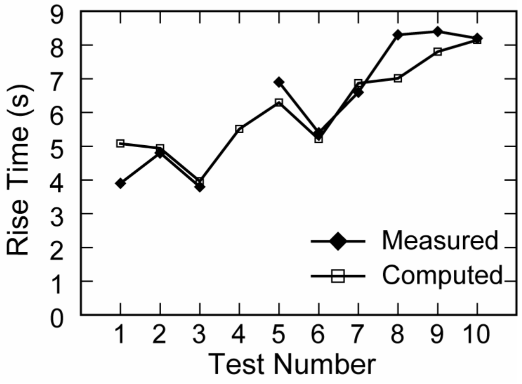

Figure 6. Shimizu rise times.

Figure 7 shows two comparisons presented on one graph. The data on the left side of the graph are for a muzzle loading, caplock Black Powder pistol, while those on the right are for a muzzle loading, flintlock Black Powder rifle. The bores are .40 and .45 caliber, respectively, and the barrel lengths are 9 and 44 in. (22.9 and 111.8 cm), respectively. Black Powder charges ranged from 20 to 40 gr (1.30 to 2.59 g) for the pistol and from 30 to 100 gr (1.94 to 6.48 g) for the rifle. The standard deviation of the comparison for the combination of pistol and rifle data is 6.4% while the experimental "variation" runs from 4.2 to 9.9% for the pistol data with no measurement error specified for the rifle data. The experimental data were for patched balls, so the model assumed a tight fit of the ball to the bore. The pistol model assumed no leakage, although the cap nipple hole would allow for some leakage, representing only 0.5% of the bore area. Countering this, the cap itself provides some sealing and the igniter charge adds to the combustion gases offsetting the leakage.

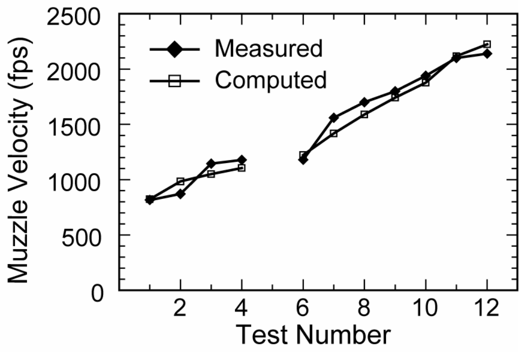

Figure 7. Dixie Gunworks data.

With all these factors, the assumed model of no leakage seems to be well within the modeling error. The rifle model assumed that there was leakage. The flash hole area represents about 2% of the bore area, and there is no obstruction to the gases escaping. To account for the leakage, the ball was modeled as having a smaller diameter producing a 0.002 in. (0.05 mm) gap between the ball and the barrel. The gap area was equal to the flash hole area. The agreement with both the pistol and rifle data seems to be within the experimental error.

Conclusions

The propellant characteristics of Black Powder and the aerodynamics of firework shells are accurately represented by the described model. The Black Powder burning model, based on the first law of thermodynamics, has a delayed release of the latent heats that is an essential element of the mortar analysis. The amount of delay is a key element in the model that allows it to analyze a wide range of test cases without changing any of the parameters. The burn rate and common thermodynamic parameters used in the model are the same or close to those found by other researchers.

A model for the leakage around the shell based on compressible flow theory appears to provide good agreement with the overall experimental data. This good agreement with experimental data ranging from large firework mortar tests down to muzzle loading rifle and pistol chronograph measurements provides confidence in the model's veracity. The numerical code based on the theoretical models provides a detailed analysis of every aspect of the thermodynamic process for mortars or muzzle-loaders.

The aerodynamic model for the shells in flight is consistent with fundamental aerodynamic principles and uses the available experimental data to determine common drag parameters that are applied equally over a wide range of test conditions. Agreement with round shell experimental data is within measurement variation. The cylindrical shell models in the code have not yet been verified but Contestabile's[13,14] experimental data should provide much of the data needed to determine the leakage and drag coefficients.

The numerical code appears to be an accurate tool that could prove useful for designing new features into display fireworks. The code could be used to design precise vertical placement of bursts. Parametric studies of mortar length, shell diameter or powder load might reveal better designs. The code can provide safety analyses (e.g., model the effects of undersized shells, incomplete insertion of a shell into the mortar or maximum barrel pressure and temperature as a function of grain size). Another safety use is for shell stress analysis wherein the computed pressure and inertial forces are required. There may even be uses for muzzle-loaders, including some of the design and safety considerations just described. The code provides a myriad of possibilities.

The model illustrates that Black Powder is a good propellant for projecting shells from a mortar because the energy release is distributed over time. This factor reduces the peak pressure to average pressure ratio thereby reducing the strength of the mortar required to contain the combustion for a given exit velocity. This same time-release factor makes Black Powder a less desirable rocket motor fuel since much of the heat is released after the combustion products pass through the nozzle thereby reducing the specific impulse.

As a final note: the characteristics of the Black Powder used for the Shimizu and Dixie Gun Works experiments were assumed to be equal except for granulation. The parameters presented in the paper are for that powder. If Black Powder of a different composition or mechanical incorporation is used, then the parameters may need to be adjusted for that powder.

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Effect of Ultrasound on Single-Base Propellants for Pyrotechnic Purposes

Valentin Grozev*, Radi Ganev†, Ivan Glavchev‡

* Artillery and Air Defense Military Academy, 1 Karel Skorpil St., 9713 Shoumen, Bulgaria
† Ministry of Defense, Armament Policy Directorate, 8 Kapitan Andreev St., Lozenets, 1421 Sofia, Bulgaria
‡ University of Chemical Technology and Metallurgy, 8 Kliment Ohridski Blvd., 1756 Sofia, Bulgaria

ABSTRACT

Investigations were conducted on the effect of ultrasound on single-base propellants. Changes in the average viscosimetric molecular weight of nitrocellulose in the solutions of propellants in acetone and in a mixture of ethyl alcohol-diethyl ether were studied. It has been established that, for at least 60 minutes, the molecular weight decreases exponentially. On-going degradation processes and the effect of cavitation during treatment of the propellants with ultrasound were analyzed. The change in nitrogen content and the heat released were also measured. The absorption coefficients and the sound velocities of the propellants were determined. Using these parameters, the dynamic modulus of elasticity was calculated. The results obtained are used in the processing of propellants for pyrotechnic purposes.

Keywords: single-base, propellants, ultrasound, degradation

Introduction

The use of ultrasound in characterization and treatment of propellants finds various applications. Reference 1 describes a technique for ultrasound measurement of propellant burning rate in a closed space. Using an ultrasound method developed in Reference 2, local regions in the propellants may be inspected to determine the defects in the composition of the individual components. Using an improved variant of the method, the inhomogeneity in the propellant elements may also be determined. Reference 3 examined changes in single-base propellants (SBP) during long term natural aging. Those same propellants were the subjects of examination after ultrasound treatment. The results obtained are to be used during their processing for pyrotechnic purposes.

The aim of the article proposed is to investigate the effect of ultrasound on propellant solutions and to determine the changes in acoustic properties of solid SBP.

Experimental

Single-base and other propellants: pyroxylin (NC), nitroglycerine (NG), and nitrodiglycol (ND or DEGN) (Arsenal, Bulgaria) with nitrogen (N_2) content of 13.05 and 12.47% were investigated. Solutions of the propellants with 3% concentration were prepared using the solvents acetone or ethyl alcohol-diethyl ether (A-E) in the ratio 1:2 (g/g). These solutions were treated with an ultrasound flaw detector USIP (Krautkrämer, Germany) with a frequency of 22 kHz and an intensity of 0.6 W/cm^2 for 60 min at 21 °C. The propellant solutions were put into open baths with distilled water without restricting the cavitation (i.e., under the conditions of an open system). Average viscosimetric molecular weight M_η was determined by drying samples of the solutions and, then, preparing new solutions with a concentration of 0.2 to 1 g per 100 cm^3. Using an Ostwald viscosimeter with a capillary diameter of 0.54 mm, the relative and specific viscosities were determined. From the relationship

$$[\eta] = \lim_{C \to 0} \frac{\eta_{sp}}{C},$$

the intrinsic viscosity $[\eta]$ was calculated. After its substitution into the Mark-Houwink equation[4] $[\eta] = KM^{\alpha}$, where K and α are the coefficient and exponent published in Reference 5, M_η was calculated. The nitrogen content was determined using a G. Lunge nitrometer,[6] and a calorimeter was used to measure heat quantity. Each point of the graph is as an arithmetic mean of five measurements. The standard error of approximation was 0.07.

The coefficient of sound absorption was determined in propellant elements 25 to 30 mm in length and 8 mm in diameter. The specimens were fixed at both ends, using sensors for excitation and reception of elastic vibrations (Brüel-Kjær, Denmark). The same flaw detector with receptors in the frequency range from 1 to 10 MHz was used. The sound velocity in SBP was measured using a pulse method with non-detected signal. The scale of the ultrasound flaw detector was adjusted in time units, using steel standards with known velocity of sound transmission. Accuracy in reading the time was 0.25×10^{-2} s, and the relative error was 1.5%. The absolute error in measuring the signal amplitude was 0.5 dB.

Results and Discussion

Effect of Ultrasound on Degradation of SBP

The molecular weight is a major factor showing the on-going degradation processes in propellants treated with ultrasound, which, according to the classification published in Reference 7, belong to the homogeneous propellant group. Those processes change the molecular characteristics of nitrocellulose (NC), which is the main component in SBP. Molecules of NC are known to be spheroids that are characterized by increased skeletal hardness, and their size depends on the content of nitro and hydroxyl groups. The change of the average viscosimetric molecular weight M_η of NC in the solutions of SBP in acetone and in a mixture of ethyl alcohol-diethyl ether after treatment with ultrasound is shown in Figure 1.

In Figure 1 the values of M_η are seen to decrease in both solvents with the duration of ultrasonic treatment. The observed exponential decrease of the molecular weight is connected with the beginning of ultrasonic degradation. This is explained by ultrasound causing equalization of the lengths of molecule fragments. Therefore, this type of degradation cannot be assigned to oxidation reactions.

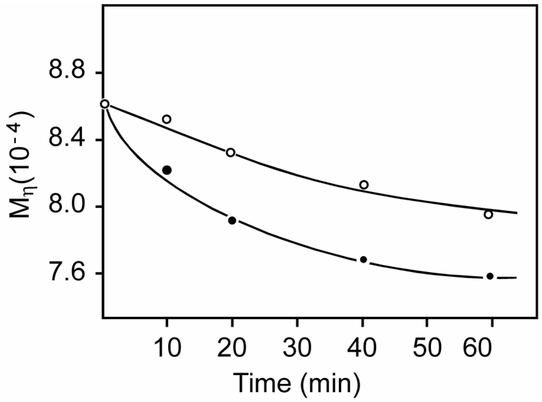

Figure 1. Dependence of molecular weight M_η on time of treatment with ultrasound of solutions of SBP in a mixture of ethyl alcohol-diethyl ether 1:2 (-○-○-) and acetone (-●-●-).

