

Journal of Pyrotechnics

Issue 11, Summer 2000

Policy Board Members:

Ettore Contestabile
Canadian Explosive Research Lab
555 Booth Street
Ottawa, Ontario K1A 0G1, Canada

Gerald Laib, Code 950X
Naval Surface Warfare Center
Indian Head Div.
101 Strauss Avenue
Indian Head, MD 20640-5035 USA

Wesley Smith
Department of Chemistry
Ricks College
Rexburg, ID 83460-0500, USA

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

Managing Editor:

Ken Kosanke
PyroLabs, Inc.
1775 Blair Road
Whitewater, CO 81527, USA

Copy Editor:

Wesley Smith
Department of Chemistry
Ricks College
Rexburg, ID 83460-0500, USA

Technical Editors for this issue:

Per Alenfelt, Hansson Pyrotech AB
Billdal, Sweden

John Bergman
Janesville, WI, USA

Tony Cardell, DERA
Fort Halstead, Kent, UK

C. James Dahn, Safety Consult. Engr.
Schaumburg, IL, USA

Dave Dillehay, Technical Consultant
Marshall, TX, USA

Frank Feher, Univ. CA – Irvine
Irvine, CA, USA

Sgt. J. R. Giacalone, WV State Police
S. Charleston, WV, USA

Ian Grose, Special Systems, DERA
Salisbury, Wilts., UK

Clive Jennings-White
Salt Lake City, UT, USA

Naminosuke Kubota, Sci. Advisor
Kamakura, Japan

Michael Petrin, Clorox Tech. Ctr.
Pleasanton, CA, USA

Barry Sturman
Mt. Waverly, VIC, Australia

Ian von Maltitz
Colorado Springs, CO, USA

Rutger Webb, TNO
Den Haag, The Netherlands

Frederic Whitehurst, Forensic Justice
Project, Washington, DC, USA

Direct Editorial Concerns and Subscription Requests to:

Journal of Pyrotechnics, Inc.

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.

Table of Contents

Issue 11 Summer 2000

A Labscale Hybrid Rocket Motor for Instrumentation Studies R. Shanks and M. K. Hudson	1
Chemical Analysis of Consumer Fireworks P. Alenfelt	11
Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures Part 3. The Effects of Stoichiometry, Particle Size and Added Materials D. Chapman, R. K. Wharton, J. E. Fletcher and A. E. Webb	16
Propellant Chemistry N. Kubota	25
Pyrotechnic Particle Morphologies — Metal Fuels K. & B. Kosanke and R. Dujay	46
Forensic Testimony: “Matches”, An Over-Inference of Data? A <i>Giglio</i> Obligation? F. Whitehurst	53
Study on Various Polyesters as Binders for Pyrotechnic Composition J.P. Agrawal, S.N. Singh, D.B. Sarwade, V.A. Mujumdar & NT Agawane	65
Communications:	
Shell Altitude vs. Mortar Length by R. Dixon.....	70
The Effect of Sample Containers on the Ignition Temperature of Sulfur/Chlorate Mixtures by D. Chapman and J. E. Fletcher	72
Errata	24
Events Calendar	62
Sponsors	75
Author Instructions	78

Publication Frequency

The *Journal of Pyrotechnics* appears approximately twice annually, typically in mid-summer and mid-winter.

Subscriptions

Anyone purchasing a copy of the Journal will be given the opportunity to receive future issues on an approval basis. Any issue not desired may be returned in good condition and nothing will be owed. So long as issues are paid for, future issues will automatically be sent. In the event that no future issues are desired, this arrangement can be terminated at any time by informing the publisher. Additional discounts are available for payment in advance for issues of the *Journal of Pyrotechnics*. Contact the publisher for more information.

Back issues of the Journal will be kept in print permanently as reference material.

A Labscale Hybrid Rocket Motor for Instrumentation Studies

Robert Shanks and M. Keith Hudson

Graduate Institute of Technology and Dept. of Applied Science
University of Arkansas at Little Rock, Little Rock, AR 72204 USA

ABSTRACT

An interest in plume spectroscopy led to the development of a labscale Hybrid Rocket Facility at the University of Arkansas at Little Rock (UALR). The goal of this project was to develop a reliable, consistent rocket motor testbed for the development of plume spectroscopy instrumentation. Hybrid motor technology was selected because it has proven to be safe and inexpensive to operate. The project included the design and construction of the labscale hybrid rocket motor, the supporting facility, the instrumentation and computer control of the motor, and the characterization of this particular thruster, including the regression rate of hydroxyl-terminated polybutadiene (HTPB) fuel grains. For plume spectroscopy experiments, the fuel is doped with metal salts, to simulate either solid motors or liquid engines. It was determined the labscale hybrid motor produces a reliable and consistent plume, resulting in an excellent tool for the development of plume spectroscopy and other instrumentation.

Keywords: hybrid rocket motor, plume spectroscopy, engine health, ground testing, rocket diagnostics

Introduction

In recent years there has been an increased interest in engine health monitoring, particularly by observation of the rocket plume. At NASA-Stennis Space Center, Space Shuttle Main Engines (SSME) are rebuilt after every flight. Several studies have indicated that severe engine wear can be detected by engine plume diagnostics, and the need for these expensive rebuilds may be eliminated.^[1] In some types of rocket

motors, especially solid motors, toxic combustion products may be produced, so it is also environmentally important to monitor emissions from rocket plumes.

The University of Arkansas at Little Rock (UALR) has been developing low cost, rugged instrumentation for plume spectroscopy for the last few years. UALR has performed joint work with NASA-Stennis, Hercules Aerospace and other aerospace companies. Testing instrumentation at other facilities, which have firing capabilities, can be accomplished; however, this is expensive, time consuming, and inconvenient, as firing schedules are usually very rigid. The need for a system to easily test new instrumentation and techniques to monitor rocket plumes provided the motivation to develop this labscale hybrid rocket motor facility at the University.

The labscale Hybrid Rocket Facility provides a significant capability for instrument testing, especially for plume spectroscopy instrumentation. Most current diagnostic work is aimed at measuring emissions from solid motors or engine component degradation in liquid engines. Facilities to test plume-monitoring instrumentation usually consist of a thruster of one of these two types. However, hybrids offer greater safety, reliability, and lower operating costs. Because UALR has the facilities to cast fuel grains, these can be doped with different metal salts for seeding the plume. This is necessary for simulating solid motors or liquid engine component degradation.

The project included the design and construction of a labscale hybrid motor, instrumentation for the motor, the design and construction of gas flow system to support the motor, a computer control system, and a data acquisition system. This facility was constructed on the Uni-

versity campus and included areas for plume monitoring instrumentation.

To test the level at which this hybrid facility meets the needs of the project, experiments were conducted to determine the quality and reliability of the plume produced, as well as the spectral characteristics of the plume when seeded. Experiments were conducted to determine the combustion stability of the motor with hydroxyl-terminated polybutadiene (HTPB) fuels and a test matrix developed to determine the regression rate of the HTPB fuel over a range of oxidizer flows. The plume was also seeded with metal salts and spectral data was collected in the UV-Vis, as reported in a separate paper.^[2]

Conversion Units

1 lbm = 1 pound mass = 454 grams

1 lb = 1 pound = 454 grams

1" = 1 in. = 1 inch = 25.4 mm

1 psia = 1 pound per square inch = 0.145 kPa

Theory of the Testbed Facility

The test facility as constructed was based loosely on the Diagnostic Testbed Facility (DTF) at NASA's John C. Stennis Space Center and other ground based test units, such as those for solid motors. Now a part of the Component Test Facility, DTF was designed to provide a testbed for development of liquid engine plume diagnostic instrumentation. A 1,200-pound-thrust, liquid-oxygen/gaseous-hydrogen thruster was used as the plume source for experimentation and instrument development. Studies have been performed to ensure the DTF thruster has been optimized to produce a plume with temperature conditions as much like the plume of the Space Shuttle Main Engine (SSME) as possible. The engine is equipped with a plume seeding device, which allows liquid seeding materials (dopants) to be injected directly into the combustion chamber.^[3] These materials simulate engine component failures, such as occur in bearings and other structural elements.

Comparatively, the Hybrid Rocket Facility at UALR provides a testbed for the development of rocket propulsion system exhaust plume di-

agnostics instrumentation for solid motors and liquid engines. A 50-pound-thrust, hybrid-rocket thruster is used as the plume source. It operates on gaseous oxygen and HTPB solid fuel. While the plume visually looks more like a solid motor plume, the combustion products are similar to a liquid engine using a kerosene fuel and liquid oxygen. The fuel grain, during casting, can be loaded with metal salts to provide the same seeding capabilities as DTF. The facility also was designed to simulate solid rocket motors. The fuel can be loaded with chloride salts to produce hydrogen chloride emissions.

Design and Materials

The facility consists of the lab-scale hybrid motor, the gas flow control system, the computer controlled operating system, the computer data acquisition system, and the instrumentation on the motor and other systems.

The initial step was the design of the hybrid motor thruster. Several specifications needed to be met with this motor. It needed to be fairly small; this would cost less to build and less to operate while offering greater safety. Most lab-scale motors consist of fuel grains 2 inches in diameter or less, and this size range fits the needs of this project.

Second, the motor needed to be capable of simulating the characteristics of larger motors. This scalability is necessary because most plume spectroscopy instrumentation is designed to operate on actual propulsion systems. To simulate those motors well, the hybrid thruster was designed with the capability of producing chamber pressures up to 500 psia, giving plume temperatures and other characteristics similar to larger motors.

Also, for spectral purposes, the oxidizer to fuel (O/F) ratio would need to be varied from below stoichiometric to well above stoichiometric for the HTPB fuel. To accomplish this, the oxidizer flow has a maximum mass flow of 10 pounds per minute of gaseous oxygen. This allows firings under a wide range of chamber pressures and oxidizer to fuel ratios. The motor design has a fuel grain 2 inches in diameter and 10 inches in length. It starts with a central circular port 0.75 inches in diameter. This size

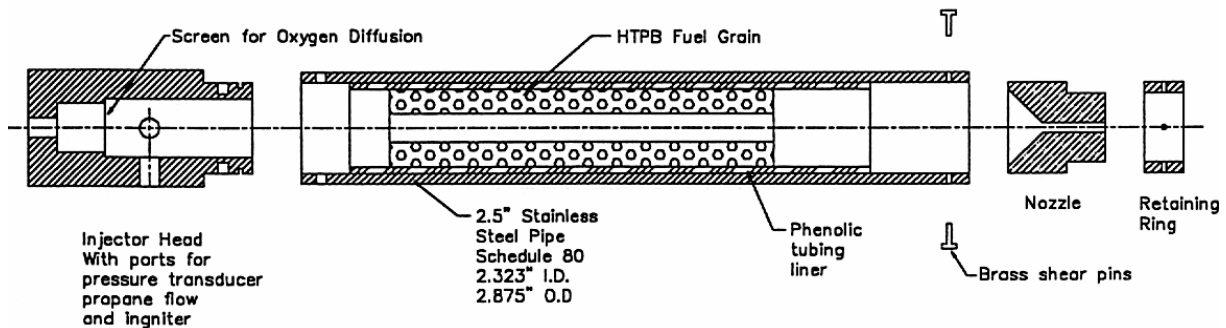


Figure 1. Layout of the lab-scale hybrid rocket motor.

fuel grain, coupled with the oxidizer flow rates attainable, can give O/F ratios from 1.5 to 4.5. This is ideal because HTPB burns stoichiometrically to CO and H₂O at an O/F ratio of 2.074.

The motor design consists of two main sections, the head assembly and the chamber body. The specifications for the mechanical design of the chamber body included the following design goals. The chamber was designed for a maximum firing pressure of 500 psia. The nozzle was designed to eject at 1000 psia in case of chamber over-pressurization. A 3-times safety factor was needed for pressure tolerance on the chamber body (3000 psia). This required a section of type 304 stainless steel, 2.5 inch, schedule 80 pipe. In addition to the 10-inch fuel grain, the chamber body would also have to house the nozzle and two chambers, one fore and one aft of the fuel grain. The design is shown in Figure 1. The head assembly is machined from a type 303 stainless steel round. This unit includes a diffusion screen, oxidizer-flow/nitrogen-purge inlet, propane ignition inlet, igniter inlet, and chamber pressure transducer port.

The nozzle is machined from a section of graphite and is 2.5 inches in length, held in place by a steel retaining ring and brass shear pins. The fore and aft chambers are lined with silica phenolic tubing used as an ablative insulator. Paper phenolic tubing is used as a sleeve in casting the fuel grain and is left on the grain during firing, which eases assembly and disassembly. For casting, the sleeve is held in a Teflon jig, with a Teflon coated rod as a central port mandrel.

Gaseous oxygen as oxidant, nitrogen for purging, and propane for ignition are needed to operate the motor. The oxygen and nitrogen are each supplied in a standard K or T cylinder and the propane in a standard "gas grill" bottle. Each gas line consists of a pressure regulator on the cylinder, a purge valve, a pressure relief valve or check valve, an electronically controlled shutoff valve, and a flow-metering device. The gas flows are set manually prior to firing by adjusting the tank regulators. The flows are started and stopped electronically using solenoid valves, allowing computer control of the firing sequence. The oxygen flow system has the capability of handling a mass flow of up to 10 pounds per minute at pressures up to 1000 psia. Flow is initiated using a pneumatic shutoff valve that is operated with nitrogen, controlled by a solenoid valve. The mass flow is controlled using a sonic flow nozzle and setting the proper regulator pressure. The actual mass flow is determined by measuring the pressure and temperature on the upstream side of the sonic flow nozzle. A pressure transducer and thermocouple are utilized to make these measurements. The flow of both the nitrogen and propane are set using regulating valves. A schematic of the gas system is shown in Figure 2.

Instrumentation

The function of the entire firing sequence is controlled and monitored by computer. This system consists of a 486DX-33 MHz computer (Gateway, Inc.), a 12-bit analog-to-digital conversion board (Computer Boards, Inc.), which includes digital input/output ports, an analog

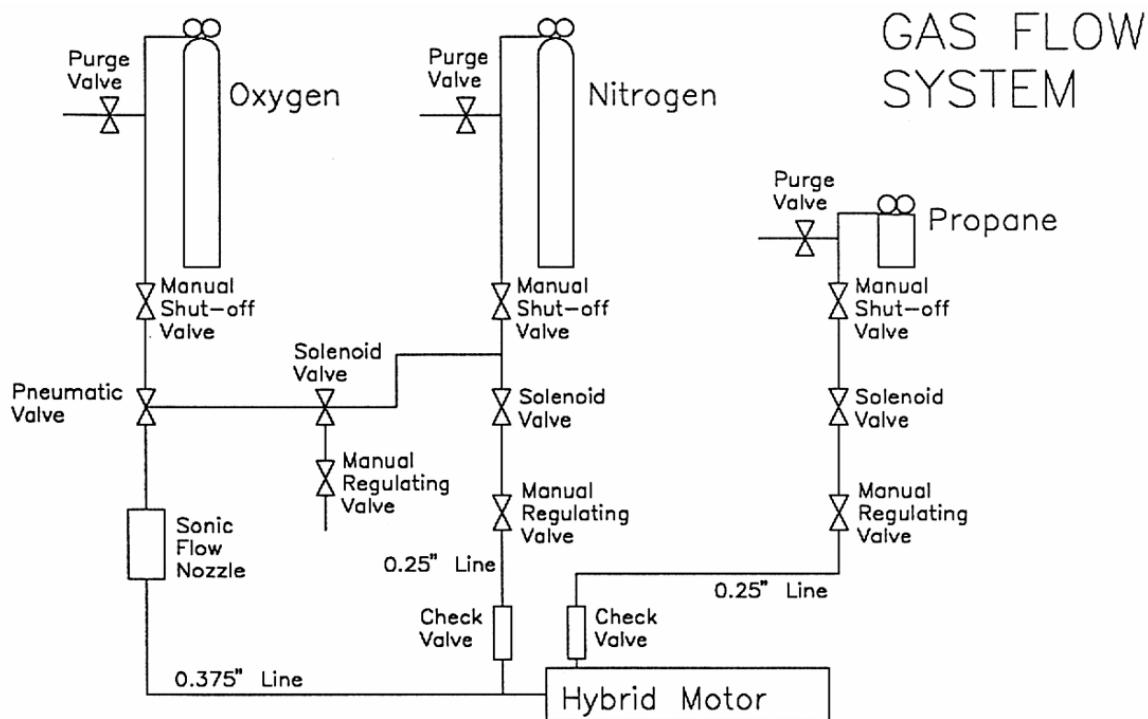


Figure 2. Gaseous materials flow system.

isolation board, and a solid-state digital input/output board.

The analog-to-digital board is installed in the computer and is connected to the remote analog isolation board. The isolation board accepts analog inputs from two pressure transducers (Keller PSI) and four thermocouples. It is capable of handling up to 8 differential inputs. One pressure transducer (1100 psia maximum) measures the oxidizer pressure on the upstream side of the sonic flow nozzle and one J type thermocouple takes the temperature at this position. The other pressure transducer (1000 psia maximum) measures the chamber pressure of the hybrid motor. The output from these pressure transducers is 0 to 5 volts DC. The other three temperature inputs are from K-type thermocouples and can be positioned where needed on the motor or test stand. All thermocouple inputs are fed into 5B-type analog isolation modules on the analog isolation board. These modules linearize and cold-junction compensate the thermocouple signal. The output from these modules is 0 to 5 volts DC so that they can be input directly to the analog-to-digital conversion board in the computer.

The digital input/output section of the board controls the gas flow system and the ignition pulse. The digital output lines go from the board in the computer to the solid-state digital input/output board. This board contains up to eight isolation modules that can control AC and DC voltage lines. Three of these control AC lines that operate the solenoid valves that control the gas flow. A fourth line controls a DC voltage line that is the igniter pulse line.

The computer firing control system consists of a graphical user interface screen, shown in Figure 3, with which the operator can control and observe all functions of the motor. Functions that can be controlled from the interface are the operation of the gas handling system, the firing duration (from 3 to 10 seconds), and the start of events for the automated firing sequence. Data is collected at 25 hertz per channel. While this is relatively slow, it is sufficient for a feed back loop to operate the hybrid motor and allows real time parameter display for the operator. The real time display includes: chamber pressure, upstream oxygen pressure, upstream oxygen temperature, oxygen mass flow rate, and the temperature at 3 separate points on

COMBUSTION DIAGNOSTICS FACILITY

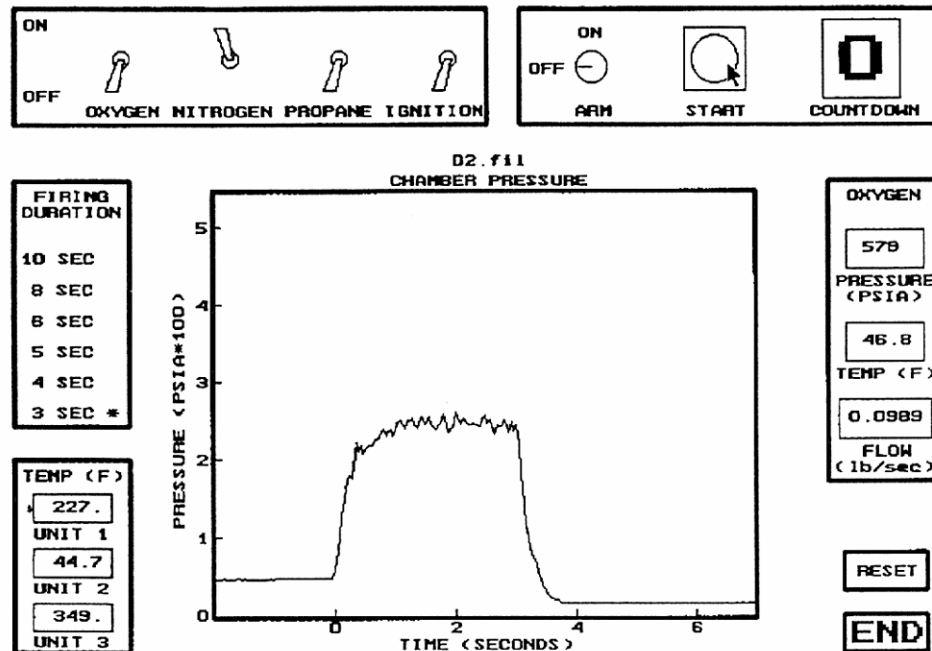


Figure 3. Graphical user interface for the Labscale Hybrid Rocket Motor Testbed Facility.

the motor. A thrust measurement can be included in the future, but was not required for the spectral monitoring experiments.