It is also necessary to note the effect of cavitation on ultrasonic degradation of solutions of SBP. Because of this, the degradation processes can take place not only mechanically, but also as oxidative degradation with a chain-radical mechanism. An initial elementary step in this process is connected with tearing NO_2 from the molecules (i.e., with dissociation of the $RO–NO_2$ bond). This assumption is warranted by the low values of the activation energy in degradation, which is 38 kcal/mol,[8] and the dissociation energy in $RO–NO_2$, which is 51.7 kcal/mol.[9] Observations showed cavitation could be limited to a considerable extent by degassing or increasing pressure before treatment of the solutions with ultrasound. By doing this, air bubbles serving as centers of cavitation were removed from the solutions.

The effects of the solvents used should also be taken into consideration. Hydroxyl and ether groups have a stronger ability to form hydrogen bonds with NC than the carbonyl groups. A portion of the ultrasonic energy is spent for destruction of the polymer-solvent associates. This portion is larger in the A-E solvent mixture than in the acetone mixture due to formation of a higher number of hydrogen bonds.

To investigate the effect of ultrasound on SBP, changes in nitrogen content N_2 and released heat Q were studied. From the exhaustion of N_2

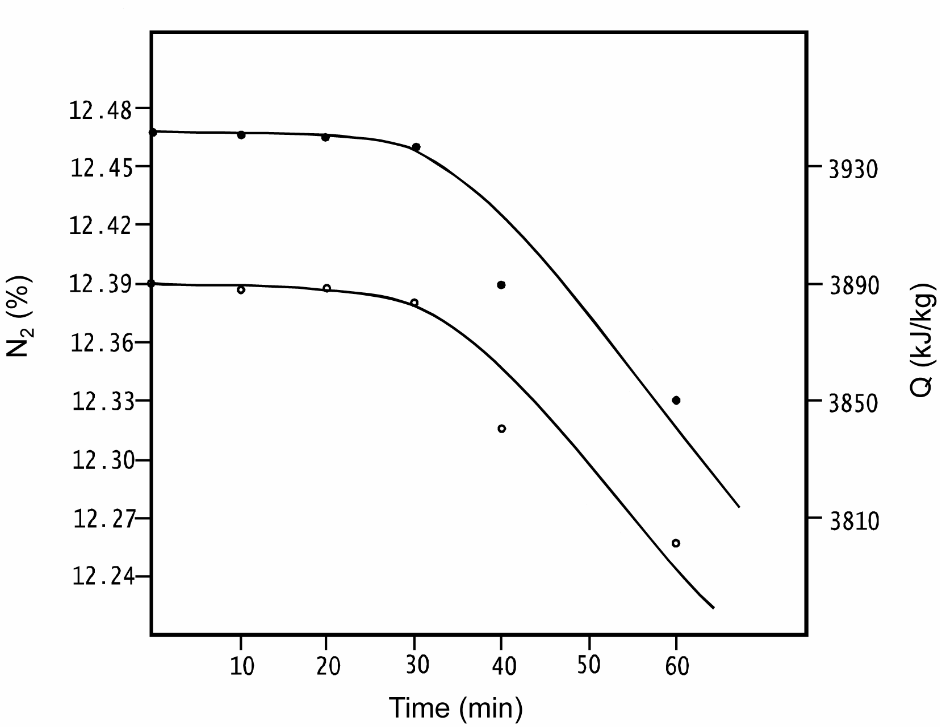

Figure 2. Dependence of N_2 (-●-●-) and Q (-○-○-) on time of treatment of SBP with ultrasound.

and changes in *Q* shown in Figure 2, one may make judgments about the degradation processes in the macromolecules of NC from the propellants.

Figure 2 shows that the nitrogen content curve has two sections. In the first section, the nitrogen content has a constant value until about the 25th minute. During this time, it can be assumed that the diphenylamine stabilizer was able to inhibit the initial oxidation processes caused by the ultrasonic degradation. In the second section, after the 25th minute, nitrogen content decreases rapidly with continued ultrasound treatment. It follows from this that the hydroxyl groups increase at the expense of NO_2 groups. The free radicals or nitrogen oxides formed by ultrasonic degradation interact with the diphenylamine and form slightly active or inactive diphenyl nitrogen oxides. The processes are of a pulsing nature due to catalytic action of released nitrogen oxides. The above-mentioned assumptions are also confirmed in Figure 2 by the graphed released heat *Q*, which correlates with that for nitrogen content N_2.

The initial elementary act of ultrasonic degradation of propellants is the breaking of the bonds between the glucose rings at $C^{(1)}$ or $C^{(4)}$ in the main chains of the macromolecules of NC in accordance with the diagram shown in Figure 3.

The proposed diagram (Figure 3) for the degradation of NC of propellants shows the formation of new molecule fragments, thereby increasing the structural disorder. The disorderly areas have more developed segmental movement, and the orderly formations have lower molecular mobility. Degradation of the super-molecular structures of propellants by the ultrasound also leads to formation of areas with various molecular mobility and duration of existence.

It may be summarized that, with ultrasonic treatment, there are two different mechanisms of degradation of SBP. Mechanical degradation begins with the breaking of bonds between the glucose rings at $C^{(1)}$ and $C^{(4)}$, and oxidative degradation occurs with the dissociation of $RO–NO_2$. Usually, neither mechanism acts separately and is not easily explained independently. They always act together or complement each other,

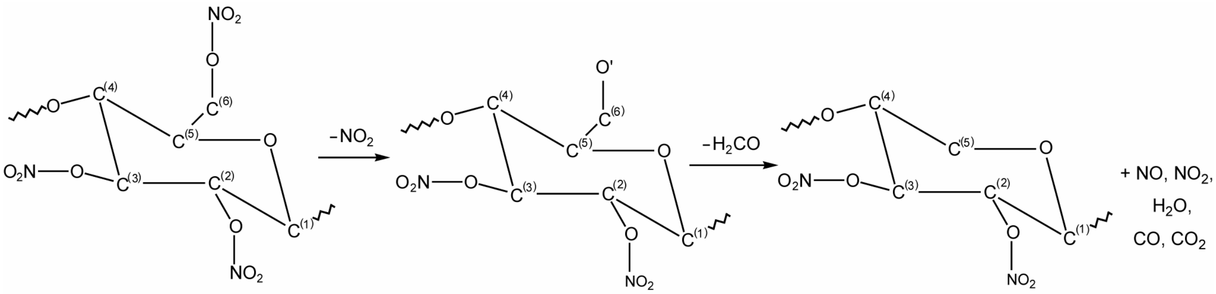

Figure 3. Probable diagram of ultrasonic degradation.

making it difficult to differentiate the action of either type of degradation.

Acoustic Properties of SBP

To obtain a fuller picture of on-going processes in SBP during treatment with ultrasound, the sound velocity C and the coefficient of sound absorption α were determined. Using these parameters, the dynamic elasticity modulus E' was determined, from which conclusions may be drawn about physicomechanical parameters and the structure of propellants used for pyrotechnic purposes.

The sound velocity C in SBP was determined using the formula:

$$C = \frac{l_2 - l_1}{t_2 - t_1} \text{ [m/s]},$$

where l_1, l_2 are the acoustic paths through the specimen examined [m]; and t_1, t_2 are the times for passing of the ultrasonic pulse through the specimen [s].

In propellants, the quantity C depends to a considerable extent on the angle between the direction traveled by the ultrasound and the axis of manufacturing of propellant elements. That is why the sound velocity in axial C_{ax} and radial C_r directions of the specimens was measured. The anisotropy index I_A was determined from the C_{ax}/C_r ratio. In Table 1, C is given for SBP, nitroglycerine (NG) and nitrodiglycol (ND) propellants.

Table 1. Sound Velocity C and Anisotropy Index I_A of SBP, NG and ND.

No.	Propellant	C_{ax} [m/s]	C_r [m/s]	I_A
1	SBP	2.493	2.228	1.12
2	NG	2.223	2.096	1.06
3	ND	2.306	2.268	1.02

The sound velocity and the anisotropy index data in Table 1 are explained by different mechanisms of transmission of ultrasonic vibrations depending on the angle between the direction of the ultrasound and the axis of the segments of the macromolecules. When the direction of ultrasound is parallel to the segments of the macromolecules, the propagation of ultrasonic vibrations is at the expense of intramolecular interaction energy. When the direction of ultrasound is perpendicular to the segments of the macromolecules, the ultrasonic vibrations propagate at the expense of the energy of intermolecular interaction. Because the energy of intramolecular interaction is considerably higher than the energy of intermolecular interaction, C_{ax} is greater than C_r.

The coefficient of sound absorption α was determined using:

$$\alpha = \frac{A_1 - A_2}{l_2 - l_1} \text{ [dB/cm]}$$

where A_1, A_2 are the amplitudes of signals that have passed though the specimens, read from the attenuator [dB]; and l_1, l_2 are the lengths of the specimens [cm].

A pulse method of measurement was used to compare the amplitudes of signals passing through the specimens with frequency f of the ultrasound. The results are shown in Figure 4.

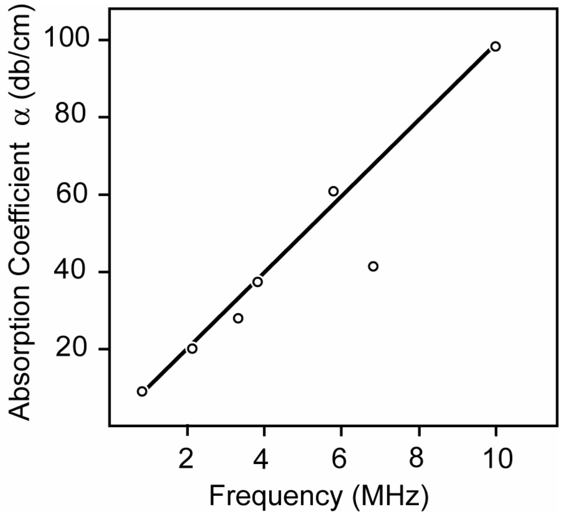

Figure 4. Determination of the absorption coefficient, α, of SBP versus the frequency, f, of the ultrasound.

Figure 4 shows that α may be plotted as a straight line with a certain slope. From it, a conclusion may be drawn about the acoustic state of the propellants, taking into account on-going relaxation processes. It is also necessary to note the special case when $\alpha = 0$ (i.e., the sound waves propagate in an ideally elastic body).

A major index characterizing mechanical behavior of the propellants during ultrasonic treatment is the dynamic modulus of elasticity E'. It is the ratio of the applied stress coinciding in phase with the strain, to the value of this strain.

After determining α and C, the modulus of elasticity is calculated using the formula:

$$E' = \frac{48\pi^2}{a_n^4} \rho \frac{l^4}{d^4} f^2 \text{ [N/m}^2\text{]},$$

where ρ is the density [kg/m^3]; l is the length of unfixed part of the specimen examined [m]; d is the diameter of the specimen examined [m]; a_n is a coefficient depending on the frequency of the ultrasound; and f is the resonance frequency [Hz].

The elasticity coefficient, E' for SBP, equals 10^9 N/m^2. This value falls between highly elastic polymers at 10^5 to 10^6 N/m^2 and harder polymers at 10^{11} N/m^2. This is one of the characteristics that allows for successful use and processing to obtain propellant elements with good mechanical properties for pyrotechnic purposes. The dynamic modulus E', α, and C allows obtaining two types of information: about mechanical properties and about structure, constitution, and condition of the propellants. From these, conclusions may be drawn about acoustic and physicomechanical properties of the propellants.

The results obtained are of substantial importance. Ultrasonic treatment of the propellants is of interest in terms of their practical application in various pyrotechnic products. A necessary requirement is that they have trouble-free operation under conditions of large loads and vibrations.

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Editorial Policy

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.

The Effects of External Fire on Fireworks Stored in Steel ISO Transport Containers

S. G. Myatt

Health and Safety Laboratory, Harpur Hill, Buxton, Derbyshire, SK17 9JN, United Kingdom

ABSTRACT

The increased use of steel ISO transport containers for storing fireworks led the UK's Health and Safety Executive (HSE) to commission research to gain a better understanding of the behaviour of fireworks in such storage when exposed to an external fire. Subsequent incidents involving storage of fireworks in ISO containers demonstrated that violent explosions could occur. This added impetus to the research programme. It was found that selection boxes of fireworks that were readily available to the general public were unlikely to present a significant hazard in bulk storage. More energetic fireworks, such as those used by professional display operators, were capable of generating sufficient pressure within the container to cause the doors to fail and for the walls and roof to become deformed. These more energetic trials used a range of firework types including star shells up to 200 mm in diameter, and resulted in unburnt stars being projected up to 140 m and unexploded fireworks being thrown to a distance of up to 32 m. Pyrotechnic effects (stars) were observed over an area in excess of 100 m diameter and thermal imaging indicated that a fireball with an effective surface temperature of 400 °C was produced over a diameter of 36 m. None of the trials produced violent mass explosion effects of the type reported in connection with recent incidents at Uffculme, UK and Enschede, The Netherlands.

Keywords: fireworks, storage, fire, explosion, ISO, container, classification, UN

Introduction

Large quantities of a whole range of materials, including fireworks, are shipped around the world in steel ISO containers. In recent years in the UK, manufacturers and retailers have used such containers to store a large proportion of their fireworks. Each container may be large enough to store tonnes of fireworks ranging from British Standard (BS) Category 1 (fireworks for indoor use) through to BS Category 4 (fireworks for professional display operators only), as defined in BS7114:1988.[1]

In 1980, tests in Seattle, WA USA,[2] demonstrated that the impingement of an external fire onto an ISO container of fireworks (2.5 tonnes) can result in a violent explosion. Two minutes after the fire was ignited, explosions projected the contents up to 61 m vertically and 213 m horizontally. Approximately 2 hectares of land sustained fire damage. Subsequently an accident at Stourbridge, Worcestershire, UK in 1996,[3] which involved 600 kg of fireworks, resulted in the doors of the storage container being blown open and the ejection of firework fragments, which caused minor damage to a fire engine. The gable end of a building some 20 m away sustained damage and a large wooden door caught fire. After the incident, the ISO container walls, roof and floor had been bowed out.

Based on this background, HSE's Explosives Inspectorate identified a need to gain a better understanding of the behaviour of fireworks stored in ISO containers when exposed to an external heat source. The Health and Safety Laboratory (HSL) was commissioned to perform tests to generate data that could form a scientific base from which future guidance on firework storage could be developed.

Figure 1. 6.1 m long ISO transport container.

The research commenced in 1996 and gained new impetus in 1998 when a serious fire and explosions occurred at a fireworks company in Uffculme, Devon, UK.[4] Eight ISO containers holding fireworks and located inside a large metal clad structure were involved in the fire. One of the ISO containers subsequently exploded causing considerable blast and fragmentation damage both on and off site. The recent accident at Enschede in The Netherlands,[5] where at least 20 people died, has highlighted the relevance of this research.

This paper describes the scientific work undertaken to date by HSL to investigate the behaviour of fireworks stored in steel containers when challenged by an external fire source and complements a previous HSE paper[4] that dealt with the wider health and safety issues raised by accidents in bulk fireworks storage.

Experimental

Mass, linear distance and peak noise measurements made during this work can be traced to national Standards.

ISO transport containers [6.1 m (20 ft) long] are commonly used for fireworks storage and were selected for these trials (Figure 1). Each container had two hinged full length doors at one end, with a rod and lever locking system to the top and bottom of the main body of the container. The floor was made of wood supported on I-section cross girders. The corrugated metal skin of the container was attached to the main structure by rivets. In the UK, a store for explosives must be maintained to a standard that prevents rust from contaminating the explosives being stored.[6] Often this requirement is met by lining the walls and ceiling of the container with wood or by maintaining a good painted

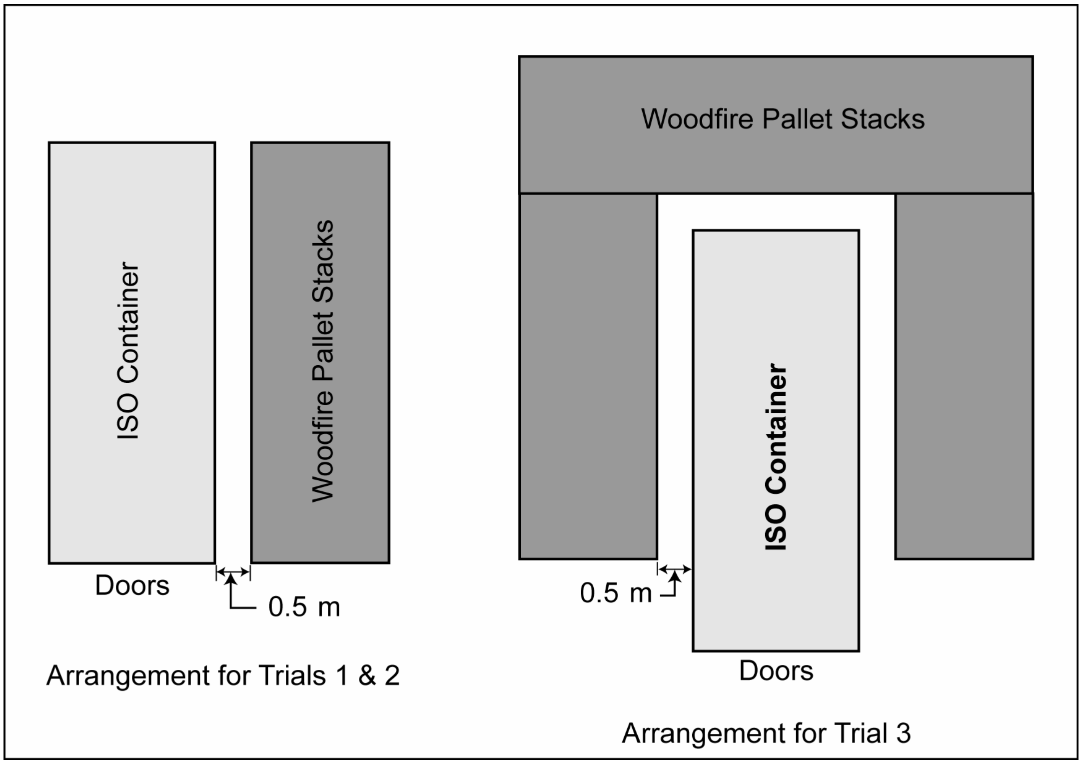

Figure 2. External fire arrangements for trials.

finish. For the purposes of these trials the containers were not wood lined.

To ensure that enough heat would be generated by the external fires, wooden pallets were stacked to the height of the containers, and 0.5 m from the container walls. Absorbent paper, doused with a small amount of kerosene (< 25 litres), was inserted into the spaces in the lower pallets and Plastic Igniter Cord (PIC) was interwoven with the doused paper along the full length of the pallets. Remote ignition of the PIC caused ignition of the doused paper along the full length of the pallets within 30 seconds; this ensured that the burning pallets provided an even flame front to act on the container.

The first two trials used relatively small volumes of fireworks stacked against the side of the container nearest to the external fire (Figure 2) whereas the third trial had fireworks stacked to both sides. Also the external fire arrangement was different in the third trial.

The three trials were intended to be representative of the bulk storage of fireworks with low, medium and high net explosive content (NEC). Details of the types of fireworks used for each trial are given in Table 1.

Labels on the selection (assortment) boxes for Trial 1 stated that they were “Display Fireworks” (i.e., BS Category 3). However, over 85% of the fireworks they contained were less energetic BS Category 2 fireworks; the remainder were BS Category 3 from which the selection boxes got their rating. Such boxes are readily available at retail outlets in Great Britain where the majority of the general public would purchase their fireworks (both these categories would generally be termed consumer fireworks in the US). They were packaged in outer cardboard transport packs, which were stacked two boxes deep along one side of the container and stacked on top of one another. The packs were pushed against the metal cladding of the container.

Trial 2 comprised a mixture of fireworks classified as UN1.3 or UN1.4, which represented a typical stock for a small professional display operator. The mixture of fireworks was agreed upon by representatives of the UK fireworks industry. The transport packs were stacked along

Table 1. Summary of Fireworks Loads Used in Trials.

Trial No.	Contents of ISO Container	No. Cases	Gross Wt. (kg)	NEC (kg)	UN Classification
1	**BS Category 3 Selection Box Fireworks** (contain > 85% BS Category 2 fireworks)				
	Assorted selection boxes readily available to UK general public	72	1000	228	1.4G
2	**Mixture of UN 1.3G and UN 1.4G Fireworks** [Proportion UN 1.3 (by NEC) = 48%]				
	Chinese cakes/crackle mines	15	345.0	90.0	1.4G
	Titanium gerbs	1	8.0	4.0	1.4G
	2 oz Sticked rockets	1	30.0	10.0	1.4G
	2 oz Rockets	1	30.0	10.0	1.4G
	4 oz Rockets	1	60.0	20.0	1.4G
	4 oz Sticked rockets	2	60.0	20.0	1.4G
	30 mm Comet candles	1	50.0	23.0	1.4G
	30 mm Bombette candles	1	50.0	14.5	1.4G
	45 mm Comet candles	2	56.0	29.6	1.3G
	45 mm Bombette candles	2	56.0	20.0	1.3G
	60 mm Candles (assorted)	3	60.0	30.0	1.3G
	Shell 75 mm dia.	4	63.6	43.2	1.4G
	Shell 100 mm dia.	6	140.4	86.4	1.4G
	Shell 125 mm dia.	11	221.8	138.6	1.4G
	Shell 150 mm dia.	13	224.6	140.4	1.3G
	Shell 200 mm dia.	10	224.0	140.0	1.3G
	75 mm dia. colour mines	1	4.4	3.0	1.4G
	Totals	**75**	**1683.8**	**822.7**	
3	UN 1.4G shells				
	Boxes of 18 x 125 mm dia. star shells with flash composition burst charges	270	4050	2600	1.4G

one side of the container, up to three rows deep, and stacked on top of one another. To represent a typical store, some of the rockets had sticks attached and were placed head down in two plastic dustbins. Where appropriate, the packs of fireworks were pushed against the metal cladding of the container.