Data is also collected on a separate 486DX-33 (assembled in house) computer that is dedicated to this purpose. It also uses a 12-bit analog-to-digital converter board (Computer Boards, Inc.) installed in the computer. This board collects pressure data at 1000 hertz per channel, while temperature data is collected at 100 hertz per channel. This data acquisition system provides high-resolution data that is stored to ASCII data files. This data can then be analyzed and plotted at a later time. This system is controlled, after initial operator setup, by the firing control system, allowing greater ease of use.

Safety

Safety considerations were of the utmost importance since this facility was set up on the UALR campus. Safety measures were also designed directly into the facility itself. The first was the mechanical design of the hybrid motor. The maximum operating chamber pressure was

designed to be 500 psia. The nozzle assembly is held in place with brass shear pins and is designed to eject if the chamber pressure exceeds 1000 psia. This would dump all chamber pressure. The body of the motor is designed to handle pressures up to 3000 psia.

The gas flow system utilizes normally closed shutoff valves, so that in the case of a power failure, all gas flow is stopped, terminating combustion. Check valves are used on the nitrogen and propane lines to prevent any over-pressurization from the combustion chamber. The oxygen gas line is designed to handle pressures in excess of 2500 psia. It also contains a pressure relief valve that is set for 1250 psia.

The computer control system has a feedback loop incorporated into the software. This checks the chamber pressure 25 times a second. If the pressure is over a preset level, the oxygen flow to the motor is terminated. There is also a manual override switch between the computer control and the solenoid valves. This remains in the off position until a few moments before the firing sequence is begun. As a final step, the entire keyboard acts as an emergency shutoff. Pressing any key during a firing will stop the oxi-

dizer flow to the motor. If the computer control system should fail, but the rest of the power remains on, the manual override switch to the solenoid valves can be used to stop the oxidizer flow.

Experimental

After construction of the lab-scale hybrid motor, initially manually controlled firings of the motor were performed, using Plexiglas (polymethyl methacrylate) fuel grains. The permanent facility had not yet been constructed, so these firings were done to assure proper function of the mechanical aspects of the motor design. Once the entire facility was completed, testing was performed to assure proper functioning of all parts of the system. The parts included the gas flow system, the instrumentation of the motor, the computer control system, and the data acquisition system. The motor was first tested to see if the ignition system was performing as intended. The ignition system was designed to use a stream of propane injected into the oxidizer flow in the motor head assembly. This was ignited by a small electric match. The motor was test fired several times to assure the combustion stability of the HTPB fuel. In general, any changes in HTPB fuel formulation or control system configuration were followed by a series of low oxidizer flow, low chamber pressure tests. After these tests, a thorough examination of all low pressure data and motor components was followed by firings at increased oxidizer flow and chamber pressure, up to the desired 500 psia level.

The first experimental objective was to characterize the regression rate of the HTPB fuel grains. The regression rate of the fuel in a hybrid rocket motor can be given by the general equation:

$$r = aG_o^n \quad (1)$$

where r is the regression rate in inches per second, a is a constant including the blowing coefficient, G_o is the oxidizer mass flux (the oxidizer mass flow divided by the port area), and n is the regression rate pressure exponent.^[4] A test matrix was developed to establish the values of a and n , and hence, the regression rate of HTPB

fuels in this hybrid motor. This was accomplished by running the motor at various oxidizer flow rates, from about 2.5 to 10.0 pounds per minute of oxygen, with the regression rate of the fuel being measured. The regression rate is particularly important for further work when the plume is seeded. The seeding material is incorporated into the fuel grain, so that the final concentration of material in the plume will depend on the oxidizer mass flow and the regression rate of the fuel.

A series of 30 firings were completed, using six fuel grains. Each grain was fired either four or six times at three seconds per firing. It is important to keep the firing duration short, as the regression rate varies with the central port diameter. However, the firing duration also needed to be long enough to reach stable combustion for the data to be valid. Experimental results showed a three second firing duration to be a reasonable compromise to meet the two criteria. The fuel grains consisted of R45 HTPB, Desmodur N100 curative, and a few drops of a tin-based catalyst (no effect on spectral output). Normally 15% by weight N100 was used. No opacifier was added to the fuel grains used in the regression rate study. Havaflex T.A.-117 (Ametek) ablative was applied to the ends of the fuel grain to prevent end grain burning. This is important since the post firing port diameter is determined by the weight loss of the grain. Tests with and without ablative showed that end grain burning could contribute to errors in the measurement. While these errors are small, it was important for characterizing the motor to have the highest confidence levels possible. Future studies may not require this ablative, depending on acceptable error.

A second part of the overall project, which is not included in this paper, was to conduct a preliminary study and characterization of the baseline spectral emissions of the plume in the ultra-violet-visible (UV-VIS) region and the infrared region (approximately 200 nanometers to 15 micrometers).^[2] That study included seeding the plume with metals and observing plume emissions in the UV-VIS region and determined that metals can be detected at low levels with good precision. This indicated that the design was a stable platform for plume spectroscopy studies.

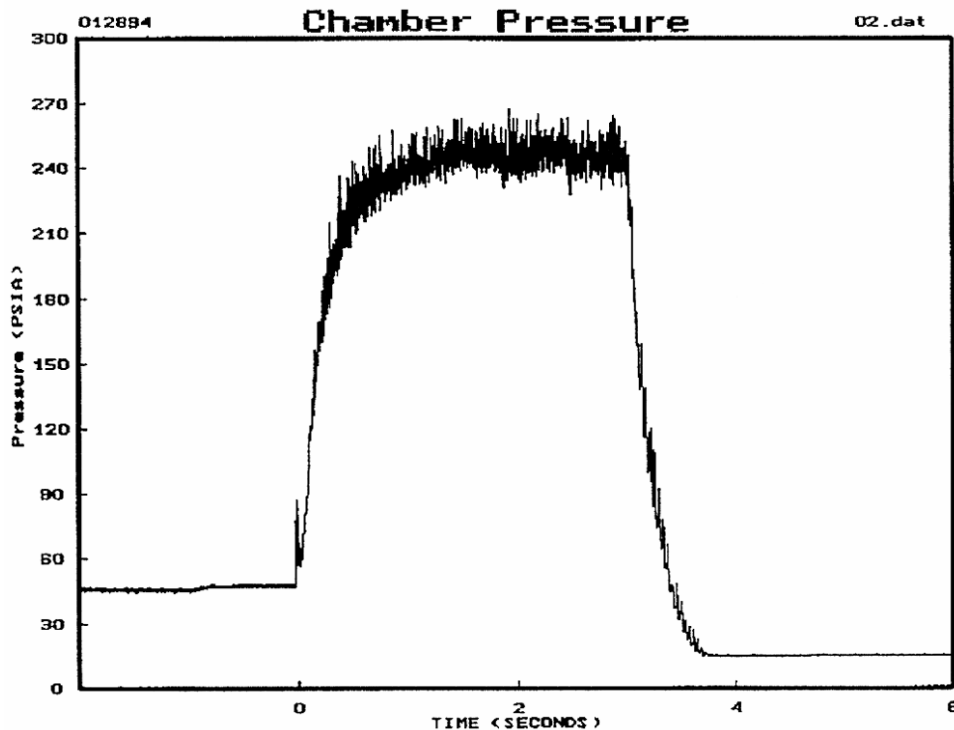


Figure 4. Chamber pressure data from the hybrid motor using HTPB fuel.

Results and Discussion

Construction of the lab-scale hybrid motor was completed in January of 1993. The motor was set up on a temporary test stand and fired using the Plexiglas fuel grains. Since this was set up on a temporary test stand, no propane was available for ignition. A different ignition system was utilized consisting of a small hobby rocket motor with a firing duration of 250 milliseconds. This was arranged so that the oxygen flow would be initiated, then the hobby rocket motor fired into the chamber upstream of the fuel grain, and ignition achieved. The ignition system worked very well. Eight firings were completed at low chamber pressures, below 200 psia. These firings demonstrated that the motor functioned as predicted, that the design of the motor was sound, and satisfied university and state safety officials that a rocket motor could safely be fired on campus.

The permanent facility was completed in September of 1993. All aspects of the facility were checked, including the gas flow system, the instrumentation of the facility, the computer

control system and the data acquisition system. This was accomplished by testing all systems separately, then bringing them together in dummy runs without ignition or installing the motor. Once initial testing of the propane ignition system was completed, optimal propane flow was determined, at which point the ignition system worked as anticipated. The oxidizer flow is initiated, then after 2 seconds to allow the flow to stabilize, the propane flow is initiated. After one more second, the igniter is fired, igniting the propane and starting combustion in the hybrid motor. Propane is allowed to flow for approximately 0.5 seconds to ensure even grain combustion. After the preprogrammed firing duration, the oxidizer flow is shut off, extinguishing combustion in the chamber. The chamber is then purged with nitrogen to assure complete combustion termination.

A series of HTPB fuel grains were cast and then fired in the motor. A slight combustion instability, which is common with hybrid motors, was noted in the motor for both the Plexiglas and the HTPB fuels. With the HTPB fuel, the pressure oscillates less than 15% of the chamber pressure during a firing. Oxidizer flow

Table 1. Regression Rate Data for Hybrid Rocket Motor Using HTPB Fuel.

Grain Number	Run Number	Oxygen Flow (lbm/sec)	Oxidizer Mass Flux, G_o (lbm/in ² -sec)	Regression Rate, r (in/sec)
01	01	0.1620	0.2713	0.0407
01	02	0.1400	0.1551	0.0390
01	03	0.1200	0.1044	0.0286
01	04	0.1030	0.0736	0.0260
02	01	0.1760	0.2981	0.0390
02	02	0.0134	0.1426	0.0367
02	03	0.1190	0.0935	0.0230
02	04	0.1010	0.0656	0.0193
03	01	0.1720	0.2900	0.0397
03	02	0.1310	0.1409	0.0333
03	03	0.1160	0.0930	0.0240
03	04	0.1000	0.0655	0.0207
04	01	0.1120	0.1955	0.0347
04	02	0.0990	0.1143	0.0307
04	03	0.0783	0.0689	0.0203
04	04	0.0740	0.0538	0.0197
04	05	0.0578	0.0363	0.0137
04	06	0.0413	0.0236	0.0100
05	01	0.1240	0.2135	0.0360
05	02	0.1060	0.1190	0.0317
05	03	0.0910	0.0803	0.0228
05	04	0.0745	0.0561	0.0193
05	05	0.0575	0.0372	0.0150
05	06	0.0408	0.0237	0.0103
06	01	0.1150	0.1952	0.0387
06	02	0.0989	0.1084	0.0320
06	03	0.0826	0.0687	0.0210
06	04	0.0736	0.0513	0.0173
06	05	0.0585	0.0356	0.0143
06	06	0.0403	0.0222	0.0103

and chamber pressure were increased until the maximum mass flow of 10 pounds per minute of oxygen and a chamber pressure of 500 psia were reached. A typical chamber pressure plot is shown in Figure 4. This completed the testing of the mechanical design of the motor and the check out of the entire facility.

The regression rate study was completed in February 1994. A total of 30 firings were completed. The fuel grains were weighed before

and after firing to determine the mass of fuel used. This mass loss was then converted into a regression rate for the firing. The ablative substance applied to the ends of the fuel grains functioned appropriately, and no end grain burning was observed. The oxidizer mass flow was accurately measured for each firing, and the oxidizer mass flux was calculated. Over the 30 firings, the oxidizer mass flow was varied from 0.0403 to 0.176 pounds mass per second

of oxygen. This range of oxygen mass flow, along with the average port diameter of the grain over the firing, gives an oxidizer mass flux that ranges from 0.022 to 0.298 lbm/in.²·sec. Regression rates from 0.0100 to 0.0407 inches per second were recorded. This data is shown in Table 1 and Figure 5. Chamber pressures varied between firings from 180 to 400 psia, depending on oxidizer flow and motor nozzle size.

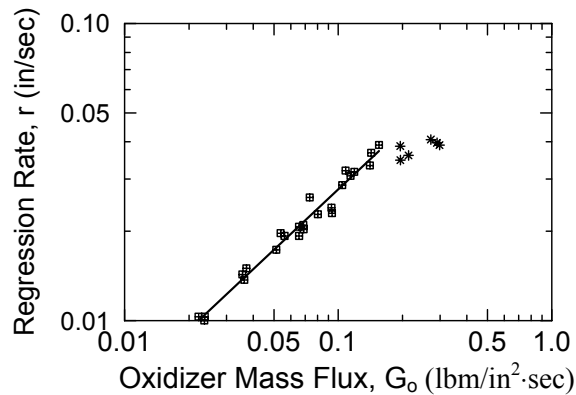


Figure 5. Plot of regression rate data for hybrid motor using HTPB fuel.

It can be noted from the data obtained that there exists a group of points that are distinctly separated from the rest of the data. These six points are for the initial firings for each fuel grain. It was hypothesized that because no opacifier was added to the fuel, the regression rate of those grains was lower. However, a char layer had been deposited on the fuel's surface at the end of these primary firings. This acted as an opacifier for the secondary firings, increasing the regression rate. This being the case, the data from the primary firings were separated from that of the secondary firings and each set used to determine the experimental results. A line was fitted through the set of secondary firings. While the six points from the primary firings do not represent enough data to fit a valid line through them, they do seem to fall on the line as described in Sutton.^[4]

For the data presented in Sutton, the constants a and n in the equation governing regression rate, were calculated to be $a = 0.104$ and $n = 0.681$. This gives the equation as follows:

$$r = 0.104 \cdot G_o^{0.681} \quad (2)$$

Since only six primary firings were completed, a more involved test matrix needs to be developed to test the theory that a char layer develops and increases regression rate.

For the data from the 24 secondary firings, the constants a and n , were calculated to be $a = 0.131$ and $n = 0.674$. When a and n are applied to equation 1, this gives

$$r = 0.131 \cdot G_o^{0.674} \quad (3)$$

This data has an error of $\pm 8.8\%$. This gives results that show a higher regression rate than shown in Sutton for HTPB fuel. It is speculated that if an opacifier is added to the HTPB grains, the primary firings would also show this increased regression rate. This was confirmed by preparing a fuel grain using carbon black as an opacifier. The regression rate of this grain on its primary firing was consistent (-3% error) with the secondary firings of the other grains. An oxidizer mass flux of 0.1562 lbm/(in²·sec) gave a regression rate of 0.0363 in/sec.

Conclusions

A lab-scale hybrid rocket motor facility was developed, designed specifically as a testbed for the development of plume spectroscopy instrumentation (Figure 6). The computer control and data acquisition systems have worked effectively and efficiently to make this facility easy to operate. The choice of hybrid motor technology made it safe and cost effective as well. The regression rate study showed that the motor design and fuel give predictable results. This makes it feasible to dope the fuel grains with metal salts and calculate the concentration of metals in the plume. This capability indicates that the UALR hybrid based facility functions well as a testbed for the development of plume monitoring systems. The design of the facility, as implemented, has proven to be reliable and to give consistent results. Additionally, the ease of use and rapidity of set-up (up to 12 or more firings a day) make this facility an excellent testbed for all types of rocket motor studies, such as fuel composition, combustion stability, and base heating effects. Other oxidizers (ni-

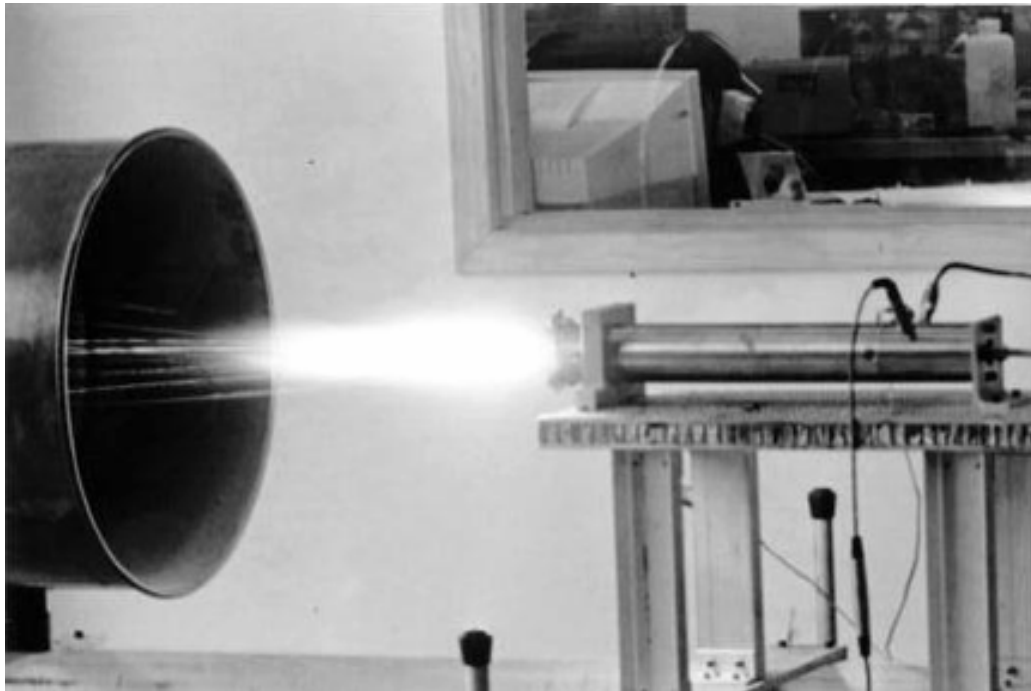


Figure 6. A typical HTPB firing of the UALR thruster.

trous oxide) could be studied, however, operating parameters would be necessarily quite different, since cylinder pressures would vary from that for gaseous oxygen.

Acknowledgments

The authors would like to thank the Arkansas Space Grant Consortium for the initial funding of the project and the NASA Stennis Space Center for the loan of equipment and for funding the bulk of the project, Grant NAG13-26. Bob Shanks was supported by a NASA Stennis GSRP Fellowship. NASA Grant NCCW-0005 also funded portions of this project. Thanks go to Armand Tomany, Fabrication Shop Manager, for aid in designing and in actual construction of the lab-scale hybrid rocket motor, and Greg Cress for additional fabrication assistance. We appreciate the assistance of Paul McLeod for his engineering expertise and design skills. This paper was presented in part at the 30th Joint Propulsion Conference, Indianapolis, IN, USA (AIAA 94-3016).

References

- 1) D. G. Garner, F. E. Bircher, G. D. Tejwani, and D. B. Van Dyke, "A Plume Diagnostic Based Engine Diagnostic System for the SSME", AIAA Paper No. 90-2235, July 1990.
- 2) M. K. Hudson, R. B. Shanks, D. H. Snider, D. M. Lindquist, C. Luchini and Sterling Rook, "UV, Visible, and Infrared Spectral Emissions in Hybrid Rocket Plumes", *International Journal of Turbo and Jet Engines*, Vol. 15, 1998, pp 71-87.
- 3) G. D. Tejwani, D. B. Van Dyke, F. E. Bircher, and D. B. Gardner, "Spectroscopic Evaluation of Rocket Engine Materials in the Exhaust Plume Environment: Spectral Line Identifications of SSME Elements and Materials", NASA Contractor Report No. 4453, NAS12-290, July 1992.
- 4) G. P. Sutton, *Rocket Propulsion Elements: An introduction to the Engineering of Rockets*, 6th ed., John Wiley and Sons, New York, 1992.

Chemical Analysis of Consumer Fireworks

Per Alenfelt

Hansson PyroTech AB, Box 93, S-427 23, Billdal, Sweden
E-mail: p.alenfelt@hansson-pyrotech.com

ABSTRACT

A chemical analysis of a selection of fireworks has been made. The products were chosen to represent the typical use of consumer fireworks in Sweden 1998. The purpose of the assignment was to estimate to what extent consumer fireworks contribute to the total emission of some undesirable elements in Sweden.

Six consumer items were examined (two of them being multi item kits). Nineteen elements were analyzed, but focus was made on the environmentally undesirable elements arsenic, cadmium, lead and mercury.

The conclusion was that, as far as arsenic, cadmium and mercury are concerned, the contribution from consumer fireworks is insignificant compared with the total emission and deposition within the country.

The emission of lead, which is a well-known constituent in crackling fireworks effects, can at most be 0.8 % of the total emission and deposition in the country.

The figures in this paper do not provide any evidence in favor of restricting the lead content of fireworks.