Fireworks for Trial 3 consisted entirely of 125 mm diameter star shells, which were classified UN1.4. These shells contained a blackpowder lift charge, stars, and a flash burst charge. The cardboard transport packs, which each contained 18 shells, were stacked 6 cases high by 5 wide, with 9 rows of cases from front to back in the container. These transport packs filled the rear 70% of the container. The remaining space between the front row of firework packs and the doors of the container was filled with boxes of vacuum packed wood shavings so that the air volume present was similar to that of a full container. Wood shavings were chosen because they had a packed density similar to that of the full firework transport packs. The fireworks and shavings were positioned centrally along the long axis of the container so that only the cartons at the back of the container were in contact with the metal cladding.

All the trials were recorded using normal speed video cameras and still photography was used to record the set-up and aftermath of each trial. In addition, Trial 3 was recorded using a thermal imaging camera to provide data on the expected fireball. After each trial the state of

Table 2. Chronology of Events for Trial 1.

Time (hrs:min:sec)	Event
00:00:00.0	External fire ignited
00:10:00.0	Audible roar from container
00:16:00.0	Effects in container continue sporadically for next 17 hrs
01:00:00.0	External fire burnt to embers
17:15:00.0	Last firework effect heard
18:10:00.0	Opened doors
18:10:01.0	Flames from doors
18:10:02.0	Effects heard and stars ejected
19:10:00.0	Frequency of effects reduced. Sporadic effects up to 23.5 hrs after external fire ignited

the container and the distance that debris had been projected was recorded.

Overpressure measurements were obtained using CEL414 soundmeters capable of recording noise levels of up to 160 dB(C). The sound pressure level obtained (in dB) was converted to the equivalent overpressure (P_{calc}), measured in kPa, by using the following expression.[7]

$$P_{calc} = P_0\left(10^{\frac{\text{dB}}{20}}\right)$$

where $P_0 = 2 \times 10^{-8}$ kPa.

Results

Trial 1 (Selection Box Fireworks)

A summary of the events from the trial is given in Table 2. Considerable firework activity was heard 10 minutes after the fire was started, but the doors remained closed and no effect, apart from smoke, was visible outside the container. Sporadic ignitions of fireworks were still being produced 17 hours after the trial started.

The majority of the surface of the ISO container was cold to the touch after 18 hours when one of the doors was opened. The wooden floor of the ISO container was burnt through in a number of places and most of the transport packs of fireworks were blackened. Virtually all the packs were in their original positions with their contents charred but unburnt. Immediately after the door had been opened, the volume of smoke being generated increased, and within 1 minute the remaining contents of the container were engulfed in flame. Firework effects were heard 2 minutes after the door had been opened and soon became too numerous to log. Only sporadic effects were being produced 1 hour after the doors were opened. After all fire activity had ceased, the floor of the container had been completely burnt away. Generally, the ash from the fireworks and packaging was in the same location as the unburnt transport cartons. This indicated that no major explosions had taken place to dissipate the ash. The main structure of the container was blackened but intact. Both doors remained on their hinges, and there was no deformation of the corrugated steel skin.

Soundmeters, positioned at 100, 150 and 200 m from the container, were only used to monitor noise levels while the container was closed. None of the measurements exceeded 100 dB(C) (2 Pa).

Table 3. Chronology of Events for Trial 2.

Time (min:sec)	Event
00:00.0	External fire ignited
07:05.3	1st explosion. Smoke from side vent
07:08.0	2nd explosion. Smoke jets from vent and door area
07:11.7	3rd explosion. Increase in power of smoke jets
07:13.7	Explosion opens doors slightly. Allows stars to be ejected
07:14.7	Multiple explosions. Increase in smoke jet strength. Smoke changes from whitish grey to black
07:20.5	1st fireball ejected from bottom of doors. Doors still closed
07:26.8	Large explosion. Assumed to blow doors open but smoke obscures view.
07:32.5	Shell ejected confirming that doors are open. Multiple explosions continue
07:49.0	Explosion frequency substantially reduced
11:35.7	Intermittent small reports continue

Trial 2
(Mixture of UN1.3 and UN1.4 Fireworks)

A summary of the events from the trial is given in Table 3. The first explosion caused smoke to emanate from the container wall vents, and subsequent explosions over the next 9 seconds increased the pressure inside the container causing smoke to 'jet' out from the seals around the doors with increasing power and a few burning stars were seen to escape from the container through the door seals even though the doors still appeared to be closed. At the end of this phase the colour of the smoke being produced changed from whitish grey to black. A fireball was ejected from the base of the doors after 7 minutes 20.5 seconds and was followed shortly after by a large explosion. The doors were certainly open 27 seconds after the first explosion because shells could be seen as they were ejected from the container. The frequency of explosions was decreasing 44 seconds after the first event, and all major explosions had occurred within the first 4 to 5 minutes. Firework casing debris was found up to 34 m in front of the container and approximately 20 m in other directions. Unburnt star shells were found at distances of up to 140 m from the front of the container.

Both doors of the container were bent by the explosion but remained on their hinges. The wooden floor had been completely consumed by the fire. The walls and roof were slightly bowed out. Three small areas of the weld had failed between the floor and walls, the largest of these being 180 mm long and 15 mm wide.

Soundmeter readings at 250 and 400 m indicated that the peak noise levels obtained were 132.8 dB(C) (87 Pa) and 131.2 dB(C) (73 Pa), respectively.

Trial 3 (125 mm Diameter Star Shells)

Still photographs of the progress of the trial are shown in Figure 3. A summary of the events from the trial are given in Table 4 and noise measurements are given in Table 5.

Table 5. Noise Measurements from Trial 3.

Distance from ISO container (m)	Peak noise level	
	dB(C)	Pa
100	147.5	474
150	141.8	246
200	140.6	214
250	137.1	143
350	138.2	159

The first large explosion occurred 12 minutes 36 seconds after the external fire was ignited and was followed by further explosions over the next 4 to 5 seconds. At this stage the colour of the smoke emanating from the door seals changed from light grey to black and was followed 1.5 seconds later by three explosions in

External Fire Engulfing Container | Main Explosion | Extent of Radiating Stars

Figure 3. Progress of Trial 3.

close succession and an increase in the flow of black smoke from the door seals. A fireball was visible at the container doors 12 minutes 45 seconds after the external fire was ignited, followed by major explosions that started 3 seconds later and continued for the next 18 seconds. During this time the visible extent of the pyrotechnic effects (stars) extended beyond the confines of the floor of the quarry in which the trial was conducted, indicating a diameter in excess of 100 m. After this period the frequency of the explosions started to subside. The last explosion occurred 2 minutes 36 seconds after the first large explosion.

Table 4. Chronology of Events for Trial 3.

Time (min:sec)	Event
00:00.0	External fire ignited
07:20.4	Fire engulfs container
08:46.9	1st bang/rumble heard. No change to container
08:48.0	2nd bang heard. No change to container
08:52.5	3rd bang heard. No change to container
10:05.6	White smoke stream from container vents
10:40.1	Copious smoke from top of doors
11:13.5	White smoke streams from vents and cracks around doors
12:36.4	1st explosion
12:39.7	2nd explosion
12:41.1	Double explosion
12:41.4	Black smoke jetting from door joints
12:42.9	Triple explosion
12:43.4	Black smoke jetting from doors. Start of multiple explosions
12:44.5	White ball of flame ejected from doors
12:47.6	Major explosions start
13:05.4	Majority of explosions complete
13:08.3	Penultimate explosion
15:12.3	Last explosion

Shell case debris was found in front of the container in an arc of 50° centred along the container main axis. The ground immediately in front of the container was blackened with ash and was almost devoid of firework debris, which had been blown out to a distance of 16 m where a pool of water arrested its travel. The majority of the shell casings collected at the water's edge although a few were found on the other side of the pool (32 m from the container doors). No complete shells were found beyond this distance. However, small fragments of shell casing were observed up to 150 m from the explosion point. Unburnt stars from the shells were found up to 100 m from the explosion point. Of the 4860 shells used, 51 were found to be intact and capable of re-use after the trial was complete.

Both doors of the container were slightly bent by the explosion but remained on their hinges. The wooden floor had been completely consumed by the fire exposing the supporting girders, some of which were also bent. The walls and roof were slightly bowed out in a manner similar to the container in Trial 2. One area of the weld had failed between the floor and walls over a distance of 100 mm.

Table 6. Fireball Dimensions for Trial 3.

Event	Start Time of Event (min:sec)	Effective Surface Temperature[EST] (°C)	Maximum Fireball Diameter (m)
External fire ignited	00:00.0	Ambient	n/a
1st fireball	12:44.5	>400	19
		>800	14
Major explosions (duration approx. 18 s)	12:47.6	>400	36
		>800	22

Analysis of the thermal images of the trial indicates that immediately prior to the first explosion the effective surface temperature (EST) of the external fire was in the range of 600 to 700 °C. This increased rapidly to over 900 °C once the explosions started. The dimensions of the fireballs produced are given in Table 6.

Discussion

Results from Trial 1 showed that 1 tonne gross weight of BS Category 2 and 3 selection box fireworks contained in cardboard transport packs are unlikely to explode with sufficient violence to breach the containment afforded by a steel ISO transport container. The fact that the ash from the fireworks and packaging was in approximately the same position as the original packaged fireworks indicates that relatively weak explosions had occurred and also supports this conclusion.

The external fire generated sufficient heat to ignite some of the contents of the container but it is thought that the insulation afforded by the cardboard boxes prevented rapid spread of the fire. This may have been further slowed by an oxygen depleted atmosphere within the container. The observation that the fireworks ignited over an extended period also supports this hypothesis. The slow ignition rate suggests that the damage sustained by the container is unlikely to increase if larger quantities of low energy fireworks of this type were stored in steel containers and exposed to external heat sources. Therefore, the UN classification[8] of 1.4G appears to be appropriate for this type of firework selection box when transported (or stored) in bulk in ISO containers.

An increased potential hazard arises once oxygen is admitted to the partially burned transport packs (i.e., when the container doors are opened). Re-ignition can occur within minutes, resulting in a fierce fire and the additional hazard of burning projectiles from the fireworks being ejected from the container. It would seem prudent to inform firefighters of these hazards and suggest that fires involving pyrotechnics such as those used in Trial 1, which are stored in ISO containers, should be allowed to burn out completely before the container is opened.

Progression of the three trials followed a similar pattern until the fireworks began to explode. The external pallet fires gained energy as more fuel was burnt until sufficient radiant heat was able to induce a fire within the container, causing the fireworks to start to ignite. This process took 7 to 10 minutes for all the trials described in this paper. After the first explosion, the less energetic fireworks used in Trial 1 were unable to produce sufficient pressure in the container to force the doors open. No deformation of the container occurred and the pyrotechnic effects were contained. Pressures generated by the more energetic fireworks used in Trials 2 and 3 were sufficient to open the container doors, but the time required to attain the necessary pressure varied. The times from first explosion to the doors opening were 22 and 11 seconds for Trials 2 and 3, respectively. This may reflect a slower increase in the rate of firework explosions for Trial 2 than for Trial 3 due to the nature of the fireworks and their packaging. However, the time for Trial 3 was probably shorter because of the larger external fire (Figure 2), which produced a larger heat input.

The explosion sequences in Trials 2 and 3 also followed a similar pattern. The first few explosions caused white smoke and steam to be ejected with increasing force from the wall vents and gaps around the doors. As the explosion frequency increased, the colour of the smoke and steam changed to black, and within a few (4–6) seconds a fireball was ejected. This was followed 3 to 6 seconds later by a larger explosion. Multiple explosions continued until the reserves of fireworks in the container had been consumed. In Trial 2, where a number of different types of fireworks were used, the period from the large explosion to completion of the trial was indistinct because some of the better protected pyrotechnics (i.e., those in thick Roman candle tubes), continued to eject effects for a further 4 hours. In contrast, Trial 3—where only shells were used—was completed within 5 minutes where all but one of the shells that exploded had functioned within 20 seconds of the first explosion. The similarities between the two trials indicate that a broadly similar mechanism may have applied during the explosion of the fireworks even though the NEC differed significantly.

In Trials 2 and 3 fireballs were generated. Data from Trial 3 indicate that, during the major explosions phase (12 minute 48 seconds to 13 minutes 5 seconds), the fireball attained an effective surface temperature (EST) of at least 400 °C over a diameter of 36 m and had a hotter core (EST of at least 800 °C) over a diameter of 22 m. Fireballs of this size and temperature could cause problems for firefighters, particularly if many ISO containers of fireworks are stored close together and result in the production of numerous fireballs.

The trials described in this paper were performed primarily to assess hazards associated with bulk storage of fireworks in ISO containers. However, the same types of container are used in many countries to transport large quantities of fireworks. Therefore, the results of these trials may have implications for the UN classification for the transport of fireworks. The UN approved test for determining the hazard division within Class 1, the UN Series 6(c) Test,[8] requires a volume of packaged articles (i.e., fireworks) of at least 0.15 m^3 to be exposed to an external fire. The test criteria indicate that if a fireball extends beyond the witness screens (4 m from the test piece), or if fiery projections are thrown more than 15 m, the product should be classified as UN1.3 for transport. Results from Trial 3 suggest that stars from 125 mm diameter shells could be projected beyond 15 m if transport packages were subjected to a UN Series 6(c) Test even though the volume of fireworks used in such a test would be much less than that used for the trial. This would necessitate a change of classification of this particular type of shell to UN1.3 from its current UN1.4 classification for transport. There is also evidence from tests with unpackaged shells to suggest that smaller shells may also need to be reclassified since Shimizu[9] estimates that shells of only 75 mm diameter can project stars over a 20 to 25 m radius, well in excess of the 15 m limit set for UN1.4 classification. However, distances that stars are projected may be affected by the packaging and further work would be necessary to evaluate this.

It has already been stated that the time from first explosion to the container doors opening in Trial 3 was approximately half that observed for Trial 2. On this basis it would be expected that Trial 3 would have generated a greater pressure more quickly than Trial 2 and hence caused more damage to the container, particularly as the NEC of that trial was 2600 kg compared to 826 kg for Trial 2. It would therefore be expected that the scatter of debris would have been greater for Trial 3. This was true for the scatter of firework casing debris, which was found 34 and 140 m from the containers in Trials 2 and 3, respectively. Noise levels were also lower for Trial 2 than for Trial 3. However, both containers suffered approximately equal damage. Their doors had been blown open and the walls and roofs were bowed out to approximately the same extent. There is evidence to suggest that the greatest overpressure was in Trial 2, not in Trial 3. Three ruptures were observed between the walls and floor of the container used in Trial 2 compared to only one in Trial 3, and unburnt stars were found 140 m from the container in Trial 2 compared to 100 m in Trial 3. The increased distance that unburnt stars were projected in Trial 2 may be due to the directional nature of some of the firework types used (i.e., Roman candles) or, more likely, the fact that Trial 2 contained some shells of up to 200 mm diame-

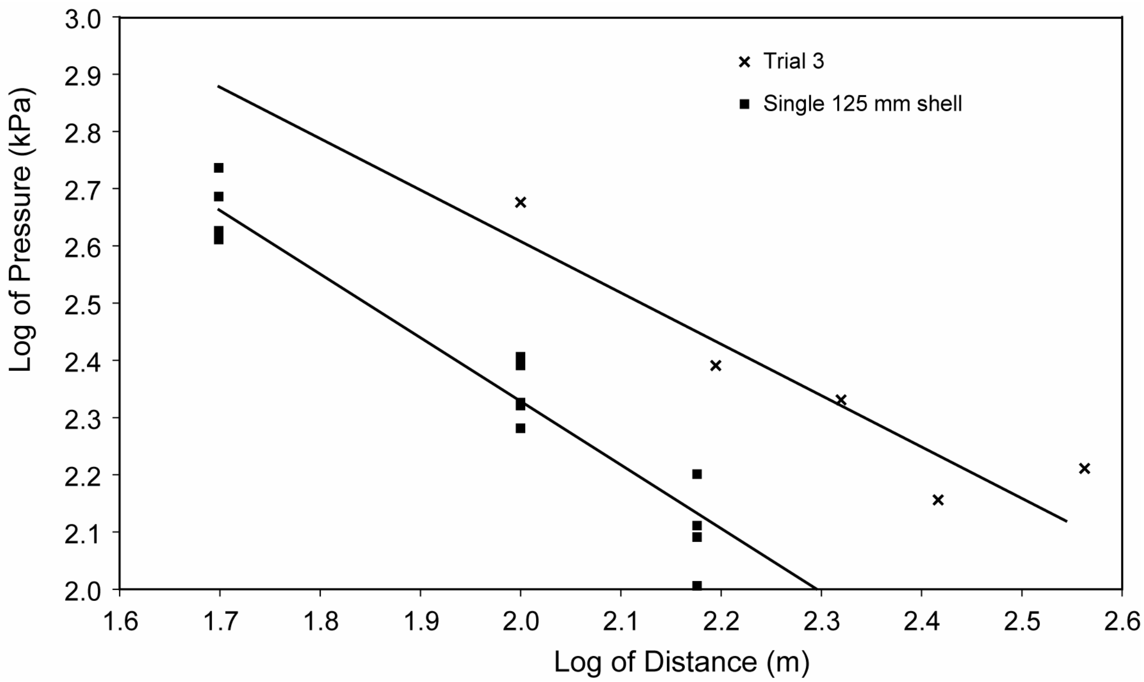

Figure 4. Overpressures measured during Trial 3 and preliminary tests using single 125 mm shells.

ter which would radiate stars to greater distances than the 125 mm diameter shells used in Trial 3. Shimizu[9] estimates the average diameter of the star burst from a 120 mm diameter shell to be 70 to 100 m compared to 130 to 150 m for a 190 mm diameter shell and 210 to 230 m for a 220 mm diameter shell. These figures compare well with the distances that unburnt stars were projected in the present trials. The presence of larger shells may also explain the additional ruptures in the container walls during Trial 2 because the burst charge would be larger and would place a higher instantaneous strain rate on the metal of the container than would a smaller shell.

The differences in the results from Trials 2 and 3, outlined above, are too small to reflect the difference in the NEC between them. These demonstrations show that the damage that a transport or storage container might sustain cannot be predicted with confidence from the net explosive content alone when an external fire occurs and firework explosions are induced inside the container. Assuming that all the pyrotechnic content of Trial 3 (2600 kg NEC) was blackpowder and that the stars in the shells would not contribute to a mass explosion because of their slow burn rate, it can be calculated that approximately 1147 kg of composition in the lift and burst charges was available for instantaneous ignition. Recent work undertaken at HSL[10] has indicated that as little as 500 g of blackpowder are sufficient to destroy a simple rectangular brick or block structure. The strength of the ISO container is likely to be greater than that of the brick or block building and a larger NEC would be required to disrupt it. However, since the much larger NEC used in the ISO container did not completely destroy the container, this indicates that the events observed did not include mass explosions of significant proportions of the contents.

Comparison of the overpressure output from Trial 3 and that from preliminary tests using single 125 mm shells (Figure 4) shows that the overpressure output from the container trial was 1.6 to 2.3 times greater than the pressure produced by individual shells over distances of 50 to 250 m, respectively. The increase in the difference in pressure between the two tests at greater distance is probably due to pressure peaks from individual shell explosions coalescing as they travel away from the explosion point. The data suggest that close to the explosion the overpressure in Trial 3 was not more than twice that obtained for a single shell. Overpressure generally increases as the cube root of the charge mass, which indicates that the observed maximum overpressure from the trial was generated from the instantaneous explosion of a maximum of 8 shells. This further confirms that, in general, shells used in Trial 3 exploded sequentially over a period of seconds or minutes. It appears that sufficient explosive needed to be consumed to generate the pressure necessary to burst open the ISO container doors. Once this had happened the energy of any remaining explosions was effectively vented to atmosphere without causing appreciable additional damage.

The debris from Trial 3 included 51 shells that were intact and capable of explosion if correctly fused. This supports the conclusion that mass explosion of the container contents did not occur. It also highlights one of the potential hazards that firefighters may be exposed to during a clean-up operation. During HSL's trials, shells were only found outside the container, but this may not necessarily be the case in all situations. Unexploded shells could be covered in ash, which could cause ignition if not damped down sufficiently. Since explosion of a shell close to a person could cause severe injury, emergency services should be informed of this hazard.

The preceding discussion attempts to explain the effects observed during the trials described in this paper. However, it does not explain the ferocity of the explosions reported from the incidents at Uffculme[4] and Enschede.[5] In both cases the contents of the storage containers started to function as described in Trials 2 and 3 of this paper, but rapidly escalated to produce effects normally identified with mass explosion events (UN classification 1.1). In these incidents blast damage was observed at a considerable distance from the source of the explosions. Assuming that only fireworks were stored in the containers, it seems likely that a large proportion of the pyrotechnics in the store must have exploded instantaneously. To simultaneously expose such large amounts of pyrotechnic composition, well-made and well-packaged fireworks would require a considerable disrupting force. This might be achieved if large shells, or more likely, fireworks containing significant quantities of flash powder, such as report shells, were present. No fireworks of this type were used in HSL's trials, which may explain why the events observed at the incidents were not reproduced.