Keywords: chemical analysis, fireworks, environment, pollutant, arsenic, cadmium, lead, mercury, crackling

Introduction

Fireworks and the Environment

Paracelsus (1493-1541) wrote^[1] "What is there that is not a poison? All things are poison and nothing (is) without poison. Solely the dose determines that a thing is not a poison." This is

the most fundamental and pervasive concept in toxicology.

When a fireworks composition is burned most of its ingredients react to produce energy and new solid and gaseous substances. The solid substances are spread in the air and will, sooner or later (depending on particle size and weather conditions), deposit on the ground. The actual bioavailability of elements from pyrotechnic emissions has not been determined and is not part of this study.

Focus was made on arsenic, cadmium, lead and mercury, since these elements are universally known to be the most toxic and most damaging of the environmental pollutants.

The Pyrotechnic Investigation

After years of lively debate concerning the connection between consumer fireworks and environmental problems the Swedish government started an official investigation^[2] aiming to shed light on the subject. Hansson PyroTech AB got the assignment to estimate the total emission of some environmentally undesirable elements from consumer fireworks in Sweden during 1998.

The work was based on the following assumptions:

- Consumer fireworks were sold for 250 million SEK (about US\$30 million) in Sweden during 1998^[3].
- The consumer got 1 g of pyrotechnic composition per SEK.
- The chosen products were representative samples of what was typically being fired.

Table 1: Total Weight and Net Explosive Weight of Analyzed Consumer Fireworks Products.

No.	Total Wt. (g)	Net explosive Wt. (g)	Description
1	401	139.2	7 rockets (5 different types)
2	803	143.8	7 rockets (4 different types) + 2 mini cakes
3	652	180.0	25-shot cake
4	729	158.5	25-shot cake
5	4807	689.0	52-shot cake
6	2283	371.5	95 mm shell in mortar

Experimental

Elements

A standard package of 19 elements was chosen for quantitative analysis:

Aluminium (Al)	Lead (Pb)
Arsenic (As)	Magnesium (Mg)
Barium (Ba)	Manganese (Mn)
Boron (B)	Mercury (Hg)
Cadmium (Cd)	Nickel (Ni)
Calcium (Ca)	Phosphorus (P)
Chromium (Cr)	Potassium (K)
Cobalt (Co)	Strontium (Sr)
Copper (Cu)	Zinc (Zn)
Iron (Fe)	

Choice of Products

The products should represent what was typically being fired in Sweden during 1998. With support from representative sales figures, six popular consumer products were chosen for analysis, see Table 1.

All products were produced in China.

Sample Preparation

The items were dissected, and all pyrotechnic compositions were weighed and documented. See Table 2 for the rough distribution of pyrotechnic compositions in each item.

Table 2: Rough Distribution of Pyrotechnic Compositions. (Numbers in Weight Percent.)

Composition	1	2	3	4	5	6
Fuse powder	2	3	2	2	3	2
Motor powder	39	44	—	—	—	—
Lift charge	—	—	25	33	21	13
Burst charge	6	2	4	4	17	31
Blue	—	—	11	6	—	—
Crackling	24	—	—	—	—	—
Glitter	6	20	—	—	21	—
Gold	—	21	20	—	17	—
Green	13	—	22	—	—	—
Red	7	—	16	—	—	—
Silver	—	4	—	55	21	2
Strobe	—	6	—	—	—	52
White	3	—	—	—	—	—

The samples were representative mixtures of the total pyrotechnic content of each firework. The compositions from each product were prepared for analysis by grinding and were mixed by sieving.

Analysis

A certified analytic laboratory^[4] analyzed the samples.

The method involved the following steps:

- Dissolution of the samples in concentrated nitric acid in a microwave oven.
- Removal of insoluble matter by filtration.
- Analysis by Inductive Coupled Plasma spectroscopy (ICP). For technical reasons

Table 3: Results of Chemical Analysis of Six Different Fireworks Products.

(Amounts in g per kg pyrotechnic composition.)

Element	1	2	3	4	5	6	Mean Value
Al	36	32	59	54	64	43	48
As	0.0024	0.044	0.013	0.010	0.046	0.0030	0.020
Ba	38	12	26	51	37	72	39
B	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Cd	0.0032	0.020	0.0037	0.0044	0.021	0.0035	0.0093
Ca	2.4	3.4	0.85	0.72	0.88	0.57	1.5
Cr	0.028	0.95	0.0076	0.0078	0.5	0.0068	0.25
Co	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Cu	10.9	0.75	23	10.4	0.77	0.31	7.7
Fe	1.3	9.2	0.58	0.57	0.25	1.4	2.2
Pb	46	3.2	6.8	2.5	5.3	0.037	11
Mg	21	22	27	30	32	42	29
Mn	0.23	0.5	0.099	0.11	0.25	0.12	0.22
Hg	0.00032	0.00044	0.00019	0.00027	0.00051	0.00018	0.00032
Ni	0.012	0.808	0.0086	0.0082	0.02	0.036	0.15
P	<0.10	<0.10	0.16	<0.10	<0.10	<0.10	<0.11
K	160	190	170	160	180	140	167
Sr	3.2	0.056	9.7	0.096	3.8	0.34	2.9
Zn	0.82	1.5	1.4	1.4	2.5	0.44	1.3

arsenic and mercury were determined by Atomic Fluorescence Spectroscopy (AFS).

General descriptions of the methods can easily be found in any book of analytical chemistry.^[5]

Results

The results from the analysis are shown in Table 3. The amounts are shown as gram of pure element per kilogram of pyrotechnic composition.

Table 4: Estimated Discharge of Selected Elements from Consumer Fireworks in Sweden 1998.

(Amounts rounded off to one significant figure.)

Element	kg	Element	kg	Element	kg
Al	10,000	Co	<1	Ni	40
As	5	Cu	2000	P	<30
Ba	10,000	Fe	600	K	40,000
B	<30	Pb	3000	Sr	700
Cd	2	Mg	7000	Zn	300
Ca	400	Mn	60		
Cr	60	Hg	0.1		

Table 5: Estimation and Comparison of Discharge from Consumer Fireworks to Total Emission of Arsenic, Cadmium, Lead and Mercury in Sweden 1998.

	Arsenic	Cadmium	Lead	Mercury
To air ^[7]	1300 kg	780 kg	38,000 kg	880 kg
To water ^[8]	830 kg	1800 kg	13,000 kg	920 kg
Hunting ^[9]	—	—	164,000 kg	—
Deposition ^[10]	10–60,000 kg	10–20,000 kg	170–760,000 kg	10–30,000 kg
Consumer Fwks.	5 kg	2 kg	3000 kg	0.1 kg
Contribution from consumer fwks. in %	0.008–0.04 %	0.009–0.02 %	0.3–0.8 %	0.0003–0.0008 %

With support from the initial assumptions, the amount of consumer fireworks sold in Sweden during 1998 corresponds to a net explosive weight of 250,000 kg. Table 4 shows the calculated total amounts rounded off to one significant figure.

Discussion

Comparison with the Total Discharge in Sweden

To judge the impact of the discharge from consumer fireworks correctly, it is important to compare it with other sources of pollution. The emission of toxic metals is steadily decreasing. For example, the emission of lead has drastically decreased since lead-free gasoline was introduced. The problem is that Northern Europe receives enormous amounts from Middle and Southern Europe as deposition with rain and snow. In Table 5 the discharge from consumer fireworks is compared to the total emission and deposition of arsenic, cadmium, lead and mercury in Sweden.

The deposition in Sweden is very difficult to estimate due to uneven distribution of the fallout and because of the randomly spread control stations in the northern parts of the country.

Table 5 clearly shows that as far as arsenic, cadmium and mercury are concerned, the contribution from consumer fireworks is insignificant compared to the total emission and deposition within the country. The levels are so low that it is very doubtful that the elements are added to the fireworks on purpose. Most proba-

bly they are introduced inadvertently as impurities.

The emission of lead, which is a well-known constituent in crackling fireworks effects, can at most be 0.8 % of the total lead emission and deposition in the country.

The figures in this paper do not provide any evidence in favor of restricting the lead content of fireworks. If all lead from fireworks were eliminated, there would be no measurable difference in the lead pollution of Sweden's environment. There may well be very good reasons for not having lead in consumer fireworks, but, on the evidence of this paper, increased environmental pollution is not one of them.

Increased Sales during 1999

Since the sales probably were doubled during 1999 it is reasonable to believe that the emission of metals from the firing of consumer fireworks also was doubled. It is furthermore believed that at least half of the fireworks sold during 1999 were fired on New Years Eve. This could mean that 3000 kg of lead were discharged from consumer fireworks that single night. The emission from display shows was probably of the same magnitude.

Comments

Low Level Elements

Commercial pyrotechnic formulations seldom contain ingredients at levels below 1 weight percent. Some exceptions are stabilizers

(boric acid, chromates) and free-flow agents (amorphous silica). The levels in table 3 imply that consumer fireworks from China do not contain ingredients based on As, P, Cd, Ca, Co, Hg, Mn, Ni or Zn. Metal powders used in pyrotechnics are often of low purity, which can explain the presence of Co, Mn, Ni and Zn, which all are common alloying additives.

Amounts of Barium and Strontium

In Table 4 the amount of strontium seems surprisingly low compared to the amount of barium. The distribution of red and green effects is usually equal in consumer fireworks, which implies that the amounts should be of the same magnitude. It is possible that the chosen products were not representative in the red/green distribution, but there are some other possible explanations of the difference. First of all, Chinese green stars are usually made with about 50 % barium nitrate whereas red stars are usually made with about 20 % strontium carbonate. Also taking in account of the difference in density (green stars are often a little heavier) the Sr/Ba ratio should be about 1/3. Furthermore barium nitrate is used for other effects than just green stars. Chinese recipes for glitter, silver, strobe and white stars also contain barium nitrate.^[10]

Consumer fireworks in Sweden

Compared to other countries in the Northern Europe, Sweden has a rather liberal fireworks regulation. Anyone of at least 18 years of age can buy shells up to 100 mm, cakes with a net explosive weight up to 1000 g and rockets with a net explosive weight up to 250 g.

The reason for this is that most of the country is thinly populated, and, even in the bigger cities, open space is never far away. However, a special permit is required from the police when shooting inside city borders.

References

- 1) Paracelsus (Theoprstus ex Hohenheim Erimita), Von der Besucht, Dillingen, 1567.
- 2) The Pyrotechnic Investigation: N 1998:7, *Ja till Fyrverkerier—men med färre skador*, Nordstedts Tryckeri AB, Stockholm, ISBN 91-7610-763-9, 1999.
- 3) Personal communication with Kenneth Jarneryd, National Inspectorate of Explosives and Flammables, Stockholm.
- 4) AnalyCen Nordic AB, Lidköping, Sweden.
- 5) D. A. Skoog, D. M. West, F. J. Holler, *Fundamentals of Analytical Chemistry*, 6th ed., Saunders Collage Publishing, ISBN 0-03-075397, 1992.
- 6) Statistics Sweden, 1995 *Metallutsläpp till luft från olika källor 1995*, <http://www.scb.se/scbswe/mhtml/miljoutslmet1.htm>.
- 7) Statistics Sweden, 1995 *Metallutsläpp till vatten från olika källor 1995*, <http://www.scb.se/scbswe/mhtml/miljoutslmet2.htm>.
- 8) National Chemicals Inspectorate *Arvecklingsprojektet: Rapport från KEMI 6/97*, 1997.
- 9) Personal communication with Karin Kindbom, Swedish Environmental Research Institute, Ltd, Göteborg (based on precipitation data from 1997).
- 10) Personal communication with Michael Zhaou, China Panda Fireworks Manufacturer, Guangzhou, China.

Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures

Part 3. The Effects of Stoichiometry, Particle Size and Added Materials

D. Chapman, R. K. Wharton, J. E. Fletcher

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

A. E. Webb

HM Explosives Inspectorate, Health and Safety Executive, St Anne's House, Trinity Road, Bootle, Merseyside, L20 3QZ, United Kingdom

ABSTRACT

The effects of stoichiometry and particle size on the thermal stability and sensitiveness of sulfur/chlorate mixtures have been investigated. Mixtures containing small particles and approximately 5% sulfur were shown to be the least thermally stable. Sulfur/chlorate mixtures containing a third component have also been investigated and compositions with up to 70% added material gave similar low ignition temperatures to mixtures of the two components. All compositions containing sulfur/chlorate were found to be friction sensitive and had limiting loads below the 80 N UN transport criterion. When iron was the third component, the compositions were also impact sensitive, with Limiting Impact Energies below the 2 J UN transport criterion.

Keywords: chlorate, sulfur, sensitiveness, thermal stability, ignition temperature

Introduction

Part 1 of this series^[1] discussed the problems posed by the presence of sulfur/chlorate in fireworks compositions, and in Part 2^[2] we reported initial studies on stoichiometric sulfur/chlorate mixtures (approximately 30:70 S:KClO₃). In this third paper we have extended the work and investigated the effect on thermal stability and

sensitiveness of varying both the proportions and particle sizes of sulfur and potassium chlorate. Additionally, we have examined the effect of adding a third component to sulfur/chlorate mixtures. Both the thermal stability and sensitiveness of the resulting mixtures have been investigated.

Experimental

Mixtures were prepared from materials purchased from laboratory suppliers. The potassium chlorate was high purity (AnalaR) grade, and the other materials were standard laboratory grade. Control samples were added to each block. These were prepared from <500 µm materials and were used to monitor any changes due to extraneous effects (e.g., ambient relative humidity). Testing was carried out up to 200 °C, the maximum temperature that could be attained in the blocks. Since initial studies^[2] had indicated that flowers of sulfur had similar properties to the sulfur used in Chinese production for a UK importer but was marginally more reactive, this sulfur was used in all the experiments reported in this paper. Additionally, as it was the most reactive sulfur, it was hoped that any subtle changes might be more apparent with this material.

For the majority of the testing undertaken, components were ground and sieved to obtain fractions that passed through a 0.5 mm mesh. When the effect of particle size was being in-

vestigated, potassium chlorate sieve fractions of <63, 63–125, 125–250, 250–500 μm , and a small amount of >500 μm were collected. The flowers of sulfur only yielded sufficient material for test in the <63 and 63–125 μm fractions.

Thermal stability of the sulfur/chlorate mixtures was measured in open cardboard fireworks tubes using 2 g samples, as previously reported.^[2] Sensitiveness^[3] measurements were made with the BAM (Bundesanstalt für Materialforschung und -prüfung) friction apparatus and Fallhammer using standard test methodologies.^[4a] In our previous work we used probit^[5] analysis to determine the limiting values. While this gives more information regarding the sensitiveness of the materials, a greater number of tests need to be carried out. Some compositions were found to change sensitiveness on standing (probably due to moisture uptake), and therefore the quicker standard method was adopted for the current experimental programme.

Wet Processed Materials

Some fireworks formulations are wet processed^[6a] to consolidate the materials (e.g., in star production). To simulate this, compositions (2 g) were mixed dry, and then 0.5 cm^3 water was added with mixing to form a paste. Such mixtures were allowed to air-dry overnight before being cautiously crushed with the back of a non-sparking metal spatula to produce powder that was sampled for test.

Co-Precipitated Potassium Chlorate/Salt Mixtures

Samples of potassium chlorate were prepared by co-precipitation with barium nitrate, strontium nitrate or copper chloride. Potassium chlorate (15 g) was dissolved in 50 cm^3 of boiling water and 2–4 g of salt ($\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$ or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) was added. The solution was carefully poured into 200 cm^3 of acetone to precipitate the mixed salts. The fine precipitates were filtered and air-dried prior to use.

Results

The Effect of Stoichiometry

Ignition temperatures for sulfur/chlorate mixtures containing between 1 and 70% sulfur were obtained from duplicate experiments in which 2 g samples were heated at 5 $^\circ\text{C hr}^{-1}$.

Table 1. Ignition Temperatures for Sulfur/Chlorate Mixtures.

% Sulfur	Ignition Temperature ($^\circ\text{C}$)	
	Sample 1	Sample 2
1	142	145
2	145	143
3	134	125
4	138	126
5	123	122
10	119	120
20	122	122
30	123	122
40	123	122
50	123	123
60	125	126
70	127	126

Effect of Particle Size

Sulfur/chlorate mixtures (30% sulfur) were prepared using the available sieve fractions of sulfur and potassium chlorate in order to investigate the effect of particle size on thermal stability, as measured by ignition temperature (Table 2).

Corresponding sensitiveness measurements were made using the available fractions to investigate the effect of particle size on friction sensitiveness (Table 3) and impact sensitiveness (Table 4). To differentiate the friction sensitivenesses, intermediate loadings were used and the “standard” BAM limiting loads are shown in parentheses.

Table 2. Effect of Particle Size on Temperature of Ignition.

Chlorate Fraction (μm)	Ignition Temperature ($^{\circ}\text{C}$)			
	Sulfur <63 μm		Sulfur 63–125 μm	
<63	119	119	119	119
63–125	119	119	119	119
125–250	125	125	125	125
250–500	134	134	132	137
Control 1 (<500)	123		124	
Control 2 (<500)	122		127	

Table 3. Friction Sensitiveness of Sieved Fractions of Sulfur/Chlorate Mixtures.

Material	Limiting Load (N) for Sulfur Fractions	
	<63 μm	63–125 μm
<63 μm chlorate	8 (10)	7 (10)
63–125 μm chlorate	5 (5)	5 (5)
125–250 μm chlorate	10 (10)	7 (10)
250–500 μm chlorate	7 (10)	14 (20)

Table 4. Impact Sensitiveness of Sieved Fractions of Sulfur/Chlorate Mixtures (63–125 μm Sulfur).

Chlorate Sieve Fraction (μm)	Limiting Impact Energy (J)
63–125	4
125–250	5
250–500	5

The Effect of Added Materials on the Thermal Stability of Sulfur/Chlorate Mixtures

Fireworks compositions generally contain a number of components. To enable a large variation in these components to be accommodated, mixtures containing 5% sulfur were selected for this part of the study.

To examine the effect of these materials on the stability of sulfur/chlorate mixtures a series of compositions containing sulfur, potassium chlorate and a third component was produced. The thermal stability of these mixtures was investigated by slow heating ($5^{\circ}\text{C hr}^{-1}$). Under these experimental conditions, control samples of 5% sulfur in potassium chlorate (i.e., no third component) ignited in the range $113\text{--}116^{\circ}\text{C}$.

Table 5. The Effect of Oxidisers on the Ignition Temperature of Sulfur/Chlorate Mixtures (<500 µm particle size, 5% Sulfur).

Added Oxidiser	Ignition Temperature (°C) for Quantity of Oxidiser				
	10%	30%	50%	70%	90%
Potassium perchlorate	117	116	117	118	N/I
Potassium nitrate	115	117	—	117 (exo)	N/I
Barium nitrate	115	114	115	116	N/I
Strontium nitrate	115	115	116	—	N/I

N/I = no ignition

exo = non-ignition exotherm

Table 6. The Effect of Fuels on the Ignition Temperature of Sulfur/Chlorate Mixtures (<500 µm particle size, 5% Sulfur)

Added Fuel	Ignition Temperature (°C) for Quantity of Fuel				
	10%	30%	50%	70%	90%
Charcoal	120	117	128	—	—
Aluminium	115	114	115	115	N/I
Magnesium	114	114	115	116	N/I
Iron filings	114	114	113	114	118 (exo)

N/I = no ignition

exo = non-ignition exotherm

Table 7. The Effect of Other Material on the Ignition of Sulfur/Chlorate Mixtures (<500 µm particle size, 5% Sulfur).

Material	Ignition Temperature (°C) for Quantity of Material				
	10%	20%	30%	40%	50%
Potassium chloride	115	115	—	116	117
Copper chloride (CuCl ₂ ·2H ₂ O)	114	115	117	123	120
Barium nitrate	115	115	116	118 (exo)	124
Strontium carbonate	115	116	116	120	123
Calcium carbonate	111	113	113	113	114

exo = non-ignition exotherm

To investigate whether wet processing exerted an effect, a number of samples were prepared and their thermal stability investigated by slow heating, Table 8.

Table 8. The Effect of Wet Mixed Materials on the Ignition of Sulfur/Chlorate Mixtures (<500 µm particle size, 5% Sulfur)

Material	Ignition Temperature (°C) for Quantity of Added Material	
	20%	40%
Potassium nitrate	114	126
Barium nitrate	115	118
Calcium carbonate	115	115
Copper chloride (CuCl ₂ ·2H ₂ O)	113	115

To further investigate the effects of wet mixing, co-precipitated materials were prepared, and ignition temperatures of the resulting “contaminated” potassium chlorate/sulfur were measured for both 5% and stoichiometric (30%) sulfur, Table 9.