Conclusions

1) Selection boxes designated 'BS Category 3 display fireworks', which contain a mixture of low energy Category 2 and 3 fireworks, similar to those used in Trial 1, are unlikely to cause explosions that will have sufficient force to damage an ISO container. Therefore, the pyrotechnic effects are likely to be contained.
2) Opening the doors of an ISO container of BS Category 3 display fireworks selection boxes—after the contents have been ignited by an external fire—can result in a rapid escalation of the fire leading to a heightened hazard from pyrotechnic effects outside the container.
3) Some fireworks types, such as the 125 mm star shells used in Trial 3, currently classified as UN1.4, are likely to throw fiery projections beyond the 15 m distance specified in the test criteria for the UN Series 6(c) Test and may require a UN1.3 classification. As a result of these findings a review of certain aspects of firework classification may be necessary.
4) If sequential explosions of fireworks in an ISO container occur, as has been demonstrated in the trials described in this paper, the weakest point of the container (the door bolts) will fail and allow subsequent explosions to vent. Although star shells of up to 200 mm diameter have been tested as part of a mixed load (Trial 2) during the current trials, larger or more energetic shells would need to be assessed before this conclusion could be widely applied.
5) These trials have not reproduced the mass explosion effects reported at the incidents in Uffculme and Enschede. This suggests that fireworks other than those tested may have been present in those incidents, or that the fireworks were confined differently. In Tri-

als 2 and 3 the initial explosions blew open the ISO container doors, which would have reduced the confinement around the fireworks.

Further Work

The current work has shown that the UN classification of fireworks may need to be reappraised in some instances. At the time of writing, papers have been submitted by The Netherlands for consideration at the UN and a European collaborative research proposal has been submitted for funding under the Framework V programme. The latter will test large quantities of a range of firework types when stored in ISO containers challenged by an external fire source. To date, however, it has not been possible to provide an adequate explanation of the mass explosion effects reported from the Uffculme and Enschede incidents. As a result, HSE has instigated research to investigate current fireworks classifications, using UN Series 6(c) Tests, to explore the possibility of high energy shells causing disruption of fireworks packaging leading to mass explosion behaviour, and is considering the merits of developing small scale methods of screening fireworks that are able to predict their likely behaviour when stored in large quantities. Findings from this research will be published in due course.

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Application of Hydroxyl (OH) Radical Ultraviolet Absorption Spectroscopy to Rocket Plumes

M. W. Teague*, Tonya Felix*, M. K. Hudson†, and R. Shanks†

*Department of Chemistry, Hendrix College, Conway, AR 72032 USA

† Dept. of Applied Science, University of Arkansas at Little Rock, Little Rock, AR 72204 USA

ABSTRACT

A spectrometer system was constructed for measurement of transient species in flames by absorption of ultraviolet radiation. The output of a xenon arc lamp was used as the source of radiation, which was focused through the flame and onto a monochromator equipped with an intensified silicon diode array detector. The system was used to measure absorption by hydroxyl (OH) radical around 306 nm in the plume of a hybrid rocket motor. Hydroxyl terminated polybutadiene (HTPB) was used as the fuel and gaseous oxygen as the oxidizer. The experimental spectra were analyzed by comparison with known vibrational and rotational lines using a multi-parameter curve-fitting program. OH radical concentration and temperature profiles of the rocket plume are presented along with details of the spectrometer specifications.

Keywords: absorption spectroscopy, hybrid rocket motor, combustion diagnostics

Introduction

By increasing the understanding of the combustion of hybrid rocket fuels, new and improved fuels can be developed. Because burning is rapid, complex, and variable, investigative methods must be fast and non-intrusive. This work is an adaptation of techniques developed by Vanderhoff, et al. in which absorption of ultraviolet and visible light was used to detect and measure species involved in solid propellant combustion at modest pressure.[1–4]

A hybrid rocket motor employs a solid fuel grain through which the oxidizer is flowed. It combines some of the advantages of a liquid-propellant motor (start-stop-restart and throttle capabilities, and safety) with some of the advantages of solid-propellant motors (less plumbing and higher propellant density).

It is commonly accepted that hybrid rocket fuel burns according to the model shown in Figure 1.

In the boundary layer between the fuel and oxidizer flow, combustion takes place at the intersection of the vaporized fuel flow and oxidizer. This combustion zone is formed within the momentum boundary layer and is the source of the heat flow to the surface to maintain fuel vaporization. The flame front is located at about the point where stoichiometric fluxes of fuel and oxidizer result and the thickness of the zone is dependent on the chemical reaction rates. Depending upon the configuration of the exit nozzle and the amount of turbulence, the respective zones of the boundary layer may extend far enough beyond the end of the rocket to be accessible to remote spectral studies.

Experimental

Spectrometer development work was performed at Hendrix College using a model hybrid rocket using polymethylethracrylate (Plexiglas) as fuel and oxygen gas (O_2) as oxidizer. The spectral measurements were then made on a 50-lb thrust (23 kg) hybrid rocket motor developed in the Dept. Applied Science, University of Arkansas at Little Rock (UALR) by K. Hudson and R. Shanks.[5,6] The principle fuel employed in the hybrid rocket was hydroxyl-terminated polybutadiene (HTPB) with gaseous O_2 as the oxidizer.

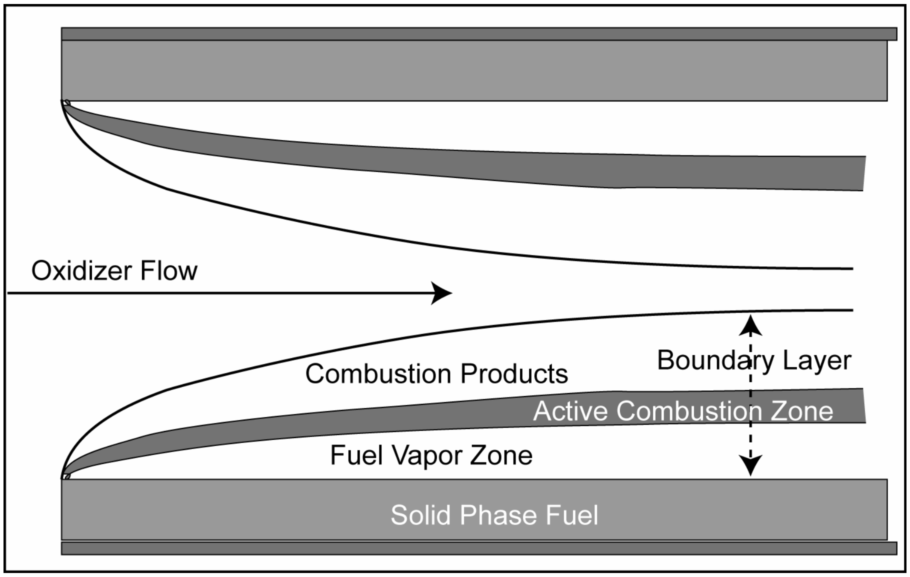

Figure 1. Hybrid rocket combustion model.

Most of the components of the experimental arrangement have been described in earlier reports,[1-4] so only a brief description will be included. The spatial arrangement is shown in Figure 2.

Time-resolved absorption measurements were made by passing a focused light beam from a xenon arc lamp through the hybrid rocket plume. Circular apertures were used to direct the beam and reduce emission interference. The transmitted beam was focused onto the slits of a 0.32-m Model HR-320 JY monochromator equipped with a 2400 groove/mm grating. UV-grade quartz lenses were used to focus the beam. The output of the monochromator was detected with a Princeton Applied Research Corporation Model 1455 intensified charge collection device. A visible filter was placed immediately in front of the monochromator entrance slits when second-order spectra were collected.

The optical bench was tested by detecting the hydroxyl (OH) radical in a "model" hybrid rocket composed of a Plexiglas fuel grain fed with gaseous oxygen. This species has been

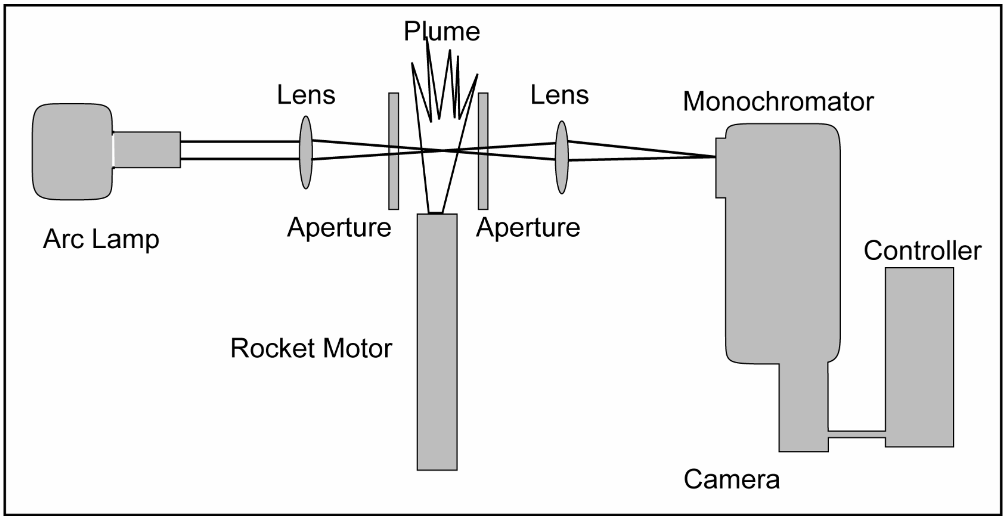

Figure 2. Experimental spectrometer setup.

studied quiet extensively in solid propellant flames and the characterization was relatively straightforward.

In the absorption measurements, the wavelength-resolved intensity of the light source is the primary measurement. This measurement is taken for conditions where the absorber of interest is absent (i.e., the incident intensity, I_0) and where the absorber is present (i.e., the transmitted intensity, I). The absorption is typically represented as the ratio, I/I_0. In this study I_0 is measured prior to combustion of the rocket fuel. During the burn the history of the transmitted beam is recorded by collecting a predetermined number of rapid scans into a number of separate memories. Typically, multiple memories were stored with 25 scans per memory at an exposure time of 20 milliseconds per scan. This provides spectra for 0.50-second time periods for a total of up to 30 seconds detection, more than adequate to provide safety for the personnel and catch the programmed 3-second burns. Background scans with no flame or lamp, and with flame only, are also collected and used to subtract background and flame emission effects, respectively.