Table 9. The Effect of Co-Precipitated Potassium Chlorate on the Ignition Temperature of Sulfur/Chlorate Mixtures (<500 µm particle size).

Material Co-Precipitated with KClO ₃	Ignition Temperature (°C)	
	5% Sulfur	30% Sulfur
Barium nitrate	104	89
Strontium nitrate	91	94
Copper chloride (CuCl ₂ ·2H ₂ O)	100	98

Note: levels of co-precipitated salt are unknown.

Effect of Added Materials on Sensitiveness of Sulfur/Chlorate Mixtures

Both the friction and impact sensitivenesses of sulfur/chlorate mixtures with an added component were measured using freshly prepared materials. Additionally, some of the mixtures were also investigated either after dry storage or after conditioning at 50 °C and 70% relative humidity for 1 week.

Table 10. The Effect of Added Materials on Sulfur/Chlorate (<500 µm particle size, 30% Sulfur) Friction Sensitiveness.

Material Added to Sulfur/Chlorate Mixture	Friction sensitiveness – Limiting Load (N)		
	Freshly Prepared	Stored Dry	Temperature and Humidity Conditioned
Charcoal (30%)	40	40	20
Iron filings (30%)	20	20	40
Aluminium (30%)	20	20	40
Magnesium (30%)	40	40	40
None	10	≤ 5	≤ 5

Table 11. The Effect of Oxidisers on the Friction Sensitiveness of Freshly Prepared Sulfur/Chlorate (<500 μm particle size, 30% Sulfur).

Material Added to Sulfur/Chlorate Mixture	Friction Sensitiveness – Limiting Load for Percentage Additional Material (N)	
	20%	40%
Potassium perchlorate	40	20
Potassium nitrate	20	40
Barium nitrate	20	40
Control sample with no addition 20 N		

Table 12. The Effect of Added Materials on Impact Sensitiveness (<500 μm particle size).

Material Added to Sulfur/Chlorate Mixture	Impact Sensitiveness – Limiting Impact Energy (J)		
	Freshly Prepared	Stored Dry	Temperature and Humidity Conditioned
Charcoal (30%)	15	5	4
Iron filings (30%)	≤ 1	≤ 1	5
Aluminium (30%)	25	7.5	20
Magnesium (30%)	20	10	5
None	3	10	15

Discussion

Previous work by Conkling^[7] using differential thermal analysis measurements indicated that the ignition temperatures of sulfur/chlorate mixtures were below 150 °C. Results from our early work^[2] using 2 g samples of sulfur/chlorate (30:70) in fireworks tubes suggested ignition temperatures of 115–140 °C. These ignition

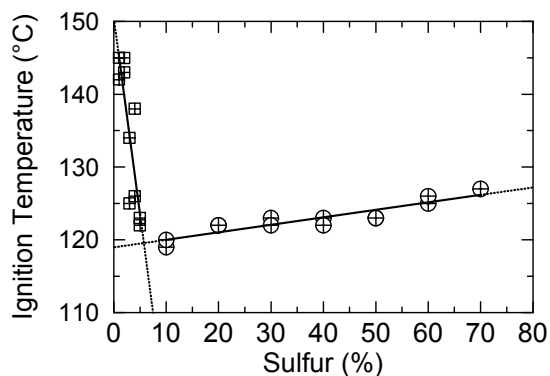


Figure 1. The effect of sulfur content on ignition temperature of sulfur/chlorate mixtures.

temperatures were dependent on the sulfur used and sample history. In extending this work, other variables have now been investigated to identify their effect on both the ignition temperatures of such mixtures and their sensitiveness to mechanical stimuli.

The Effect of Stoichiometry on the Thermal Stability of Sulfur/Chlorate Mixtures.

Sulfur/chlorate mixtures containing a low percentage (1–5%) of sulfur showed a reduction in ignition temperature with increasing sulfur content, whereas above 5% sulfur there was a gradual small increase in the ignition temperature with increasing sulfur content. Figure 1 illustrates the experimental data and indicates that the minimum ignition temperature is at approximately 5% sulfur. The majority of subsequent thermal stability testing was therefore carried out on mixtures with 5% sulfur.

The Effect of Particle Size on the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures

Similar series of experiments were carried out to ascertain the effect of the particle size of the components on the reactivity of mixtures of 30% sulfur and potassium chlorate. The sulfur fractions were limited by the small amount of material greater than 125 μm . It was possible to obtain two workable sieve fractions from sulfur and four from potassium chlorate. Table 2 shows that particle size has little effect on thermal stability when the materials are below 125 μm . When the potassium chlorate sieve fraction was larger than 125 μm there was an increase in ignition temperature, presumably due to the decreased surface area of the material reducing the reactivity. As firework compositions tend to be finely divided materials, any sulfur/chlorate mixtures present in a fireworks composition could be expected to lower the ignition temperatures of the mixtures provided that there were no specific interactions with other constituents.

All the combinations of sieve fraction that were tested for friction sensitiveness were found to be very sensitive with limiting loads below the 80 N UN transport criterion.^[4a] For comparison, a typical explosive (RDX) has a limiting load of 120 N^[8] and a typical primary explosive (lead azide) a limiting load of 10 N.^[4b] Thus, the sulfur/chlorate mixtures in Table 3 generally have friction sensitivenesses similar to primary explosives. The impact study indicated that the materials from all the fractions tested had Limiting Impact Energies (LIE's) above the 2 J UN transport criterion.^[4a] There was little variation in impact sensitiveness with particle size and no consistent trend was observed. For comparison, a typical explosive (RDX) has a LIE of 7.5 J^[8] and a typical primary explosive (lead azide) has a value of 2.5 J.^[4c] Hence, the sulfur/chlorate mixtures in Table 4 are less sensitive than primary explosives to impact.

The Effect of Added Materials on the Thermal Stability of Sulfur/Chlorate Mixtures

It could be anticipated that the inclusion of a third component in a sulfur/chlorate mixture would exert some effect on thermal stability and sensitiveness. There are likely to be some materials that would stabilise the mixtures, and others that would destabilise the mixtures. Also, certain materials would have no effect by interaction but would dilute the material. Bases are reported to be included in sulfur used in UK military pyrotechnics to counteract the effect of any acidity from the sulfur.^[9] Conversely copper(II) salts are known^[10] to destabilise potassium chlorate. Surprisingly, most tests indicated that there was little effect on ignition temperature until high percentages of a third component were added. For most compositions, the addition of up to 70% of a third added material had little effect on the ignition temperatures, which were similar to those for the basic sulfur/chlorate mixture. Beyond this level non-ignition exotherms or no reaction was observed. Charcoal showed the most marked stabilising effect, being the only fuel or oxidiser to increase ignition temperature by 10 °C at 50% addition. This may be due to the ability of charcoal to absorb materials, particularly gases. The other components found to give similar stabilising effect were the bases strontium carbonate and barium carbonate. Carbonates have been reported as stabilising sulfur/chlorate-containing compositions in military pyrotechnics.^[9]

Chlorates of many metals (other than the alkali metals) mixed with sulfur are reported to be less thermally stable than potassium chlorate/sulfur mixtures.^[11-13] It could be anticipated that the inclusion of barium, strontium or copper salts might lower the ignition temperature of sulfur/chlorate mixtures if there was an interaction with the salt. However, freshly prepared, dry compositions containing barium nitrate, strontium nitrate (Table 5) or copper chloride (Table 7) in sulfur/chlorate did not display reduced ignition temperatures. Copper chloride and the carbonates of both strontium and barium had a slight stabilising effect when present in high percentage in the compositions. The copper chloride presumably exerts an effect by diluting the mixture, while the carbonates may

also have a chemical effect by neutralising any acidic species. Similarly, freshly prepared, wet processed materials (Table 8) did not produce compositions with lower ignition temperatures. However, when the potassium chlorate was co-precipitated with these salts, the resulting sulfur/chlorate mixtures had lower ignition temperatures (Table 10). The co-precipitated materials may equate to poor quality potassium chlorate, the inclusion of potassium chlorate having been cited as one of the main causes of many of the early fireworks accidents.^[6b] In the co-precipitated materials there will be more intimate mixing of the salts and the possibility of double decomposition reactions leading to small amounts of other chlorates being formed.

The Effect of Added Materials on Sensitiveness of Sulfur/Chlorate Mixtures

Most compositions investigated had friction sensitivenesses below the UN transport criterion of 80 N and impact sensitivenesses above the 2 J criterion. However, the inclusion of iron into the composition produced material that was below both criteria. The inclusion of hard metallic components in pyrotechnic compositions has been reported to increase sensitiveness.^[14] For example, when up to 25% titanium was added to Black Powder, mixtures were obtained that had enhanced mechanical sensitiveness.^[15]

Conclusions

The present study has indicated that sulfur/chlorate mixtures, with up to 70% other material, are likely to ignite at temperatures below the melting temperature of sulfur (119 °C). This is low compared with normal fireworks compositions. Such mixtures are also friction sensitive, having values well below the UN transport criterion and with some compositions approaching the friction sensitiveness of primary explosives. The inclusion of hard metallic materials is likely to produce mixtures that are not only friction sensitive but also impact sensitive.

Acknowledgement

The authors are grateful to Black Cat Fireworks Limited for the supply of card tubes and clay for preparing the test specimens.

References

- 1) D. Chapman, R. K. Wharton and G. E. Williamson, "Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures Part 1. Introduction", *Journal of Pyrotechnics*, No. 6, 1997, pp 30–35.
- 2) D. Chapman, R. K. Wharton, J. E. Fletcher and G. E. Williamson, "Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures Part 2. Stoichiometric Mixtures", *Journal of Pyrotechnics*, No. 7, 1998, pp 51–57.
- 3) R. K. Wharton and D. Chapman, "Use of the Term Sensitiveness To Describe the Response of Pyrotechnics to Accidental Stimuli", *Journal of Pyrotechnics*, No. 7, 1998, pp 65–68.
- 4) "Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria", ST/SG/AC.10/11/Rev. 2, 2nd rev. ed., United Nations, New York and Geneva, 1995; [a] pp 74–83 and pp 105–106; [b] p 107; [c] p 76.
- 5) D. J. Finney, *Probit Analysis a Statistical Treatment of Sigmoid Response Curve*, Cambridge University Press, London, 1952, p 2.
- 6) R. Lancaster, *Fireworks Principles and Practice*, 3rd ed., Chemical Publishing Co. Inc., New York, 1998; [a] p 382; [b] p 16.
- 7) J. A. Conkling, *Chemistry of Pyrotechnics*, Marcel Dekker, New York, 1985, p 107.
- 8) J. Köhler and R. Meyer, *Explosives* 4th ed., VCH Publishers, Weinheim, 1993, p 71.
- 9) A. Bailey and S. G. Murray, *Land Warfare: Brassey's New Battlefield Weapons Systems & Technology Series, Vol. 2, Explosives, Propellants and Pyrotechnics*, Brassey's (UK), London, 1989, p 119.

- 10) J. H. McLain, *Pyrotechnics*, The Franklin Institute Press, Philadelphia, 1980, p 78.
- 11) J. Amiel, "Action of chlorates on Sulfur, Selenium and Tellurium", *Comptes Rendus de L'Académie des Sciences*, Vol. 198, 1934, p 1033.
- 12) F. Taradoire, "Actions of Sulfur on Chlorate", *Comptes Rendus de L'Académie des Sciences*, Vol. 199, 1934, p 603.
- 13) J. Amiel, "Damp Mixtures of Chlorates and Sulfur and other Reactions of Damp Chlorates", *Comptes Rendus de L'Académie des Sciences*, Vol. 199, 1934, p 787.
- 14) W. Ofca, Bill Ofca's *Technique in Fire*, Vol. 10, *Working Safely with Chlorate*, B&C Products, Inc., Hyde Park, NY. 1994, p 39.
- 15) R. K. Wharton, R. J. Rapley and J. A. Harding, "The Mechanical Sensitiveness of Titanium/Blackpowder Pyrotechnic Compositions", *Propellants, Explosives, Pyrotechnics*, Vol. 18, 1993, pp 25–28.

©British Crown copyright, 1999.

Errata

Issue 10, Winter 1999

Page 6, Equation 7 should read: $v_s = (\frac{1}{4}\pi d_s^2/m_s) \int p_s dt$

Page 6, Equation 8 should read: $v_s = \eta_b (\frac{1}{4}\pi d_s^2/m_s) \int p_s dt$

Propellant Chemistry

Naminosuke Kubota

Scientific Advisor, Mitsubishi Electric Corporation, Kamimachiya 325, Kamakura 247-0065, Japan
email: Naminosuke.Kubota@kama.melco.co.jp

ABSTRACT

Propellants used for pyrotechnics are composed of energetic materials that produce high-temperature and high-pressure gaseous products. The propellants are classified into three types by their physical structure and the ingredients used: (1) homogeneous propellants consisting of chemically bonded oxidizer and fuel components in the same molecule, (2) heterogeneous propellants consisting of physically mixed oxidizer and fuel components, and (3) granulated propellants consisting of energetic solid particles. While the energy content of a propellant is determined by the chemical properties of the ingredients, the physical properties and chemical processes of the ingredients determine the ballistic characteristics such as burn rate and pressure and temperature sensitivities.

Keywords: propellant chemistry, activation energy, burn rate

Nomenclature

a = burn rate constant defined in equation 8
 A_b = burn area, m^2
 A_t = nozzle throat area, m^2
 c = specific heat, kJ/kgK
 c_d = mass discharge coefficient
 c_f = thrust coefficient
 d = dark zone pressure exponent
 E = activation energy, $kJ/kmol$
 H_{exp} = heat of explosion, MJ/kg
 I = radiative heat flux, kW/m^2
 k = reaction order
 K_n = area ratio defined by A_b/A_t
 m = mass flow rate, kg/m^2s or reaction order in the dark zone
 m_d = mass discharge rate, kg/s

m_g = mass generation rate, kg/s
 M = molecular mass, $kg/kmol$
 n = pressure exponent of burn rate
[OB] = oxygen balance
 p = pressure, MPa
 q_{cond} = conductive heat flux, kW/m^2
 q_{conv} = convective heat flux, kW/m^2
 q_{reac} = rate of heat production, kW/m^2
 Q = heat release, kJ/kg
 r = burn rate, m/s
 R = gas constant, $8.315 kJ/kmolK$
 T = temperature, K
 u = flow velocity, m/s
 x = distance, m
 Z = pre-exponential factor, $(kg/m^3s)(MPa)^{-\kappa}$
 α = thermal diffusivity, m^2/s
 β = radiative heat flux factor defined in equation 26, kW/m^2K^4
 γ = specific heat ratio
 Γ = heat flux at the burning surface, kW/m^2
 δ = reaction distance, mm
 ΔH_f° = heat of formation, MJ/kg
 λ = thermal conductivity, kW/mK
 Λ = heat flux in the gas phase or in the condensed phase, kW/m^2
 ξ = mass fraction
 π_k = temperature sensitivity of chamber pressure, K^{-1}
 ρ = density, kg/m^3 or g/cm^3
 σ_p = temperature sensitivity of burn rate, K^{-1}
 ϕ = temperature gradient, K/m
 φ = temperature defined in equation 32, K
 ω = reaction rate in the gas phase, kg/m^3s

Subscripts

- c = combustion
- d = decomposition or dark zone
- f = flame or fizz zone
- g = gas phase
- m = melting point
- p = propellant, condensed phase, or product
- r = reactant
- s = burning surface
- 0 = initial condition

1. Introduction

When a propellant is ignited and burned in a closed chamber, gaseous species at high temperature and pressure are formed. These energetic gaseous species generate propulsive forces used for rockets, guns, and fireworks. The specific impulse (I_{sp}) is a parameter used to identify the energy content of propellants and is represented by

$$I_{sp} \sim (T_c/M_c)^{1/2} \quad (1)$$

where T_c is combustion temperature and M_c is molecular weight of the combustion products. Though I_{sp} is also a function of the specific heat ratio (γ) of the combustion products, γ is relatively constant among propellants. It is evident from equation 1 that an energetic material that produces high T_c and high M_c combustion products may not be a useful propellant. A propellant that generates low T_c can also be useful if the M_c is sufficiently low. For example, a pyrolant containing metal powders is not used as a propellant because it generates metallic oxides with a high M_c even though a high T_c is generated by metal combustion.

Solid propellants may be classified into three types by their physical structures: (1) homogeneous propellant, (2) heterogeneous propellant, and (3) granulated propellant. A homogeneous propellant consists of fuel and oxidizer components that are bonded chemically in the same molecule, and the physical structure appears to be homogeneous. A typical example of homogeneous propellant is nitrocellulose (NC) that is composed of $-O-NO_2$ chemical bonds and hydrocarbon structure. Breaking the $O-NO_2$ bond produces NO_2 gaseous species, which act

as an oxidizer fragment, and the hydrocarbon structure acts as a fuel fragment. The physical structure of NC is homogeneous, and it is known as a single-base propellant. The mixture of NC with nitroglycerin (NG) forms a homogeneous gelled propellant known as a double-base propellant. The physical structure of a double-base propellant is also homogeneous.

On the other hand, a heterogeneous propellant is made as a mixture of fuel and oxidizer components, and the physical structure of the propellant is heterogeneous. A typical heterogeneous propellant is a mixture of crystalline particles and a polymeric hydrocarbon, a so-called "composite propellant". The crystalline particles act as the oxidizer component, and the polymeric hydrocarbon acts as a fuel component when these are decomposed. The chemical reaction that produces heat and combustion products occurs on and above the burning surface of the propellant.

A granulated propellant consists of numerous granulated grains or powders that are made from energetic materials. When a granulated propellant is used for a propulsion system, the propellant is a loosely packed shape. Black Powder is a typical example of this class of propellant. However, in some applications (model rocket motors, skyrockets, and signal rockets) Black Powder may be compressed into a single grain and performs as a heterogeneous propellant.

These three types of propellants are fundamentally different from each other in various aspects: chemical ingredients, decomposition processes, burn rate characteristics, combustion products, etc. In this paper the chemical properties of propellants, their ingredients, and combustion characteristics are described in order to understand the ballistic properties of solid propellants.

2. Energetics of Propellants

2.1 Generation of Heat Energy

When a propellant burns, heat and combustion products are produced. In general, the heat produced is evaluated by the “heat of explosion” H_{exp} . H_{exp} is defined as the difference between the heats of formation of the reactants, $\Sigma\Delta H_f^\circ$ (reactants), and the heats of formation of the products, $\Sigma\Delta H_f^\circ$ (products) as represented by

$$H_{exp} = \Sigma\Delta H_f^\circ(\text{reactants}) - \Sigma\Delta H_f^\circ(\text{products}) \quad (2)$$

Each heat of formation, ΔH_f° , is dependent on the chemical structure and chemical bond energy of each molecule of propellant ingredient and combustion products. Equation 2 indicates that a higher H_{exp} is obtained when a higher $\Sigma\Delta H_f^\circ$ (reactants) is used for the propellant and also when a lower $\Sigma\Delta H_f^\circ$ (products) results from the combustion products.

Table 1 shows ΔH_f° for typical energetic reactant ingredients used for propellants, and Table 2 shows ΔH_f° for typical propellant combustion products. It is evident from the data in Table 1 that higher ΔH_f° (reactants) is generally obtained with oxidizers or materials containing nitrogen atoms.

Table 3 shows H_{exp} , percent nitrogen (N%), density (ρ), and melting point temperature (T_m) for typical energetic materials used as major components of propellants. To obtain higher H_{exp} of propellants, various types of chemicals are mixed to formulate propellants. The major chemicals are fuel and oxidizer. The oxidizer oxidizes the fuel to produce heat and gaseous products. Even though $\Sigma\Delta H_f^\circ$ (reactants) of the fuel and oxidizer may be low, a higher H_{exp} is obtained if the oxidizer has a potential to oxidize the fuel completely. The complete oxidation reaction (i.e., complete combustion) produces lower $\Sigma\Delta H_f^\circ$ (products) as the combustion products. Thus, the concentration of oxygen atoms within the oxidizer represented by “oxygen balance: [OB]” is an important parameter to identify the potential of oxidizers. Oxygen balance is the amount of oxygen remaining after oxidizing hydrogen, carbon, magnesium, aluminum, etc. to produce H_2O , CO_2 , MgO , Al_2O_3 , etc. If excess oxygen molecules remain after the oxidation reaction, the oxidizer

Table 1. ΔH_f° for Propellant Reactant Ingredients.

Reactant	ΔH_f° (MJ/kg)
NG	-1.70
NC	-2.60
HMX	+0.25
NH_4ClO_4	-2.52
$KClO_4$	-3.12
NH_4NO_3	-4.56
KNO_3	-4.87
CTPB	-0.89
HTPB	-0.31
GAP	+0.96
BAMO	+2.46
Cubane	+5.47
Al	0
Mg	0
B	0

Table 2. ΔH_f° for Propellant Combustion Products.

Product	ΔH_f° (MJ/kg)
CO	-3.94
CO_2	-8.94
H_2	0
$H_2O_{(g)}$	-13.42
N_2	0
Al_2O_3	-16.4
B_2O_3	-18.30
MgO	-14.93

is termed to have a “positive” oxygen balance. If the oxygen molecules are completely consumed and excess fuel molecules remain, the oxidizer is termed to have a “negative” oxygen balance.

Since the reaction of an oxidizer composed of a $C_aH_bN_cO_dCl_eS_f$ oxidizer is represented by

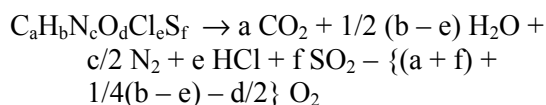


Table 3. Physicochemical Properties of Ingredients Used for Propellants.

Propellant Ingredient	Short-hand	Formula	N (%)	Density (ρ) (g/cm ³)	H_{exp} (MJ/kg)	T_m (°C)	[OB] (%)
nitroglycerine	NG	(ONO ₂) ₃ (CH ₂) ₂ CH	18.50	1.59	6.322	13.2	+3.5
nitrocellulose	NC	C ₁₂ H ₁₄ N ₆ O ₂₂	14.14	1.67	4.13	D	-28.7
ammonium perchlorate	AP	NH ₄ ClO ₄	11.04	1.95	1.114	D	+34.04
ammonium nitrate	AN	NH ₄ NO ₃	35.0	1.72	1.601	169.6	+19.99
nitroguanidine	NQ	CH ₄ N ₄ O ₂	53.83	1.71	2.88	232	-30.7
triaminoguanidine nitrate	TAGN	CH ₉ N ₇ O ₃	58.68	1.5	3.67	216	-33.5
cyclotetramethylene tetranitramine	HMX	(NNO ₂) ₄ (CH ₂) ₄	37.83	1.90	5.36	275	-21.6
cyclotrimethylene trinitramine	RDX	(NNO ₂) ₃ (CH ₂) ₃	37.84	1.82	5.40	204	-21.6
hexanitrohexaazatetradecyclododecane	CL-20	(NNO ₂) ₆ (CH) ₆	38.45	2.04	6.8	260	-10.95

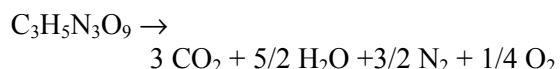
D = decomposes instead of melting.

Note: H_{exp} is for H₂O as a gas.

the oxygen balance, expressed as mass percent, is given by

$$[OB] = - \{ (a + f) + 1/4(b - e) - d/2 \} \times \{ 32 / (\text{molecular mass of oxidizer}) \} \times 100\%$$

For example, NG produces excess oxygen molecules during its combustion as given by



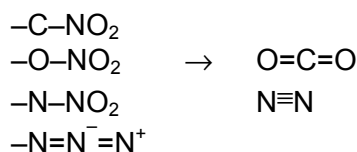
The oxygen balance of NG is given by

$$[OB]_{NG} = \{ + 1/4 \} \times \{ 32 / 227 \} \times 100\% = + 3.52\%$$

The oxygen balance for any type of oxidizer can be obtained by assuming the oxidized products as shown above. Table 3 shows the oxygen balance for some ingredients used in propellants.

2.2 Characterization of Energetic Materials

Typical materials containing oxygen and nitrogen atoms are known as nitrate esters and include nitrocellulose (NC) and nitroglycerin (NG). Nitrate esters consist of -O-NO₂ chemical bonds in their structures. The oxidizer component is oxygen, and the fuel components are carbon and hydrogen. The oxidized combustion products are CO₂ and H₂O_(g) for which ΔH°_f are -8.94 and -13.42 MJ/kg, respectively, as shown in Table 2. The nitrogen atoms in the reactants produce nitrogen gas for which ΔH°_f is zero (Table 2). Also materials containing a -C-NO₂ bond such as trinitrotoluene (TNT: C₇H₅N₃O₆) and tetryl (C₇H₅N₅O₈), those containing a -N-NO₂ bond such as RDX (C₃H₆N₆O₆) and HMX (C₄H₈N₈O₈), and those containing a -N=N=N⁺ bond such as lead azide (Pb(N₃)₂) and glycidyl azide polymer (GAP: C₃H₅N₃O) are high-energy materials useful for propellants. These materials act to produce CO₂ and N₂ through the following combustion reaction



Thus, a high H_{exp} as shown in equation 2 is obtained by the combustion of materials containing these chemical bonds.

Crystalline materials such as KNO_3 , NH_4NO_3 , and NH_4ClO_4 are used as oxidizers due to the high concentration of oxygen atoms in their molecules. These materials generate oxidizing fragments when thermally decomposed. On the other hand, hydrocarbon polymers such as polyurethane and polybutadiene generate gaseous fuel fragments when thermally decomposed. Thus, the mixture of an oxidizer and a hydrocarbon polymer forms a composite propellant. Accordingly, a composite propellant generates high temperature gases during combustion.

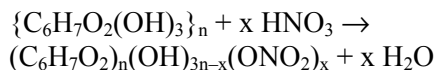
The mechanical properties of propellants are important to produce desirable propellant grains. The mass burn rate of propellant is dependent not only on the linear burn rate of the propellant but also on the burning surface area of the propellant grain. During pressure transient processes, such as ignition and oscillatory burning in a rocket motor, very high mechanical stresses are produced in the propellant grain. If the internal grain shape is complicated, these stresses may damage the propellant grain. The increased burning surface area caused by unexpected damage, such as cracks, to the grain increases pressure in the combustion chamber. Furthermore, the elongation property (elasticity) decreases as the temperature decreases. This may cause damage to the grain when mechanical shock is applied to the grain at low temperature. On the other hand, mechanical strength decreases as temperature increases. This may allow deformation of the grain due to its mass. Accordingly, the propellant grain geometry should be maintained by adequate elongation and strength properties of the propellant.

3. Propellant Ingredients

3.1 Homogeneous Propellants

Nitrocellulose (NC) is a major energetic ingredient used for single-base and double-base propellants. As shown in Table 3, NC is a nitrate ester composed of carbon, hydrogen, oxygen, and nitrogen atoms. The oxygen atoms are attached as $-\text{O}-\text{NO}_2$ with a nitrogen atom. When NC is thermally heated, NO_2 is formed because the $\text{O}-\text{N}$ bond is the weakest of the NC chemical bonds. The remaining oxygen then forms aldehydes such as HCHO and CH_3CHO . The reaction between NO_2 and aldehydes produces heat and the combustion gases that are used for propulsive forces in rockets, guns, and pyrotechnics.

In general, NC is produced from the cellulose, $\{\text{C}_6\text{H}_7\text{O}_2(\text{OH})_3\}_n$, of cotton or wood, which is nitrated using nitric acid (HNO_3) to gain $-\text{O}-\text{NO}_2$ bonds in its structure as



Through this nitration the $-\text{OH}$ contained within the cellulose is replaced with $-\text{O}-\text{NO}_2$; the degree of nitration determines the energy available to form high temperature combustion gases. The maximum nitration is obtained when the nitrogen mass becomes 14.14% within NC.

The major ingredient of single-base propellant is NC. Diphenylamine, $(\text{C}_6\text{H}_5)_2\text{NH}$, is also added as a chemical stabilizer. In some cases, a small amount of K_2SO_4 or KNO_3 is mixed as a flame-suppressor. Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) or diethylether ($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$) is mixed within the NC to soften it and to gain an adequate size and shape of the propellant grain. The grain surface is coated with carbon black to keep the surface smooth.

A double-base propellant is also known as smokeless powder [propellant] when used for guns and rockets. Two major ingredients are used to formulate double-base propellant grains: NC and nitroglycerin (NG). NG, $\text{C}_3\text{H}_5(\text{ONO}_2)_3$, is also a nitrate ester characterized with the $-\text{O}-\text{NO}_2$ structure and is a high explosive. Since NG is liquid at room temperature, NG is absorbed by the NC and acts to gelatinize NC to form double-base propellant grains.

Table 4. Physicochemical Properties of Nitrate Esters Used for Double-base Propellants.

Nitrate Ester	N (%)	Density (ρ) (g/cm ³)	$\Delta H_f^{\circ}(r)$ (MJ/kg)	H_{exp} (MJ/kg)	T_m (°C)	[OB] (%)
diethyleneglycol dinitrate (DEGDN) (CH ₂) ₄ O(ONO ₂) ₂	14.29	1.38	-2.208	4.852	2	-40.8
triethyleneglycol dinitrate (TEGDN) (CH ₂) ₆ O ₂ (ONO ₂) ₂	11.67	1.34	-2.526	3.140	-19	-66.7
trimethylolethane trinitrate (TMETN) CH ₃ C(CH ₂) ₃ (ONO ₂) ₃	16.46	1.47	-1.610	5.527	-3	-34.5

Since NG is highly shock sensitive, other types of nitrate esters can be used to formulate non-NG double-base propellants. Diethyleneglycol dinitrate (DEGDN), (CH₂)₄O(ONO₂)₂, triethyleneglycol dinitrate (TEGDN), (CH₂)₆O₂(ONO₂)₂, and trimethylolethane trinitrate (TMETN), CH₃C(CH₂)₃(ONO₂)₃ are typical examples of energetic nitrate esters that are mixed with NC. Though these nitrate esters are less energetic than NG, the required mass fraction of desensitizers required is less for the nitrate esters than it is for NC/NG double-base propellants. The physicochemical properties of these nitrate esters are shown in Table 4.

Two production methods are used to produce double-base propellant grains: (1) extrusion using an external mechanical press and (2) casting using finely divided NC powders or NC/NG powders. The extrusion method is used for grains less than 0.1 kg, typically used in guns and pyrotechnics. The casting method is used for grains larger than 1 kg such as rockets. Since NG is a detonative explosive, the concentration of NG is kept approximately less than $\xi(0.5)$ for double-base propellants. Furthermore, various chemicals such as plasticizers, stabilizers, and burn rate modifiers are added to NC/NG mixtures to improve the physicochemical properties of double-base propellants.

The mechanical properties and shock sensitivities of double-base propellants are highly dependent on the mixture ratio of NC and NG. Though the specific impulse of double-base propellants increases with the concentration of NG, the strength of the propellant decreases. It becomes difficult to maintain grain shape when the concentration of NG is as high as $\xi(0.5)$. For example, dynamites contain more than $\xi(0.8)$ NG, and their grains are very soft and have high shock sensitivity. When the concentration of NC becomes higher than $\xi(0.6)$, the elongation properties become poor. Thus, double-base propellants need to contain desensitizers, stabilizers, and chemicals to improve mechanical properties. In order to obtain superior mechanical properties, plasticizers such as dibutylphthalate (DBP), C₁₆H₂₂O₄; diethylphthalate (DEP), C₁₂H₁₄O₄; triacetin (TA), C₉H₁₄O₆; and stabilizers such as ethyl centralite (EC), CO{N(C₆H₅)(C₂H₅)}₂ are added. Table 5 shows the physicochemical properties of the plasticizers and stabilizers used for double-base propellants. These chemicals are used to obtain superior grain formation and to improve mechanical properties, shock sensitiveness and chemical stability.

Table 5. Plasticizers and Stabilizers Used for Double-base Propellants.

Plasticizers and Stabilizers	N (%)	Density (ρ) (g/cm ³)	$\Delta H_f^{\circ}(r)$ (MJ/kg)	[OB] (%)
dibutylphthalate (DBP) C ₁₆ H ₂₂ O ₄	0	1.045	-3.027	-224.2
triacetin (TA) C ₉ H ₁₄ O ₆	0	1.15	-5.606	-139.4

Table 6. Ingredients Used for Double-Base Propellants.

Plasticizer (Oxidizer and Fuel)		Plasticizer (Energetic Fuel)	
NG	nitroglycerin	GAP	glycidylazido polymer
TMETN	trimethylolethane trinitrate	BAMO	bis-azide methyloxetane
TEGDN	triethyleneglycol dinitrate	AMMO	3-azidomethyl-3-methyloxetane
DEGDN	diethyleneglycol dinitrate		
DNT	dinitrotoluene		
Plasticizer (Fuel)		Binder (Fuel and Oxidizer)	
DEP	diethylphthalate	NC	nitrocellulose
DBP	dibutylphthalate		
TA	triacetine		
PU	polyurethane		
Burn Rate Catalyst		Stabilizer	
PbSa	lead salicylate	EC	ethyl centralite
PbSt	lead stearate	2NDPA	2-nitrodiphenylamine
Pb2EH	lead 2-ethylhexanoate	DPA	diphenylamine
CuSa	copper salicylate		
CuSt	copper stearate		
LiF	lithium fluoride		
High Energy Additive (CMDB Propellant)		Burn Rate Catalyst Modifier	
RDX	cyclotrimethylene trinitramine	C	carbon black (used with lead or copper salts)
NQ	nitroguanidine		
HMX	cyclotetramethylene tetranitramine		
CL-20	hexanitrohexaazatetracyclodecane		
ADN	ammonium dinitramide		
Combustion Instability Suppressant		Oxidizer (CMDB Propellant)	
Al	aluminum	AP	ammonium perchlorate
Zr	zirconium	HNF	hydrazinium nitroformate
ZrC	zirconium carbide		
		Coolant (Fuel)	
		OXM	oxamide
		TAGN	triaminoguanidine nitrate
		Opacifier	
		C	carbon black
		Metal Fuel	
		Al	aluminum

The I_{sp} and T_f (T_f is the adiabatic flame temperature) of double-base propellants are dependent on the mass fraction of NG, $\xi(\text{NG})$, mixed within the NC and other chemicals. When a double-base propellant is composed of NG, NC, and DEP (the additional mass fraction of DEP is 0.10), the maximum I_{sp} and T_f are obtained at $\xi(\text{NG}) = 1.0$ as shown in Figure 1. It should be noted that the I_{sp} and T_f of the double-

base propellants composed of NC and NG without plasticizers and stabilizers are maximized at $\xi(\text{NG}) = 0.75$.

Table 6 shows materials used to formulate double-base propellants. Typical examples of chemical compositions and energetics of double-base propellants are shown in Table 7.

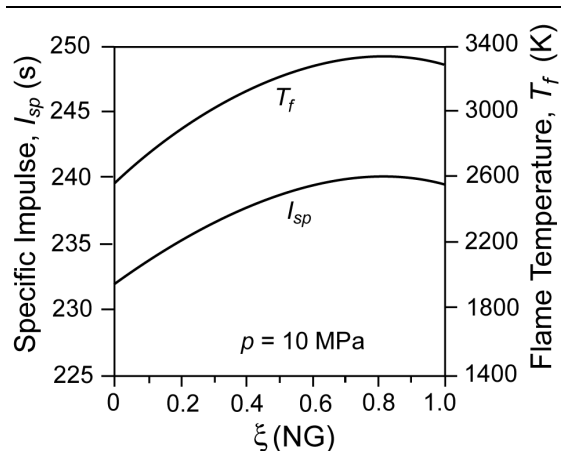
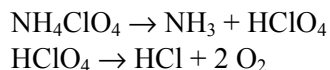


Figure 1. Combustion performance of double-base propellant as a function of NG (the propellant contains an additional mass fraction of 0.1 DEP).

3.2 Heterogeneous Propellants

When crystalline oxidizer particles are mixed with a hydrocarbon polymer, a heterogeneous propellant, or “composite propellant”, is formed. Unlike double-base propellants, the physical structure of composite propellants is heterogeneous due to the dispersed crystalline particles within the polymer. As described previously, at the burning surface of the propellant, the oxidizer particles generate gaseous oxidizing fragments, and the polymer generates gaseous fuel fragments. Both gaseous fragments diffuse with each other and react to generate heat and combustion products. Accordingly, ballistic properties, such as burn rate and pressure sensitivity, are dependent not only on the chemical properties of oxidizers and binders but also are dependent on the shape and size of the oxidizer particles.

The major oxidizer used for composite propellants is ammonium perchlorate (AP), NH_4ClO_4 . When AP is heated, it decomposes as



The oxidizing fragments react with fuel fragments when these crystalline materials are mixed with fuel components, for example,

Table 7. Chemical Compositions and Energetics of Typical Double-Base Propellants.

NC	NG	DEP	2NDPA	T_f (K)	H_{exp} (MJ/kg)
53.0	40.5	4.0	2.5	2800	4.62
48.0	36.7	13.0	2.3	2200	3.78



This reaction produces significant heat and gaseous molecules, which yields a high I_{sp} as defined in equation 1.

Ammonium nitrate (AN), NH_4NO_3 , is a halogen-free oxidizer, which produces nontoxic combustion products. However, disadvantages of AN compared with AP are hygroscopicity and crystal structure transitions at 125.2, 84.2, 32.3, and -16.9 °C. These transitions produce internal mechanical stresses in the propellant grain, which sometimes damages the grain. Though potassium nitrate (PN), KNO_3 , and potassium perchlorate (PP), KClO_4 , produce high temperature combustion products, the combustion products contain potassium oxide (K_2O), which has high M_c and significantly reduced I_{sp} . PN is a well-known oxidizer used as the oxidizer in Black Powder. PP is also used as an oxidizer in pyrotechnic compositions.

The binders, used to adhere oxidizer particles to form propellant grains, are also fuel ingredients. Table 8 shows typical polymers used for composite propellants.

The binders are based on hydrocarbon polymers that have a relatively low viscosity during the process of mixing the oxidizer particles and the polymer before the curing process. Two types of polymers are commonly used for modern propellants: (1) polyurethane copolymer and (2) polybutadiene copolymer. Polyether and polyester types of polyurethane copolymers are used. The molecular concentration of hydrogen contained within polybutadiene copolymers is relatively high, and the heat of formation is also high. Also, the viscosity of the copolymer is low enough to allow mixing with oxidizer particles before curing.

Table 8. Type of Polymers Used for Composite Propellants.

Polymeric Binder	Basic Polymer Unit
Polyethylene	$-\text{CH}_2-\text{CH}_2-$
Polyester	$-(\text{CH}_2)-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$
Polyurethane	$-\text{O}-(\text{CH}_2)_n-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-(\text{CH}_2)_n-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-$
Polybutadiene	$-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$

Polybutadiene-acrylonitrile (PBAN) is used as the binder in the booster propellant of the Space Shuttle. Carboxy-terminated polybutadiene (CTPB) and hydroxy-terminated polybutadiene (HTPB) are used widely for modern composite propellants. CTPB and HTPB form regularly distributed matrices of polymers through crosslinking reactions. For example, HTPB polymer, $\text{HO}-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n-\text{OH}$, is cured using isophorone diisocyanate (IPDI) to form a polymeric binder. Using this binder, it is possible to achieve a high loading percentage of oxidizer. To gain superior mechanical properties a small amount of bonding

agent is added to adhere each oxidizer particle to the binder. As shown in Figure 2a, the maximum I_{sp} , 259 s, ($p = 10$ MPa), is obtained when the mass fraction of AP, $\xi(\text{AP})$, is 0.89 mixed with a mass fraction of HTPB binder of 0.11.

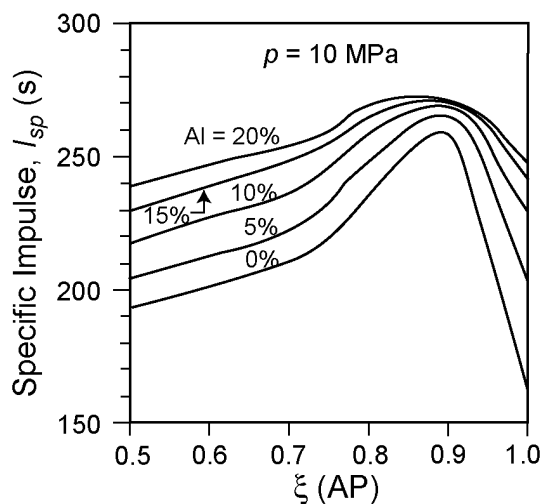


Figure 2a. Specific impulse of AP/HTPB/Al propellant as a function of the mass fraction of AP.