Results and Discussion

OH radical absorption spectra were obtained in both first and second order in the 306-nm region of the ultraviolet radiation. Figure 3 is a typical transmittance spectrum from the plume of a Plexiglas model hybrid rocket. This particular one was obtained as a second-order spectrum in the blue flame region approximately 75 mm beyond the rocket body. The absorption includes distinct contributions from the R_1, R_2, and Q_2 bands in the $A^2\Sigma - X^2\Pi$ electronic transition of the OH radical.

Absorption measurements were then made at three different points in the plume of the hybrid rocket motor on three successive firings. The rocket firings were for approximately three seconds: absorption data were collected for 30-second intervals, producing six or seven spectra for each firing. The files were converted to MS-DOS files, edited, and loaded into the program for data analysis.

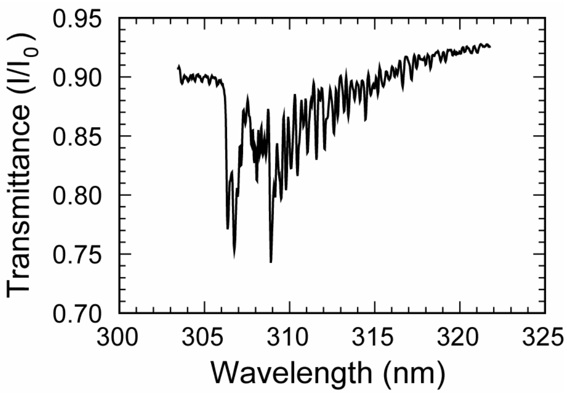

Figure 3. OH radical ultraviolet absorption spectrum.

Absorption path lengths (i.e., plume diameters) were estimated from video records of the rocket firings. The tapes were projected on a large screen and frame-by-frame examinations were performed to obtain the measurements. Rocket diameter and nozzle-to-beam distances were used as reference lengths to determine the video system magnification factor.

The data were analyzed using a multi-parameter curve-fitting routine provided by A. Kotlar .[7] This program utilized 153 rotational transitions over the three vibrational bands, R_1, R_2, and Q_2, in the spectral region of 306 to 312 nm. By comparing known spectral lines, absorption sensitivities, and temperature dependencies to the experimental spectra, a "best fit" is determined, which provides number density and temperature of the OH radical molecules in the flame. Parameters specific to the particular monochromator and detector system were provided to the program for all determinations. Each specific data set was then loaded along with the estimated pathlength for the curve-fitting routine. In most cases, the following parameters were varied to determine the appropriate temperature and number density: number density, temperature, baseline level (background offset), slope, slit width, pixel width, and reference channel.

Figure 4 shows a plot of the experimental and fitted data for one spectrum over the approximately 5-nanometer range covered by the 153 transitions available in the fitting routine.

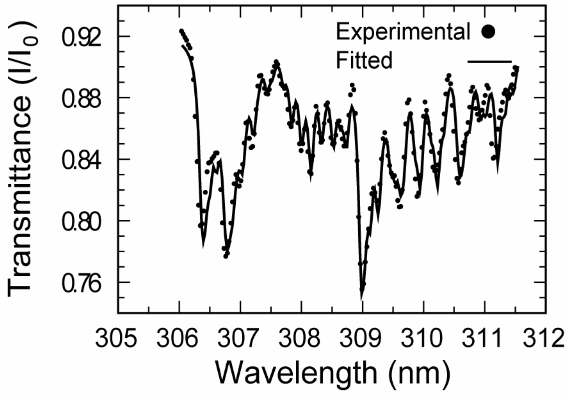

Figure 4. Experimental and fitted spectra.

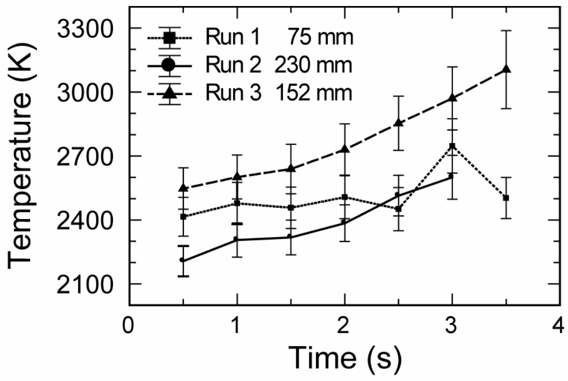

Figure 5. Rocket plume temperature profiles.

The pertinent curve-fitted results are compiled in Table 1. The measured plume diameters are listed in column 3. Each value represents an average over the half-second signal accumulation time; in some cases there were significant fluctuations in plume size, but these were usually cyclical in nature and averaged out well. In most cases the plume became irregular toward the end of the burn, so these data are not as reliable as those during the early and middle parts of the firings. The experimental uncertainty is indicated by standard deviation in the table and by error bars on the graphs.

Figure 5 represents the results of the measurement of the temperature of the OH radicals in the rocket motor plume at the three different distances. In all cases, the temperature rises during the burn. Since these data were taken on three different burns, no conclusion should be drawn about a spatial temperature profile along the axis of the plume. Figure 6 shows the results of the number density calculations. In all

Table 1. Temperature and OH density values in a hybrid rocket motor plume.

Run	Time (s)	Path Length (cm)	Temp (K)	Std. Dev.	Number Density	Std. Dev.
1	0.50	4.40	2415	91	2.43E+16	1.02E+16
	1.00	5.27	2478	98	2.23E+16	9.30E+14
	1.50	5.73	2457	97	2.08E+16	8.90E+14
	2.00	6.31	2507	101	1.37E+16	8.20E+14
	2.50	6.14	2451	101	2.10E+16	9.30E+14
	3.00	6.48	2747	127	1.78E+16	8.20E+14
	3.50	8.50	2503	96	7.00E+15	3.10E+14
2	0.50	3.50	2207	71	2.15E+16	7.70E+14
	1.00	5.04	2306	80	1.86E+16	7.10E+14
	1.50	5.83	2318	81	1.72E+16	6.50E+14
	2.00	8.82	2385	86	1.22E+16	4.70E+14
	2.50	10.68	2514	95	1.08E+16	4.30E+14
	3.00	10.07	2600	103	1.09E+16	4.80E+14
3	0.50	5.70	2547	97	1.95E+16	8.00E+14
	1.50	8.86	2639	116	1.52E+16	7.30E+14
	2.00	9.55	2730	120	1.42E+16	6.70E+14
	2.50	9.71	2853	127	1.65E+16	8.20E+14
	3.00	10.32	2970	148	1.34E+16	7.10E+14
	3.50	11.41	3105	183	5.50E+15	3.80E+14

cases, the number density decreases during the burn, although these data are not as smooth as the temperature profiles. Again, since the curves represent different burns as well as different distances from the rocket motor nozzle, conjecture about relative values is risky at this point, so no attempt is made to propose a spatial density distribution.

Conclusions

The results of this investigation show that ultraviolet radiation absorption measurements are a convenient, non-intrusive method of measuring temperature and OH radical concentration in a hybrid rocket motor plume. Using the motor at UALR, it was found that the temperature typically varied between 2500 and 3200 K, rising during a firing. Number densities decreased during a typical burn starting at about 2 × 10^{16} particles/cm^3.

Acknowledgements

We would like to thank the following for assistance on this project:

- Financial: Arkansas Space Grant Consortium; NASA, John C. Stennis Space Center; NASA Grant NCCW-55; NASA Graduate Student Researchers Program, Stennis Space Center, (R.B. Shanks).
- Instrument loan: Dr. John Vanderhoff, Army Research Laboratory, Aberdeen Proving Ground, MD.
- Curve fitting: Dr. Tony Kotlar, Army Research Laboratory, Aberdeen Proving Ground, MD.
- Video analysis: Vicki Pillow, The Jennings Snoddy Academic Resource Center, Hendrix College, Conway, AR.

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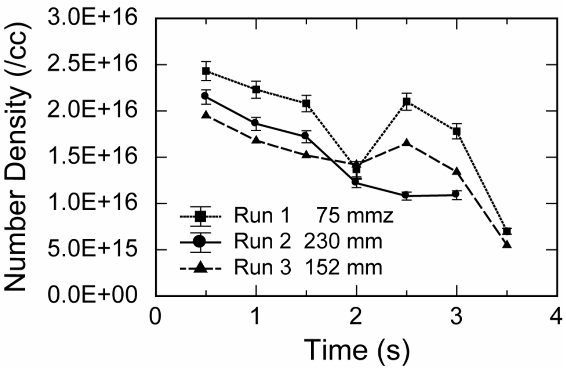

Figure 6. Rocket plume OH radical density profiles.

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Communications

Brief technical articles, comments on prior articles and book reviews

The following was brought to our attention by Barry Sturman. It originally appeared in *Quarterly Journal and Transactions of the Pharmaceutical Society of Victoria*, Vol. 1, No. 3 (1858) pp 119–120.

CORRESPONDENCE.

GRASS TREE GUM—(AUSTRALIAN DRAGON'S BLOOD)

Letter from Dr. McCrea, Chief Medical Officer.
C. M. O. Office, Melbourne, 23rd May, 1858.

Sir,— The accompanying specimens of gum, from the grass tree, have been transmitted to me, and I shall be glad if you will bring them before the Pharmaceutical Society, with the view of testing their properties.

I have the honor to be,
Your obedient servant,
W. McCREA,
CHIEF MEDICAL OFFICER.

The Secretary of the Pharmaceutical Society

ANSWER TO THE ABOVE.

Pharmaceutical Society's Office, 3 Commercial Chambers,
Swanston Street, Melbourne, 17th June, 1858.

Sir,— In reply to your letter, accompanying some specimens of gum from the grass-tree, growing in Gipps' Land, which I had the honor to receive on the 23rd day of May 1858, I beg to inform you that I, on the first opportunity, laid the gum before the Council of the Pharmaceutical Society, as intimated in your letter.

The Council having commissioned me to make a careful chemical examination of the gum, I now beg to communicate to you the result of the investigations on its properties.

The gum originates from *Xanthorrea Australis Rob. Brown*, which occurs abundantly in Gipps' Land, and. on several ranges of mountains in this colony. It resembles so much, in every respect, dragon's blood that it might be called Australian dragon's blood. The dark-brown globulous, nutmeg-sized lumps, are very brittle, and easily rubbed up into a saffron-yellow powder.

The gum is not soluble in water or turpentine, sparingly or partly in fatty oils, but very readily in diluted spirits of wine and ether. The solution in spirits of wine forms a splendid varnish, or lac, which appears to be useful for many purposes.

When heated to about 200 degrees the gum melts, and fumes arise of a peculiar, but very agreeable smell similar to benzoin and styrax, owing to an etherial oil, benzoic and cinnamic acid. With the alkalies it unites, very readily, to the production of combinations very soluble in water; with the earthy and metallic bases the gum combines also.