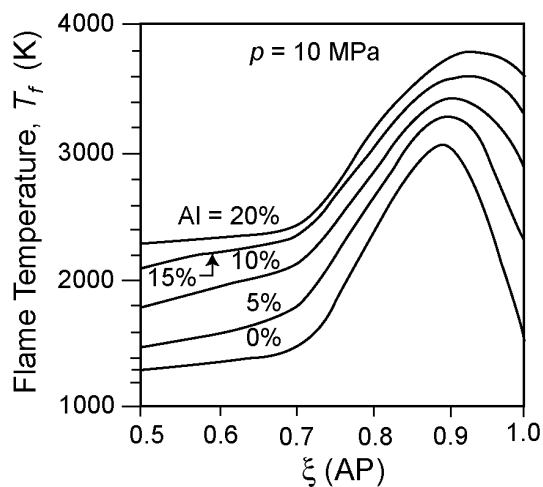


Figure 2b. Adiabatic flame temperature of AP/HTPB/Al as a function of the mass fraction of AP.

To gain higher I_{sp} with AP-based composite propellants, aluminum particles are added as a fuel component. Though the addition of aluminum particles increases the M_c , the increase of T_f is the larger effect resulting in higher I_{sp} . The effect of aluminum addition on the adiabatic flame temperature is shown in Figure 2b. However, it should be noted that the maximum solid fraction within composite propellants is limited to approximately 0.85 due to mixing difficulties.

When aluminum particles are added to composite propellants, white smoke is generated due to the combustion product, aluminum oxide. If the smoke is not desirable because of military requirements or use in a fireworks display, aluminum particles cannot be used. Furthermore, if the atmosphere is very humid, white smoke is also generated due to the HCl – produced as a combustion product. This is because the HCl molecule acts as a nucleus for moisture from the atmosphere, and relatively large-sized water drops are formed producing a fog or a mist. This occurs only when the humidity in the atmosphere is high or the temperature is low (below $-10\text{ }^\circ\text{C}$). Double-base propellants are classified as smokeless propellants, and composite propellants, using AN as an oxidizer without halogen molecules, are also known as smokeless propellants.

Since composite propellants consist of crystalline particles and polymeric binders, the mechanical properties of propellant grains are dependent on the physical and chemical properties of these ingredients and also of the additives such as bonding agents, surfactants, crosslinkers, and curing agents. The binder, as well as the mass fraction and particle size of the oxidizer, determine the characteristics of mechanical strength and elongation.

The polymers chosen for composite propellants are dependent on application conditions. Low viscosity is needed to allow high concentrations of AP particles, aluminum powders, and metallic powders used for burn rate modifiers, to achieve high I_{sp} . HTPB is considered to be the best binder to obtain both high combustion performance and superior elongation properties at low temperatures. HTPB is characterized with $-\text{OH}$ terminal of butadiene polymer. Another useful butadiene polymer is carboxy-

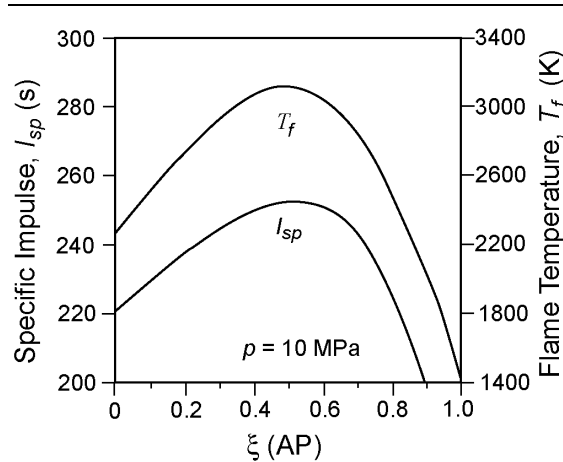


Figure 3. Combustion performance of AP-CMDB propellant as a function of the mass fraction of AP.

terminated polybutadiene (CTPB). The prepolymer of HTPB is cured and crosslinked using isophorone diisocyanate (IPDI) to form HTPB polymer, useful as a binder. The functionality of the HTPB prepolymer is also an important chemical parameter during the process of curing and crosslinking to achieve superior mechanical properties of the HTPB binder.

The propellant composed of AP particles with NC/NG used as a binder is the so-called “ammonium perchlorate based composite modified double-base propellant (AP-CMDB propellant)”. AP-CMDB propellant is called a composite propellant because of its physical structure. However, the binder of NC/NG burns by itself and produces numerous diffusional flamelets around each AP particle at the burning surface. The AP particles act as an oxidizer to increase T_f and I_{sp} . Figure 3 shows the T_f and I_{sp} of AP-CMDB propellants at $p = 10\text{ MPa}$ as a function of $\xi(\text{AP})$. The base matrix used as a binder is composed of NC/NG = 1/1. The maximum T_f and I_{sp} are obtained at $\xi(\text{AP}) = 0.5$.

Table 9 shows the materials used to formulate composite propellants. An example of the chemical composition of a composite propellant is shown in Table 10.

Table 9. Chemical Ingredients Used for Composite Propellants.

Oxidizer		Binder (Fuel)	
AP	ammonium perchlorate	HTPB	hydroxy-terminated polybutadiene
AN	ammonium nitrate	CTPB	carboxy-terminated polybutadiene
HNF	hydrazinium nitroformate	PU	polyurethane
		PS	polysulfide
		PVC	polyvinyl chloride
Curing and/or Crosslinking Agent		Binder (Energetic Fuel)	
IPDI	isophorone diisocyanate	GAP	glycidylazido polymer
TDI	toluene-2,4-diisocyanate	BAMO	bis-azidemethyloxetane
PQD	paraquinone dioxime	AMMO	3-azidomethyl-3-methyloxetane
HMDI	hexamethylene diisocyanate		
MAPO	tris(1-(2-methyl)aziridinyl) phosphine oxide		
Metal Fuel		Bonding Agent	
Al	aluminum	MAPO	tris(1-(2-methyl)aziridinyl) phosphine oxide
		TEA	triethanolamine
		MT-4	adduct of 2.0 moles MAPO, 0.7 mole adipic acid, and 0.3 mole tartaric acid
Plasticizer		Burn Rate Catalyst	
DOA	dioctyl adipate	Fe ₂ O ₃	ferric oxide
IDP	isodecyl pelargonate	FeO(OH)	hydrated ferric oxide
DOP	dioctylphthalate	NBF	n-butyl ferrocene
		LiF	lithium fluoride
High Energy Additive		HCl Suppressant	
RDX	cyclotrimethylenetrinitramine	Mg	magnesium
HMX	cyclotetramethylenetetranitramine	MgAl	magnalium
NQ	nitroguanidine	NaNO ₃	sodium nitrate
CL-20	hexanitrohexaazatetracyclo- dodecane		
ADN	ammonium dinitramide		
Combustion Instability Suppressant			
Al	aluminum		
Zr	zirconium		
ZrC	zirconium carbide		

3.3 Granulated Propellants

Granulated propellants are used in a loosely packed shape containing numerous individual grains or powders. Though single-base propellants normally are classified as homogeneous propellants, some propulsion applications use a

packed shape consisting of granulated single-base propellant.

Black Powder is a typical granulated propellant used for propulsion and is used as a propellant for small-sized rockets, guns, and fireworks. Though the theoretical I_{sp} of Black Powder is less than that of single-base, double-base, and

Table 10. Chemical Composition and Combustion Products of a Typical Composite Propellant.

Ingredients (weight %)		T_f , K	Products (mole fractions)					
AP	HTPB		CO	CO ₂	HCl	H ₂ O	N ₂	H ₂
80.0	20.0	2358	0.251	0.055	0.143	0.244	0.075	0.213

AP-based composite propellants, Black Powder is useful for short-duration operations of simplified propulsive systems. The advantages of Black Powder are low cost, very low aging effect, and simple adjustment of propulsive forces by the amount used.

Black Powder is a mechanically mixed material of PN powder (60–80%), charcoal (10–25%), and sulfur (8–25%) that is pressed, granulated, and formed as a packed shape for use. When Black Powder is ignited, combustion occurs over all granulated surfaces. Thus, the rate of gas production becomes much higher than that of conventional propellants used for rockets. However, this combustion phenomenon is deflagration, not detonation. The burn rate of Black Powder is not defined as that of rocket propellants because of the nature of the granulated combustion, except when pressed in some applications. The overall gas production rate is an important combustion parameter, and it is dependent on the granulation size of the powder as well as the density of the packed shape. The specific impulse, I_{sp} , ranges from 60 to 150 s, and the combustion temperature ranges from 1400 to 3200 K. These values are determined by the mixture ratio of the ingredients.

In general, powdered grains made of single-base, double-base, and triple-base propellants are classified as granulated propellants. These are used as gun propellants, and the burn time is on the order of 10 to 100 ms. The mass burn rate of these grains is very high because the web thickness is very thin compared to rocket propellants, and the burning pressure is on the order of 100 to 1000 MPa. Though the physical structures of single-base and double-base granulated grains are essentially homogeneous, these grains burn independently in combustion chambers. Thus, the flame structures appear to be heterogeneous in nature. The shape of each grain is designed to obtain the desired pressure versus time relationship during burning. The reaction products of granulated propellants are essentially the same as Black Powder, single-base gun propellant, or double-base rocket propellant. Table 11 shows the chemical composition of a typical single-base propellant. Table 12 shows the chemical composition and properties of typical Black Powder.

Table 11. Chemical Composition and Combustion Products of a Typical Granulated Single-base Propellant.

Ingredients (weight %)				T_f , K	Products (moles/kg)				
NC	DNT	DBP	DPA		CO ₂	CO	H ₂ O	H ₂	N ₂
85.0	10.0	5.0	1.0	1598	2.32	22.84	5.81	9.55	4.39

Table 12. Chemical Compositions and Properties of Typical Black Powders.

Ingredient	Percentage
potassium nitrate	60 – 80
charcoal	10 – 25
sulfur	8 – 25

Property	Range of Values
I_{sp} , s	60 – 150
Density, g/cm ³	1.2 – 2.0
Flame temperature, K	1400 – 3200

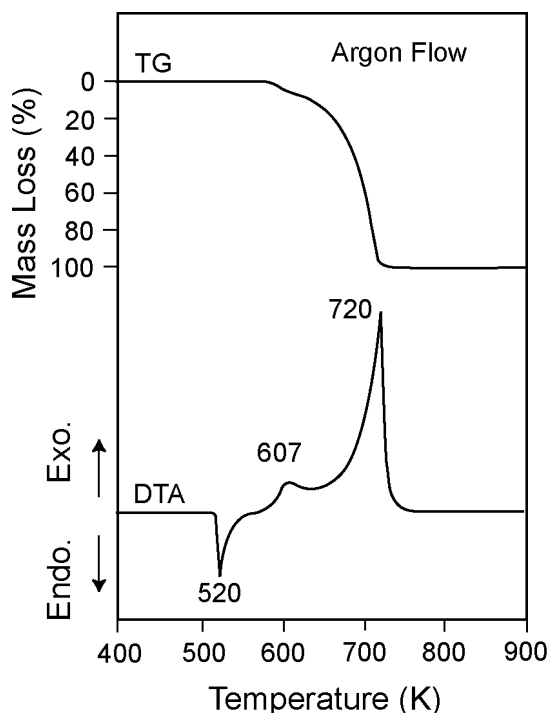


Figure 4. Thermochemical data of AP obtained by DTA and TG showing an endothermic peak at 520 K and an exothermic peak at 720 K.

4. Reaction of Propellants

4.1 Thermal Decomposition Process

There have been numerous studies on the decomposition of propellants and their ingredients to elucidate the aging mechanisms and burn rate characteristics. Various types of experimental techniques are used: (1) differential thermal analysis (DTA), (2) thermogravimetric analysis (TG), (3) Fourier transform infrared analysis (FTIR), (4) Raman spectrum (RS), (5) gas chromatography (GC), and (6) scanning electron microscopy (SEM). Since the chemical process of aging is very slow and the decomposition process for combustion is very fast, the experimental techniques shown above are applied at accelerated conditions for aging analysis and at decelerated conditions for combustion process analysis.

Typical examples of the thermal decomposition process of AP as obtained by DTA and TG are shown in Figure 4. These experiments are conducted to determine the endothermicity

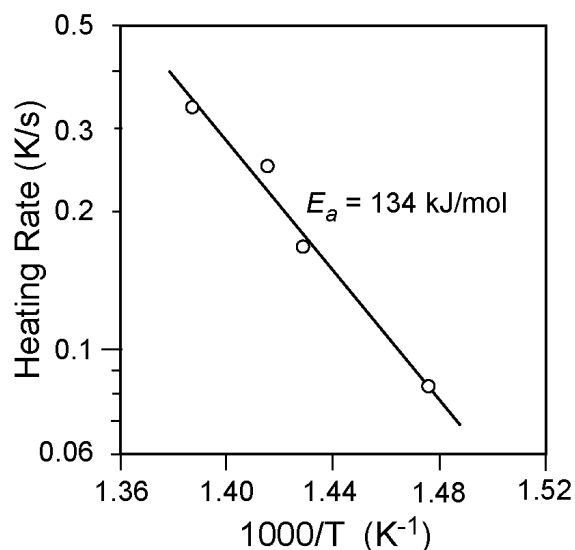


Figure 5. Arrhenius plot of reciprocal exothermic peak temperature as a function of heating rate obtained by DTA.

and/or exothermicity of AP decomposition. The AP sample size was 5 mg in a quartz cell under an argon atmosphere. The heating rate is varied from test to test and ranged from 0.08 to 0.33 K/s. An endothermic peak is seen at 520 K, and an exothermic peak temperature is seen at 720 K using a heating rate 0.33 K/s.

When the heating rate is increased, these peaks shift toward higher temperatures. As shown in Figure 5, the plot of reciprocal temperature versus heating rate produces a straight line that determines the activation energy of the observed phenomenon. Based on data at different heating rates, the activation energy E_a for the decomposition is determined to be 134 kJ/mol. The activation energy of the burning surface decomposition is used to determine burn rate characteristics at high-pressure conditions.

4.2 Characteristics of Thermal Decomposition

The thermal decomposition process is different for each material. For example, the exothermicity of NG is different from that of NC even though both are nitrate esters. Also, the exothermicity of a double-base propellant that is a mixture of NG and NC appears to be different from that of either NG or NC and is also different from an averaged value of NG and

NC. This indicates that the thermal decomposition property of propellant is not an averaged value of each propellant ingredient. Furthermore, the exothermicity of an AP-based composite propellant is much higher than the sum of the exothermicity of each ingredient because an exothermic oxidation reaction occurs between AP and binder.

Though the aging chemistry of propellants is complicated, the surface chemistry between oxidizer particles and binder plays a dominant role in determining the aging period. No definite methods are available to quantify such a very slow reaction mechanism, however, one can estimate it through theoretical analysis based on the data from DTA, TG, and other thermal measurement equipment.

The thermal decomposition at the burning surface of a propellant is more than 10^4 times higher than that of DTA and TG heating rates. Though the data obtained by DTA and TG cannot be applied to determine ballistic characteristics, these are used to determine the thermal properties of propellant burning.

5. Propellant Combustion

5.1 Stable Combustion of Rocket Motor

The thrust of a rocket motor is expressed by

$$F = c_f A_t p_c \quad (3)$$

where F is thrust, p_c is pressure in the combustion chamber of the rocket motor, A_t is the nozzle throat area, and c_f is the dimensionless thrust coefficient, which is determined by the nozzle expansion ratio of the rocket motor, the specific heat ratio, and the atmospheric and chamber pressures.

The mass generation rate in the combustion chamber, m_g , is given by

$$m_g = \rho_p A_b r \quad (4)$$

where r is burn rate of the propellant, A_b is the burning surface area of the propellant, and ρ_p is the density of the propellant. The mass discharge rate from the nozzle, m_d , is then given by

$$m_d = c_d A_t p_c \quad (5)$$

where c_d is the nozzle discharge coefficient that is determined by the combustion properties of propellant such as combustion temperature, molecular mass and specific heat ratio of the combustion products.

The mass balance of the rocket motor at steady-state is given by

$$m_g = m_d \quad (6)$$

From equations 4, 5 and 6, the chamber pressure is determined to be

$$p_c = \rho_p K_n r / c_d \quad (7)$$

where $K_n = A_b / A_t$, which is determined by the physical dimensions of the rocket motor design. In general, the burn rate of the propellant increases linearly as the pressure increases in a $\ln p$ versus $\ln r$ plot at constant initial temperature T_0 , where r is the burn rate and p is the pressure. Thus, the burn rate is represented by the experimental law, Vieille's law or Saint Robert's law, as

$$r = ap^n \quad (8)$$

where n is the pressure exponent of the burn rate and a is constant at constant initial propellant temperature T_0 . Substituting equation 8 into equation 7, one obtains

$$p_c = (a \rho_p K_n / c_d)^{1/(1-n)} \quad (9)$$

The mass balance of a rocket motor is illustrated in Figure 6.

5.2 Burn Rate Characteristics

The pressure sensitivity of the burn rate is expressed as

$$n = d(\ln r) / d(\ln p) \quad \text{at constant } T_0 \quad (10)$$

The burn rate increases also as T_0 increases at constant pressure. A typical example of the results obtained by a strand burner at $T_0 = 233$ and 333 K is shown in Figure 7, which is a $\log p$ vs $\log r$ plot. The temperature sensitivity of burn rate, σ_p , is defined as the fraction of burn rate increase per K as when the initial propellant temperature is increased at constant pressure

$$\sigma_p = (r_1 - r_0) / \{(T_1 - T_0)r\} \quad (11)$$

where r_0 and r_1 are the burn rates at temperatures T_0 and T_1 , respectively. The differential form of σ_p is

$$\sigma_p = d(\ln r) / dT_0 \quad \text{at constant } p \quad (12)$$

Substituting equation 8 into equation 12, one gets

$$\sigma_p = d(\ln(ap^n)) / dT_0 = (da/dT_0) / a \quad \text{at constant } p \quad (13)$$

When T_0 of the propellant in the combustion chamber is changed, p_c is changed according to the relationship of equation 7. The temperature sensitivity of the chamber pressure π_k is defined as

$$\pi_k = (p_{c1} - p_{c0}) / \{(T_1 - T_0)p_c\} \quad \text{at constant } K_n \quad (14)$$

where p_{c0} and p_{c1} are the chamber pressures at T_0 and T_1 , respectively. The differential form of equation 14 is given by

$$\pi_k = d(\ln p_c) / dT_0 \quad \text{at constant } K_n \quad (15)$$

Substituting equation 9 into equation 15, one obtains

$$\pi_k = (da/dT_0) / a(1-n) = \sigma_p / (1-n) \quad (16)$$

Thus, it should be noted that the initial propellant temperature, T_0 , and the pressure exponent of the burn rate n are important parameters in determining the chamber pressure p_c (i.e., thrust

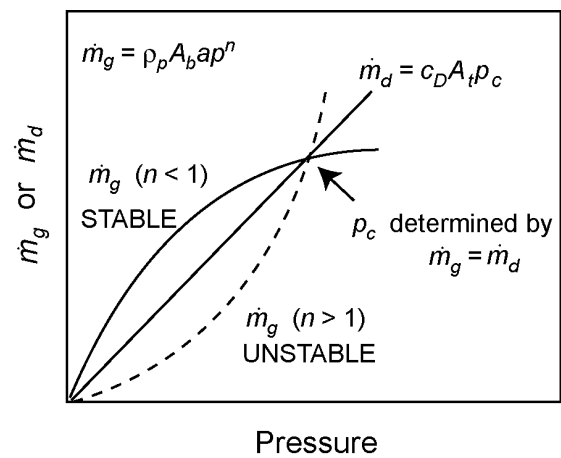


Figure 6. Mass balance of the mass generation in chamber and the mass discharge from nozzle showing the conditions of stable and unstable burning.

of the rocket motor) as shown by equation 3 at different initial propellant temperatures. Figure 8 shows a typical result of rocket-motor firing tests at $T_0 = 233$ and 333 K (constant K_n). The propellant used is an HTPB/AP composite propellant composed of $\xi(\text{AP}) = 0.84$ with $\sigma_p = 0.003/\text{K}$ and $n = 0.5$ ($\pi_k = 0.006/\text{K}$). It is important to note that the chamber pressure increased from 4.9 MPa ($T_0 = 233$ K) to 8.0 MPa ($T_0 = 333$ K).

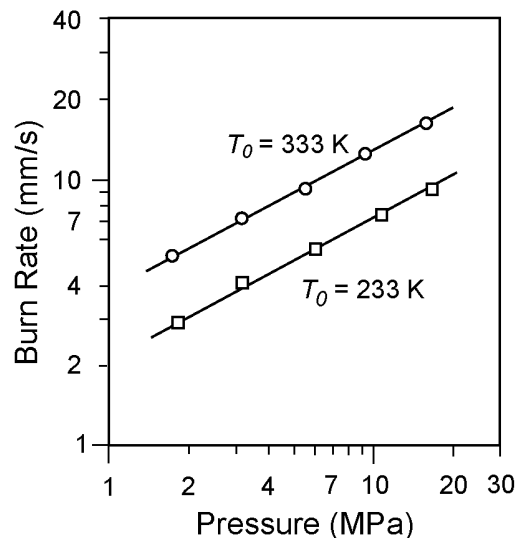


Figure 7. Burn rate versus pressure at different initial-propellant temperatures.

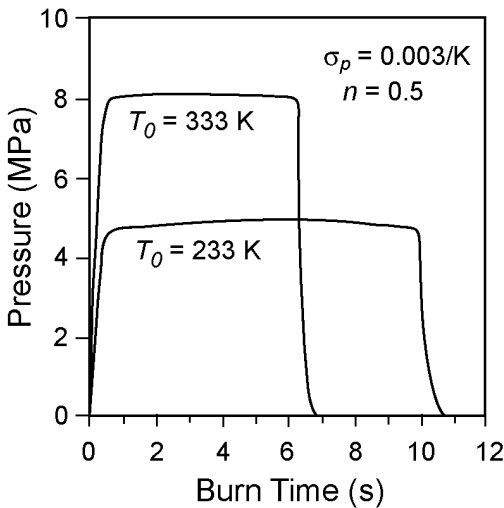


Figure 8. Firing test results of a rocket motor at different temperatures.

5.3 Combustion Wave Structure of Propellants

The burn rate of solid propellant is dependent on various physicochemical parameters such as propellant chemical ingredients, particle size of crystalline oxidizers, chamber pressure, initial propellant temperature, and burn rate catalysts. A schematic representation of the combustion wave of a solid propellant is shown in Figure 9a. In the condensed phase zone (zone I), no chemical reactions occur, and the temperature increases from the initial temperature (T_0) to the decomposition temperature (T_d). In the solid phase reaction zone (zone II), the temperature increases from T_d to the burning surface temperature (T_s), where a phase change from solid to liquid and/or to gas occurs, and reactive gaseous species are formed. In the gas phase reaction zone (zone III), the temperature increases rapidly from T_s to the flame temperature (T_f), where an exothermic gas phase reaction takes place.

During steady state burning of a propellant, the heat transfer in the combustion wave occurs as illustrated in Figure 9b. The energy conservation equation in the combustion wave is represented by

$$q_{cond}(x) + q_{conv}(x) + q_{reac}(x) = 0 \quad (17)$$

where

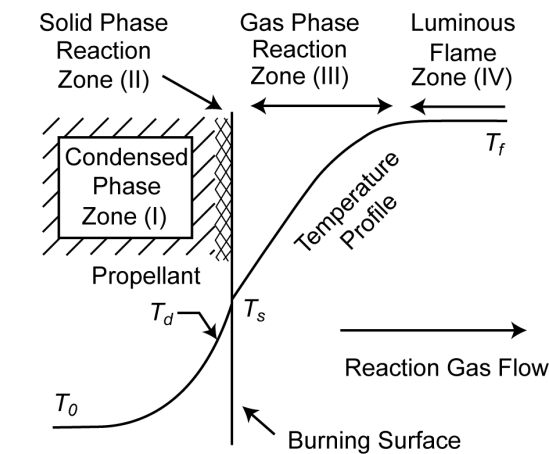


Figure 9a. Thermochemical structure of combustion wave of a solid propellant.

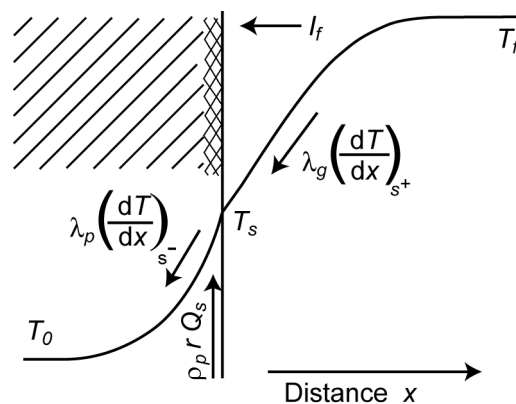


Figure 9b. Heat balance in combustion wave of a solid propellant.

$$q_{cond}(x) = \lambda_g d\phi/dx \quad (18)$$

$$q_{conv}(x) = -mc_g\phi \quad (19)$$

$$q_{reac}(x) = Q_g\omega_g(x) \quad (20)$$

If one assumes that physical properties λ_g and c_g are constant in the gas phase, equation 17 is represented by

$$\lambda_g d\phi/dx - \rho_p rc_g\phi + Q_g\omega_g(x) = 0 \quad (21)$$

where the mass conservation-equation is represented by

$$m = \rho_g u_g = \rho_p r \quad (22)$$

The over-all reaction rate in the gas phase can be represented by

$$\omega_g \delta = \int \omega_g(x) dx = m \quad (23)$$

At the burning surface, the heat flux feedback from the gas phase reaction (zone III) to the burning surface (zone II) by conductive heat transfer is given by

$$\Lambda_g = \lambda_g \phi \quad (24)$$

where ϕ is the temperature gradient in zone III at the burning surface represented by

$$\phi = (dT/dx)_{s,III} \quad (25)$$

The heat flux feedback from zone III to zone II by radiative heat transfer is given by

$$I_f = \beta T^4 \quad (26)$$

The heat flux produced in zone II is given by

$$\Gamma_s = \rho_p r Q_s \quad (27)$$

The heat flux feedback from the burning surface to the condensed phase (zone I) is given by

$$\Lambda_p = \rho_p c_p (T_s - T_0) \quad (28)$$

The overall heat balance at the gas/condensed phase interface is represented by

$$\Lambda_p = \Lambda_g + I_f + \Gamma_s \quad (29)$$

The determination of the magnitude of each term of equation 29 is the center of research on the combustion study of energetic materials.

If one assumes that the radiative heat flux feedback from zone III to zone II is much smaller than the other terms, the burn rate is obtained by substituting equations 24, 27 and 28 into equation 29 and then solving for r

$$r = \alpha_s \phi / \varphi \quad (30)$$

where

$$\alpha_s = \lambda_g / \rho_p c_p \quad (31)$$

$$\varphi = T_s - T_0 - Q_s / c_p \quad (32)$$

Equation 30 indicates that the burn rate of solid propellants is determined by two parameters: the gas phase parameter ϕ , which is determined by the physical and chemical properties in the gas phase, and the condensed phase pa-

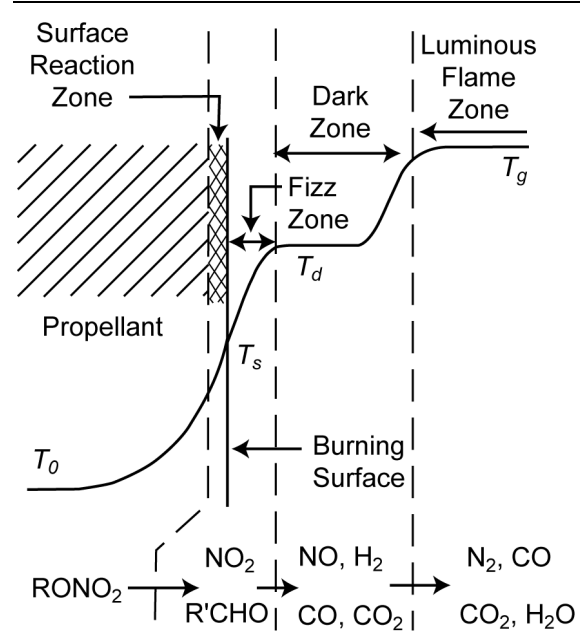


Figure 10. Combustion wave structure of a double-base propellant.

rameter φ , which is determined by the physical and chemical properties in the condensed phase.

5.4 Combustion of Homogeneous Propellant

The combustion wave of a homogeneous propellant is known to consist of successive one-dimensional, homogeneous reaction zones. Figure 10 shows a typical example of the combustion wave of double-base propellants. There exist four reaction zones: surface, fizz, dark, and flame zones. The temperature increases smoothly from the initial propellant temperature T_0 to the burning surface temperature T_s , to the dark zone temperature T_d , and to the flame zone temperature T_g .

At the surface reaction zone (including sub-surface reaction), NO_2 is formed due to the breaking of $\text{O}-\text{NO}_2$ bonds in the nitro groups of NC and NG. The decomposition of the remaining fragments follows, producing fuel components such as aldehydes. These combustible gaseous species react rapidly in the fizz zone and produce large amounts of heat. Thus, a steep temperature rise is observed in the fizz zone. In the succeeding dark zone, the NO produced by the reduction of NO_2 in the fizz zone reacts slowly, and the temperature also rises slowly. The NO and the rest of the fuel prod-

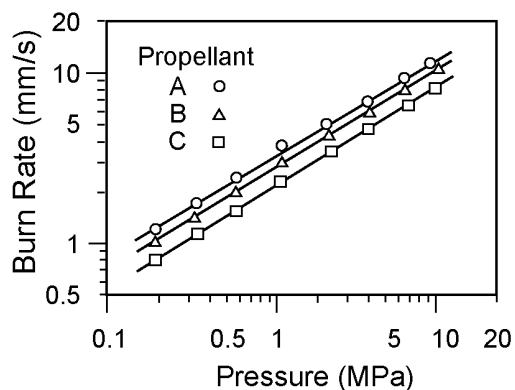


Figure 11. Burn rate of double-base propellants as a function of pressure showing that the pressure exponent remains unchanged when the mixture ratio of NC/NG is changed.

ucts react more rapidly after some elevated temperature is achieved at some distance from the burning surface and form the luminous flame zone. In this flame zone, the final combustion products, such as N_2 , CO_2 , H_2O , etc., are produced, and the temperature reaches its maximum. These reaction processes are largely dependent on pressure.

The burn rate of a double-base propellant is approximately a straight line in a $\log p$ versus $\log r$ plot. As shown in Figure 11, the pressure exponent is unchanged when the mixture ratio of NC/NG is changed. Table 13 shows the chemical compositions of double-base propellants—A, B, and C. The pressure exponent, n , of the burn rate is determined to be 0.60.

The photographic observation of the flame structure shows that the luminous flame zone approaches the burning surface as the pressure increases. The dark zone length, which is approximately equal to the luminous flame stand-off distance, L_d , (the fizz zone length is much shorter than that of the dark zone length), is

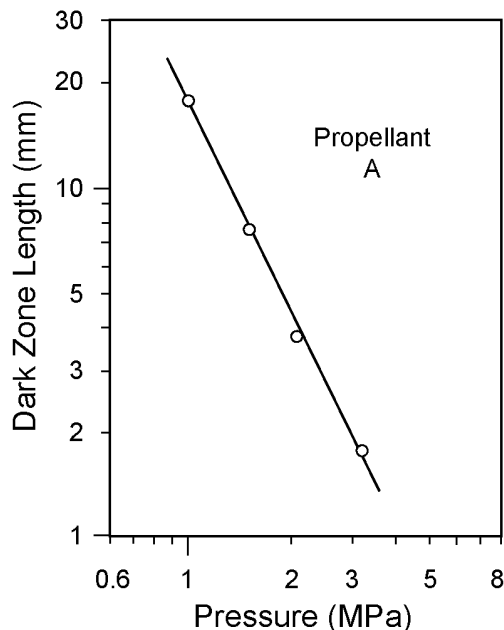


Figure 12. Dark zone length versus pressure for a double-base propellant A.

represented by

$$L_d = ap^d = ap^{n-m} \quad (33)$$

where d is the dark-zone pressure exponent, m is the overall reaction order in the dark zone, n is the pressure exponent of the burn rate, and a is a constant. From the data shown in Figure 12, d is determined to be -2.0 . The overall reaction order in the dark zone is determined to be approximately 2.6. This reaction order indicates that the reaction in the dark zone is more pressure sensitive than other gas-phase reactions of which reaction orders are approximately 2.0. It has been reported that the reaction involving NO as an oxidizer is a termolecular (or trimolecular) reaction (i.e., larger than 2.0). Thus, the reaction in the dark zone is responsible for the NO reduction to produce the final combus-

Table 13. Chemical Compositions of Propellants—A, B, and C.

Propellant	NC	NG	DEP	2NDPA	H_{exp} (MJ/kg)
A	53.0	40.5	4.0	2.5	4.59
B	51.3	39.3	7.0	2.4	4.21
C	48.0	36.7	13.0	2.3	3.47

(a) The percent nitrogen for NC is 12.20%.

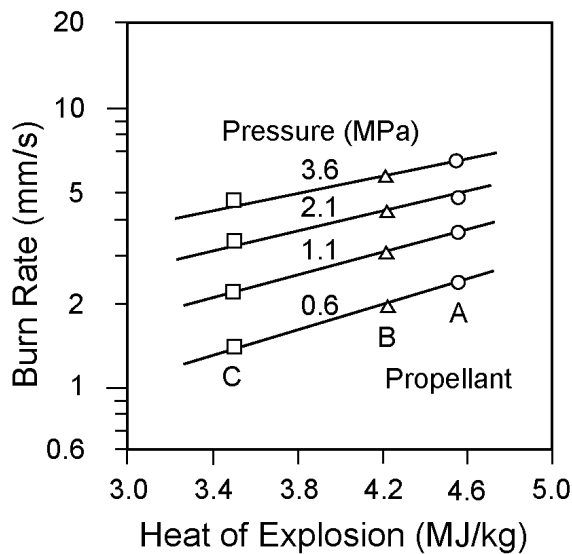


Figure 13. The burn rate of a double-base propellant increases as the heat of explosion increases.

tion product.

The temperature gradient in the fizz zone, $(dT/dx)_{s,f}$, is represented by

$$(dT/dx)_{s,f} = \omega_f Q_f / \rho_p c_p r \quad (34)$$

where Q_f is the heat of reaction in the fizz zone. The reaction rate in the gas phase is given by

$$\omega_f = p^k Z_f \exp(-E_f/RT_f) \quad (35)$$

Substituting equation 35 into equation 34, one obtains the relationship between $(dT/dx)_{s,f}$ and pressure as

$$(dT/dx)_{s,f} = p^{k-n} \quad (36)$$

The results of the measurement of $(dT/dx)_{s,f}$ as a function of pressure show that $k-n$ appears to be constant for double-base propellants and is determined to be $k-n = 0.85$. Thus, the reaction order in the fizz zone is determined to be $k = 1.7$.

As shown in equation 30, the burn rate is dependent on the flame temperature, T_g , at constant pressure. However, the temperature in the dark zone, T_d determines the heat flux feedback from the gas phase to the burning surface of double-base propellants. Since the mixture ratio of NC and NG alters the temperature profile in the gas phase, the heat flux is also altered. Fig-

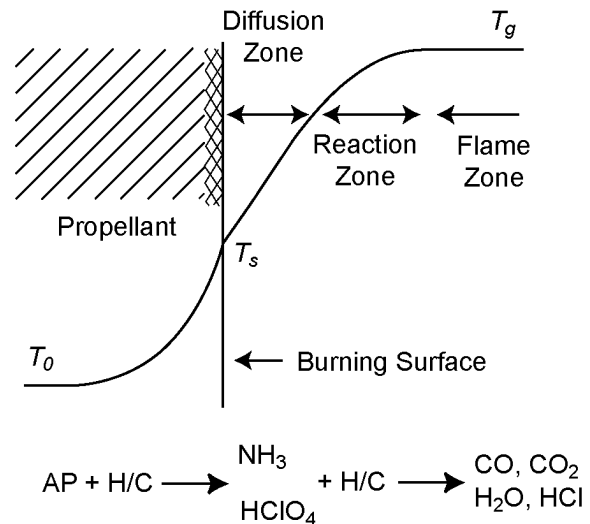


Figure 14. Combustion wave structure of an AP composite propellant.

ure 13 shows the results of the burn rate and pressure relationship as a function of H_{exp} . It is evident that the burn rate of double-base propellants is increased by increases of H_{exp} .

5.5 Combustion of Heterogeneous Propellant

Heterogeneous propellants consist of crystalline oxidizer particles and a polymeric fuel binder. The decomposition process of these materials occurs on and above the burning surface of the propellant. The gaseous oxidizer and the fuel fragments generated at the burning surface diffuse and mix together above the burning surface. This binary diffusion process produces a reactive gaseous fragment that reacts to produce heat and a combustion product.

Figure 14 shows the combustion wave structure of an AP/HTPB composite propellant. Unlike those of a double-base propellant, the surface and gas phase reaction zones are heterogeneous because the AP particles decompose to produce an oxidizer fragment through the reaction process described in Section 3.2, and the HTPB binder decomposes to produce gaseous hydrocarbon fragments at the burning surface. These gaseous fragments diffuse with each other to produce reactive gases that combine to produce its final reaction product. Since the thermochemical properties of AP and HTPB

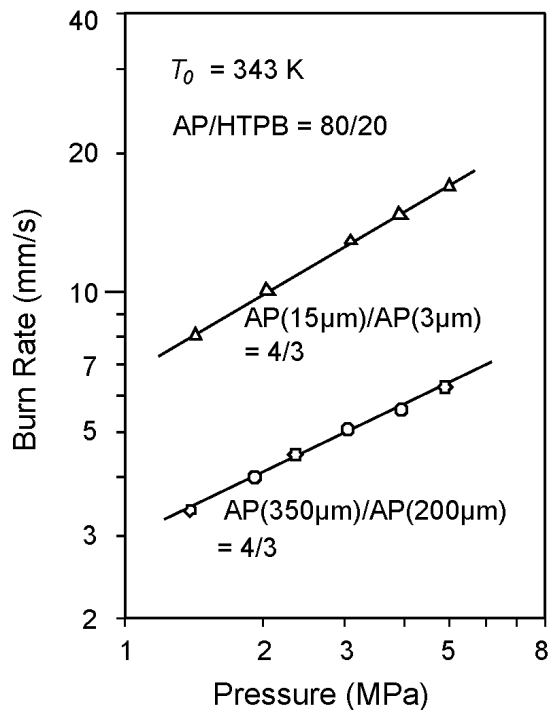


Figure 15. Burn rate of AP composite propellant showing that the burn rate increased with the mixing of fine AP particles.

are different, the temperatures of decomposition are different. In addition, the rates of decomposition of AP and HTPB are also different. Thus, not only the physical structure but also the thermal structure of the burning surface of the propellant becomes heterogeneous. As shown in Figure 14, the time-averaged temperature increases from the initial propellant temperature T_0 to the burning surface temperature T_s , and then to the flame temperature T_g .

The heat feedback from the gas phase to the burning surface is not only dependent on the reaction rate of the reactive gases above the burning surface, but also on the diffusion rate between the oxidizer and fuel fragments. Accordingly, the particle size of the oxidizer plays an important role in the determination of the heat flux feedback from the gas phase to the burning surface. The diffusion rate increases as the AP particle size decreases. As shown in equation 30, the burn rate is dependent on the heat flux feedback to the burning surface. Thus, one can conclude that the burn rate increases as the AP particle size decreases. Figure 15 shows a typical example of burn rate versus pressure

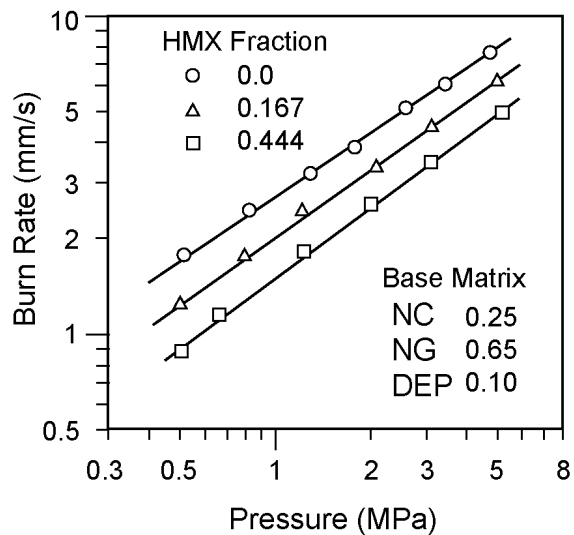


Figure 16. Burn rate of HMX-CMDB propellant as a function of the mass fraction of HMX.

relationship of AP/HTPB composite propellant as a function of AP particle size.