The most important and interesting chemical results are obtained by treating the gum with nitric acid, as well in a scientific as an industrial point of view. If on one part of the gum in powder be poured 10 or 12 parts of nitric acid, a violent effect takes place, and the gum soon disappears. After boiling for about half-an-hour, the brown color of the solution at first produced is changed into deep yellow and is then evaporated, in a vapor bath, to dryness. In this way; about fifty per cent of the very important chemical substance, picric acid, may be obtained from the gum used, mixed with a small quantity of oxalic and nitro-benzoic acid.

For purification, the picric acid is combined with potash; the resulting salt crystallized once or twice, and, finally, decomposed by muriatic acid. The picric acid (sparingly soluble in water) is redissolved in spirit, and made to crystallize.

I have the honor to forward you a sample of the acid so prepared.

Besides the scientific interest attaching to this substance, picric acid is a most valuable yellow dye for silks and wools, which it colors of any tint from a light straw to a brilliant canary.

Picric acid has a very remarkable bitter taste, and has been recommended as a remedy in intermittent fever.

The Society owes to you the sincerest thanks for having drawn its attention to a substance which promises such interesting results to science and to industry.

I have the honor to be, sir,
Your most obedient servant,
JOHN KRUSE, Sec. Phar. Society.

Review of:
Propellants and Explosives: Thermochemical Aspects of Combustion

Naminosuke Kubota
Wiley VCH [ISBN 3-527-30210-7], 2002

M. K. Hudson
Dept. of Applied Science, University of Arkansas at Little Rock, Little Rock, AR 72204 USA

Kubota's new title covers a wide area, as its name suggests. However, as its subtitle indicates, the author has focused on the thermo aspects of combustible materials. An examination of the book shows that it contains nine chapters, which can be broken down into three major groupings (the author indicates four). Chapters one to three cover the thermodynamics concepts necessary to understand energetic materials used in the combustion field, as well as reviewing some of the phenomena of combustion. Topics covered in these sections include the formation of shock and detonation waves, equilibrium and reaction rates, as well as flame structure and ignition processes, which provide a good, in-depth review. While presenting a considerable number of equations, necessary to explain the phenomena and basis for combustion, the author uses figures and good explanations in the text to guide both the combustion scientist and technical users along.

The second portion of the book actually deals with the combustion of energetic materials, with Chapter four providing a general overview. Chapters five through seven provide a fairly in-depth look at the uses and thermodynamics of these materials, discussing the combustion wave structure, burning rates, and associated parameters for each type of material presented. Each type of material is covered in a similar manner, which allows them to be compared. Again, the author makes good use of graphs, tables, and figures to make his points and instruct the reader in many of the finer points. In particular, I found the use of flame photographs from strand burners interesting, as he illustrated the various zones (dark and luminous) seen for the conditions of the experiments involved. Related to these figures, the author also provides a very good explanation of then use of strand burners in appendix B.

The last part of the book covers the uses and applications of this knowledge. Chapters eight and nine present materials on the combustion of explosives and rocket motors. In particular, the sections on the use of explosives for blasting, gun propellants, and rocket propulsion were very informative. The explanation of co-axial burning and end burning rocket propellant grains, along with an excellent discussion of the phenomena observed during a solid motor run will be put to good use by students and others seeking practical knowledge on such topics. The equations concerning and the discussion of instabilities in rockets provided a fresh view to this reader, and will be used in future classes. Also, the discussion on ignition and transients that are seen will be of significant use to our research group as we design new experiment and attempt to model similar behavior that we are studying.

In summary, I find Kubota's book to be a very good work, and I plan to utilize it in the classroom as well as in our research. While it is not meant to replace the classics by Glassman and others, it does provide a discussion of the combustion of solid materials. It does a good job of providing updated examples and a new look at combustion phenomena, particularly that of solid energetic materials. While his audience appears to be the advanced undergraduate or graduate student, others working in the combustion field should be able to put the topics presented to good use, and it is recommended for inclusion in their technical libraries.

Review of: *Explosives*

Fifth Completely Revised Edition

Rudolf Meyer (deceased), Josef Köhler, and Axel Homburg

Wiley VCH [ISBN 3-527-30267-0], 2002

L. Weinman
Schneier/Weinman Consultants, LLC
9051 Sugartree Trail, Huntsville, AL 35802

This book, for those who are not familiar with it, it is a compendium of short references to various explosives and related items of interest. There are some limited references to pyrotechnic materials and items, but the material is strongly oriented toward high explosives both civilian and military.

This book is of particular interest to those needing some sort of reference to many older, or obscure, materials. While most entries are not very extensive, they often have enough information to either provide sufficient information or, at least, give some indication of where further information may be sought. A sometimes useful feature is that many of the entry names are given in German and French as well as English.

In briefly comparing this 5th edition to the older 2nd edition, additions and deletions were moderately numerous. An unfortunate matter is that although this is the 5th edition, there are still entirely too many typos or "odd" word selections to call this a completely "English" version.

An example of where the book may be most useful is the article on Impact Sensitivity (Testing). This article is approximately 4-1/2 pages long and gives some detail and comparison about how various national standard tests are performed. Similarly, the Airbag entry describes typical airbag gas generators and even has a table of expected effluents and their specified limits.

On the other hand, the entry for Black Powder only takes about 1/2 page and this covers composition, use, and manufacture.

One of the few directly pyrotechnic items is Illuminant Composition, which has no actual composition information and the text implies that illuminant composition is always pressed into a container.

As a further indication of the primarily high explosive orientation, the entry for Detonation runs to about 12 pages plus a 2 page bibliography.

This 5th edition was also supplied with a CD ROM containing a database and compilation of thermochemical data for 500 substances. Also available from the publisher is a more complete database containing information on over 6000 substances. This might prove useful to those doing such work or needing to add information to the database contained in PEP (Propellant Evaluation Program).

For those who either do not have a copy of this book, or who have a much earlier edition, it may prove useful to examine a copy for possible use.

Events Calendar

Pyrotechnics and Fireworks

Recent Advances in Pyrotechnics

June 8–12 2003, 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

30th Int'l Pyrotechnics Seminar held in conjunction with Euro Pyro 2003.

June 23–27 2003, Saint-Malo, France

Contact: Claude Prisset, Seminar Chairman
AFP, PO Box 121
45240, La Ferte, Saint Aubin, France
e-mail: europyro.2003@club-internet.fr
web: www.perso.club-internet.fr/afpyro

Chemistry of Pyrotechnics & Explosives

July 27 – Aug. 1 2003, 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. 9–15 2003, Gillette, WY, 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

31st Int'l Pyrotechnics Seminar

mid to late July, 2004, will be in USA

Ms. Linda Reese, Applied Res. Assoc., Inc.
5941 S. Middlefield Rd., Suite 100
Littleton, CO 80123, USA
Phone: +1-303-795-8106
FAX: 1-303-795-0125
email: lreese@ara.com

7th Int'l. Symp. on Fireworks

October 6–10 2003, Valencia Spain

Contact: Fred Wade
Box 100
Grand Pré, NS, B0P 1M0, Canada
Phone: +1-902-542-2292
FAX: +1-902-542-1445
email: fireworks@fireworksfx.com
web: www.ISFireworks.com

Energetic Materials

Computational Mech. Assoc. Courses–2003

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email: 74047.530@compuserve.com
web: www.compmechanics.com

6th Int'l. Seminar "New Trends in Research of Energetic Materials"

April 23–25 2003, Pardubice, Czech Republic

Contact: Prof. Svatopluk Zeman, D.Sc.
Dept. Theory & Tech. Explo., Univ. Pardubice
CZ-432 10, Pardubice, Czech Republic
Phone: +420-46-603-8023
FAX: +420-46-603-8024
email: kttv.fcht@upce.cz
web: www.upce.cz/~kttv

34rd Int'l Annual Conf. ICT – Energetic Materials - Synthesis, Production & Application

June 24–27 2003, Karlsruhe, Germany

Contact: Manuella Wolff
Fraunhofer-Inst. für Chem. Technologie (ICT)
P. O. Box 1240
D-76318 Pfinztal (Berghausen), Germany
Phone: +49-(0)721-4640-121
FAX: +49-(0)721-4640-120
email: mw@ict.fhg.de
web: www.ict.fhg.de

29th ISEE Conf. on Explosions and Blasting Technique

Feb 2–5 2003 Nashville, TN, USA

Contact: Lynn Mangol
Phone: 440-349-4400

2003 Insensitive Munitions & Energetic Materials Technology Symposium

March 10–13 2003, Orlando, FL, USA

Contact:Christina Buck at NDIA,
Phone: +1-703-522-1820
email: cbuck@ndia.org.)
web: www.ndia.org/events

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

May 2004 (tentative) Sweden

Contact: Stig Johansson
Johan Skyttes väg 18, SE 55448
Jönköping, Sweden
Phone/FAX: +46-3616-3734
email: srj@telia.com

Propulsion

41st Aerospace Sciences Meeting & Exhibit

January 6–9 2003, Reno, NV, USA

Contact:
Phone: 703-264-7500 or 800-639-2422
Web: http://www.aiaa.org/calendar

AIAA/ASME/SAE/ASEE Joint Propulsion Conference

July 14–17 2003, Huntsville, AL, USA

Contact:
Phone: +1-703-264-7500 / 800-639-2422
web: www.aiaa.org

High Power Rocketry

LDRS 2003

Contact: see web site
www.tripoli.org/calendar.htm

Model Rocketry

NARAM 2003

Contact: — see web site for details:
web: www.naram2003.org
For other launch information visit the NAR
Web site: www.nar.org

Future Events Information

If have information concerning future—explosives, pyrotechnics, or rocketry—meetings, training courses or other events that you would like to have published in the *Journal of Pyrotechnics*, please provide the following information:

Name of Event

Date and Place (City, State, Country) of Event

Contact information — including, if possible, name of contact person, postal address, telephone and fax numbers, email address and web site information.

This information will also be published on the Journal of Pyrotechnics Web Site:
http://www.jpyro.com

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4808 Moorland Lane - Ste 109
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Dr. Phil Lightfoot, Manager
CANMET - 555 Booth St.
Ottawa, ON K1A 0G1, Canada
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Grenadiersweg 55
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Fawkes Fireworks
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Subject Areas

Fireworks, Pyrotechnic Special Effects, Propellants, Rocketry and Civilian Pyrotechnics

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Submissions should be made directly to the publisher at the address at bottom of page. Upon receipt of an article, the author will be sent an acknowledgment and a tentative publication date. For specific requests regarding editors, etc. please include a note with that information. Preferably the text and graphics will be submitted electronically or on a 3-1/2" diskette or CD in IBM format with a print copy as backup. The Journal is currently using Microsoft Word 2002, which allows for the import of several text formats. Graphics can also be accepted in several formats. Please also inform us if any materials need to be returned to the author.

General Writing Style

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

Format

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

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

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

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

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

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

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

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

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Contact Bonnie Kosanke, Publisher, the Journal of Pyrotechnics, Inc., 1775 Blair Road, Whitewater, CO 81527, USA.
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