The flame temperature T_f is dependent on the mass fraction of AP, $\xi(\text{AP})$, as shown in Figure 2b. It is shown that T_f increases as $\xi(\text{AP})$ increases at constant AP particle size. However, T_f reaches a maximum at $\xi(0.87)$ and thereafter decreases as $\xi(\text{AP})$ increases. Since the burn rate is dependent on T_f as shown in equation 30, the burn rate becomes a function of $\xi(\text{AP})$. Thus the burn rate increases as $\xi(\text{AP})$ increases in the range of $\xi(\text{AP}) < \xi(0.87)$ at constant AP particle size. Figure 15 shows the results of the effect of AP particle size on the burn rate of AP/HTPB propellants. It is evident that the burn rate increases as the particle size of AP particles decreases at constant $\xi(\text{AP})$. In addition, the burn rate increases as $\xi(\text{AP})$ decreases when the same size of AP particles is used.

As shown in Figure 16, the burn rate of HMX-CMDB propellant increases as pressure increases when $\xi(\text{HMX})$ remains constant. However, the burn rate decreases as $\xi(\text{HMX})$ increases at constant pressure. This indicates that the burn rate decreases as the energy contained within the unit mass of HMX-CMDB propellant increases.

5.6 Combustion of Granulated Propellant

Each grain within a granulated propellant burns independently. When the grains are composed of a double-base propellant used for rockets, the linear burn rate r of each grain appears to be the same as the burn rate of the double-base propellant in a rocket motor. Accordingly, the combustion wave structure of the granulated propellant made of a double-base propellant is the same as that of the double-base propellant. However, the difference between a granulated propellant and a rocket propellant is evident. The mass burn rate m_g of the granulated grains is much faster than that of rocket grains because the burning surface area A_b of the granulated grains is much larger than that of rocket grains as shown in equation 4.

When Black Powder is used as a propellant, the mass burn rate is much greater than granulated single-base and double-base propellants. This is due to the high porosity and small size of each grain of Black Powder. The burn rate is also dependent on the type of charcoal. Various charcoals are made from different types of trees. The porosity of charcoal is dependent on the type of tree used.

In general, granulated propellants are used to eject projectiles from launch tubes such as gun projectiles and to burst fireworks shells because they produce high pressure almost instantaneously. The ejection velocity of a projectile is determined by various parameters: projectile mass, launch tube length, pressure versus time in the launch tube. Detailed examination of the ejection process is accomplished by the analysis of interior ballistics.

References

- 1) G. P. Sutton, *Rocket Propulsion Elements*, 6th ed., John Wiley & Sons, New York, 1992.
- 2) N. Kubota, *Fundamentals of Rocket Combustion*, Nikkan Kogyo Press, Inc., Tokyo, 1995.
- 3) Y. M. Timnat, *Advanced Chemical Rocket Propulsion*, Academic Press, London, 1987.
- 4) S. F. Sarnar, *Propellant Chemistry*, Reinhold Publishing, New York, 1966.
- 5) K. F. Meyer, *Explosives*, Verlag Chemie, Weinheim, 1977.
- 6) N. Kubota, "Survey of Rocket Propellants and Their Combustion Characteristics", *Fundamentals of Solid-Propellant Combustion*, Chap. 1, Edited by K. K. Kuo and M. Summerfield, *Progress in Astronautics and Aeronautics*, Vol. 90, New York, 1984.
- 7) G. Lengelle, A. Bizot, J. Duterque, and J. F. Trubert, "Steady-State Burning of Homogeneous Propellants", *Fundamentals of Solid-Propellant Combustion*, Chap. 7, Edited by K. K. Kuo and M. Summerfield, *Progress in Astronautics and Aeronautics*, Vol. 90, New York, 1984.
- 8) N. Kubota, "Flame Structures of Modern Solid Propellants" and "Temperature Sensitivity of Solid Propellants and Affecting Factors; Experimental Results", *Nonsteady Burning and Combustion Stability of Solid Propellants*, Edited by L. DeLuca and M. Summerfield, *Progress in Astronautics and Aeronautics*, Vol. 143, New York, 1992.
- 9) N. S. Cohen and Flanigan, "Mechanisms and Models of Solid-Propellant Burn Rate Temperature Sensitivity: A Review", *AIAA Journal*, Vol. 23, 1985, pp 1538–1547.
- 10) R. L. Glick, "Temperature Sensitivity of Solid Propellant Burning Rate", *AIAA Journal*, Vol. 5, 1967, pp 586–587.
- 11) N. Kubota, "Combustion of Energetic Azide Polymers", *Journal of Propulsion and Power*, Vol. 11, No. 4, 1995, pp 677–682.

Pyrotechnic Particle Morphologies — Metal Fuels

K. L. & B. J. Kosanke

PyroLabs, Inc., Whitewater, CO 81527, USA

and

Richard C. Dujay

Mesa State College, Electron Microscopy Facility, Grand Junction, CO 81501, USA

ABSTRACT

The morphology (size, shape and surface features) of the constituent particles in a pyrotechnic composition affects its performance. This is particularly true of metal fuel particles in the composition. Particle morphology can also constitute an important part of forensically establishing a match between materials of known origin and evidence. This article catalogs and briefly discusses some characteristic features commonly associated with metal fuels in pyrotechnic compositions.

Keywords: morphology, metal fuels, forensics, pyrotechnics

Introduction

Morphology is a term borrowed from biology for describing the appearance of organisms. In pyrotechnics and forensics the term is often used to denote information about the size, shape and surface features of particles, where knowledge of these attributes is frequently important. In pyrotechnics, particle morphology influences such things as the ease of ignition and burn rate of a composition.^[1] While this is true in general, it is especially true for the fuel particles in those compositions. This is because the oxidizer(s) will usually have melted below the ignition temperature of the composition, whereas the fuel particles usually will not have. (See Table 1 for examples.) Large particle size, rounded shape, and smooth surface features all tend to make ignition more difficult and burn rate slower. Accordingly, knowledge of a composi-

tion's particle morphology is important in any attempt to predict (or control) the ignition and propagation properties of a pyrotechnic composition.

Table 1. Examples of Melting Points (in °C) of Some Common Fuels and Oxidizers.

Fuel	T_m	Oxidizer	T_m
Aluminum	660	Ammonium perchlorate	d ~150
Boron	2300	Barium peroxide	450
Iron	1535	Potassium chlorate	356
Magnesium	649	Potassium nitrate	334
Silicon	1410	Potassium perchlorate	d ~400
Titanium	1660	Sodium nitrate	307

Note:

- T_m is melting point in degrees Celsius; values are taken from references 2 and 3.
- d is the decomposition temperature and means the oxidizer decomposes before melting.

An important aspect of forensic science is the recognition and identification of materials, often for the purpose of determining the source of the material. Typically this would be accomplished by attempting to physically and chemically compare items of evidence with materials from known sources. In attempting to determine whether two materials match, various attributes

of the two are compared and contrasted. The degree of certainty of the match is a function of the number of attributes compared and the degree to which they are identical.^[4] For pyrotechnic compositions, one important part of this matching process should be a comparison of the morphologies of the materials. Probably the best known and most complete work on this subject are the writings of McCrone and Delly.^[5] This multi-volume treatise provides extensive overall information. However, of necessity, it tends to include only a few of the most common chemicals, and then only in one form. The emphasis is on identification of the nature of the chemical. This is valuable information but it falls short of what is needed to determine whether a firm match exists between materials.

This article presents general information about particle morphology of metal fuel particles used in pyrotechnics. This is augmented with a series of electron micrographs as illustrations.

Particle Size

As a rule, the size of metal fuel particles in a pyrotechnic composition is smaller than 100 mesh, and they are often smaller than 400 mesh (see Table 2 for a list of some common mesh sizes and their openings). An exception is those metal particles added to a composition for the purpose of producing spark effects. This requires that the particles be large enough so as not to be completely consumed during their passage through the reaction zone and flame of a burning pyrotechnic composition.^[6] Such particles may be as large as 10 mesh. Table 3 is a list of metals commonly present in pyrotechnic compositions. Some examples of aluminum particle types and sizes used in pyrotechnics and fireworks are presented in Table 4.

All metal powders used in pyrotechnics have a range of individual particle sizes; for some the range is narrow, for others it is quite broad. (Collectively, the figures in this article are examples of the typical range of particle size for metal powders commonly used in pyrotechnics.) Further, in the authors' experience, both the average particle size and the range of particle size can differ somewhat from lot to lot

Table 2. Information for Some Common US Sieve Mesh Sizes.

Mesh Number	Opening (in./1000)	Opening (micron)
10	79	2000
20	33	850
40	16	425
60	9.8	250
100	5.9	150
140	4.1	106
200	2.9	75
325	1.7	45
400	1.5	38

Note that the particles smaller than about 400 mesh are typically only described in terms of their physical size, usually in microns.

from the same manufacturer. In terms of consistent performance, this can be frustrating for the pyrotechnists. However, for a forensic analyst this can help determine the degree to which a match exists between two materials. (As a word of caution, it must be recognized that even between different points within a single drum, there can be some differences in average particle size and the range of size, although gener-

Table 3. Metals Used in Pyrotechnics.

Commonly Used	Occasionally Used ^[a]
Aluminum	Chromium
Boron ^[b]	Copper
Iron	Manganese
Magnesium	Molybdenum
Silicon ^[b]	Nickel
Titanium	Selenium
	Tellurium
	Tungsten
	Zinc
	Zirconium

[a] Many of these are only used in military items, some of which are being phased out.

[b] Not strictly a metal.

Table 4. Information about Some of the Aluminum Powders Used in Pyrotechnics.¹⁷¹

Description — Common Name (Approximate Size Range)	Commonly Used In	Purpose — Effect Produced
Flake — Coarse Flitters (10–28 mesh / 700–2000 μ)	Fireworks Comet Stars, Waterfalls, and Fountains	Long Duration White Sparks
Flake — Fine Flitters (20–80 mesh / 200–850 μ)	Fireworks Comet Stars, Waterfalls, and Fountains	Medium Duration White Sparks
Flake — Bright (\approx 325 mesh / \approx 35 μ)	Fireworks Comet Stars & Fountains Large Fireworks Salutes	Short Duration White Sparks Explosive Sound or Report
Flake — Dark (\approx 15 μ)	Medium Fireworks Salutes Military Simulators	Explosive Sound or Report Explosive Sound or Report
Flake — German Dark (\approx 5 μ)	Small Fireworks Salutes	Explosive Sound or Report
Atomized — Granular Blown (50–150 mesh/100–350 μ)	Fireworks Comet Stars & Fountains Military Thermite	Long Duration White Sparks Heat and Molten Iron
Atomized — Spherical (\approx 400 mesh/ \approx 30 μ)	Fireworks Glitter Stars/Fountains Composite Rocket Propellant	Delayed Trailing Flashes Energy Production
Atomized — Spheroidal (\approx 20 μ)	Fireworks Color Stars Military Photo-Flash	Flame Brightening Intense Light Production
Atomized — Spherical (\approx 10 μ)	Fireworks Glitter Stars/Fountains Military Igniters	Delayed Trailing Flashes Thermal Energy
Atomized — Spheroidal (\approx 5 μ)	Large Fireworks Salutes Fireworks Color Stars	Explosive Sound or Report Flame Brightening

ally these would be rather subtle differences.)

In general, the most expeditious method for determining particle size of bulk powders is by performing a sieve analysis. In this process, a sample of powder is passed through a series of successively finer sieves (typically in a stack that is mechanically agitated). The fraction (by mass) of material that is retained on each sieve is then reported, along with the amount passing the finest sieve. However, for mixed materials such as a pyrotechnic composition, or when only very small amounts of material are available, a sieve analysis to report such “mesh fractions” is often not possible. In that case a microscopic investigation is a common approach, whereby the physical dimensions of a large number of individual particles are measured and reported. For a light microscope this involves the use of a calibrated reticule in the eyepiece or associated with the slide mounting. For an electron microscope, the instrument pro-

vides scale information associated with the images produced. These procedures can be performed manually. However, in many cases, computer assisted image analysis can be used.

Particle Shape

A range of particle shapes are used in pyrotechnic compositions, and like particle size, shape also affects ignition and propagation characteristics.^[1] Details of particle shape can also provide the basis for forensic comparison of metal powders. Normally it is the manner of production of the material that is the determining factor for particle shape. Atomization (spraying molten metal through an orifice and allowing it to solidify as it falls to a collection area) produces particles that are spheroids. Often, atomization produces nearly perfect spheres, see Figure 1. However, when the metal is quite reactive and when the atmosphere into

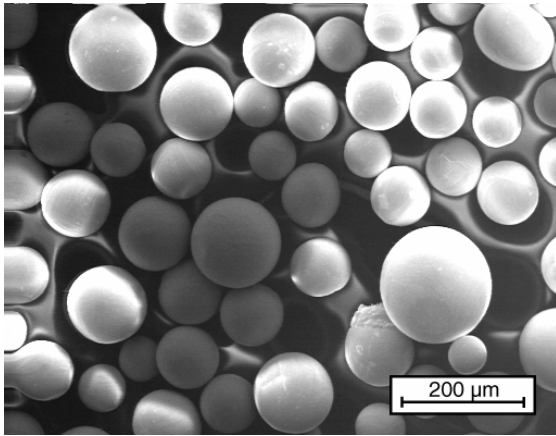


Figure 1. Illustration of nearly perfect spherical particles of titanium produced by atomization (100 \times).

which the metal is sprayed is not completely inert, much less perfect spheres are often produced. Aluminum, because of its ability to quickly form a rigid oxide coating, produces a good example of this. Even when using relatively inert atmospheres, the so-called spherical atomized aluminum particles are less than perfect spheres, see Figure 2. Further, when the atmosphere used contains even a modest amount of oxygen, highly distorted spheroids are produced; see Figure 3.

Depending to some extent on the physical properties of the metal, mechanical diminution such as grinding is possible. This produces metal particles that tend to have sharp angular features like those illustrated in Figure 4. While it is somewhat unusual to produce granular aluminum powders, it is common for some aluminum alloys, such as those with iron and magnesium, to be produced by grinding. Because of their sharp, angular features, particles that have been ground will be more reactive than those of the same size produced by atomization. Also, the sharp, angular features of the ground particles make them fairly easy to differentiate from atomized particles. However, one type of atomized aluminum, so-called "blown" aluminum, has surface features (coarse texturing) that may at first appear somewhat similar to ground particles, see Figure 5. This type of aluminum powder is generally atomized as fairly large particles (20 to 100 mesh / 150–850 μ) and in an atmosphere that has a rela-

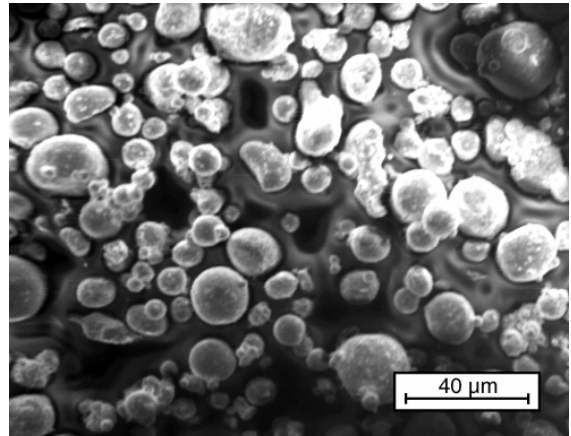


Figure 2. Illustration of so-called spherical atomized aluminum (500 \times).

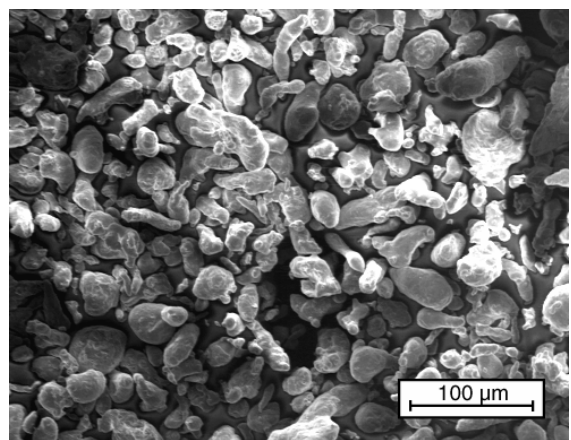


Figure 3. Illustration of so-called spheroidal atomized aluminum (200 \times).

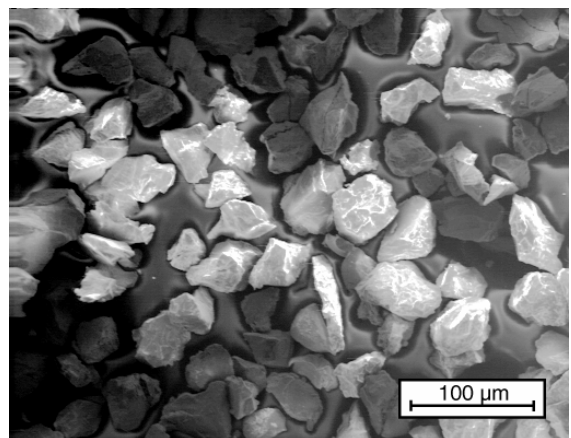


Figure 4. Illustration of ferro-aluminum alloy particles prepared by grinding (200 \times).

tively large oxygen content. This causes the rapid formation of an aluminum oxide crust, and the resulting particles are far from being spherical. The diagnostic feature differentiating blown atomized aluminum from granular aluminum powders is the nature of their edges and surface features. For blown aluminum these appear rounded and not sharp, as is the case for ground aluminum particles.

Another type of mechanical particle size reduction is by chipping. This may be the primary intent of the operation, or it may be that the material is a byproduct produced when machining metal parts (turning or milling). These particles tend to have two dimensions that are relatively large and a third that is less, either producing large flake-like particles, or long thin strips of material. The large flake-like particles are generally too large for use directly as a pyrotechnic fuel, but may be suitable for producing pyrotechnic spark effects. Chipped material is often further reduced in size by a secondary process such as hammer milling. Figure 6 is an example of titanium metal turnings that have been hammer milled to break the largest particles into smaller ones (hammer milling will not reduce such particles' thin dimension). That these large flake-like particles were produced from machine turnings, is fairly obvious in the higher magnification micrograph where tool marks are obvious.

A third type of mechanical particle diminution is the stamping or milling of already tiny particles to produce thin flakes. For malleable metals, this method is quite common, and it is probably the most common method for the production of aluminum metal powders, especially for those with the greatest surface area to mass ratios. For the same nominal mesh size materials, flakes tend to have the greatest reactivity as compared with the other powder forms. This is because, while one or two flake dimensions may be substantial, the third dimension is quite small in comparison. Accordingly flakes can be raised more quickly to their ignition temperature, tending to make pyrotechnic compositions containing them easier to ignite and faster to propagate. Flaked metal powders have a physical appearance that is fairly distinct and identifiable, see Figure 7.

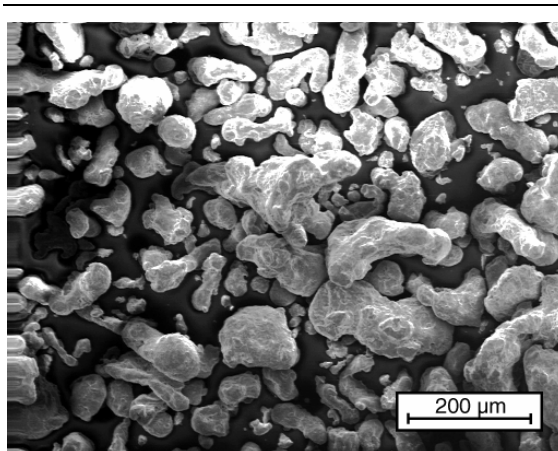


Figure 5. Illustration of “blown” atomized aluminum particles (100 \times).

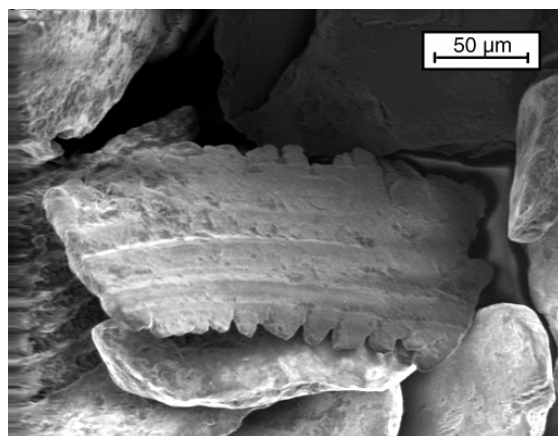
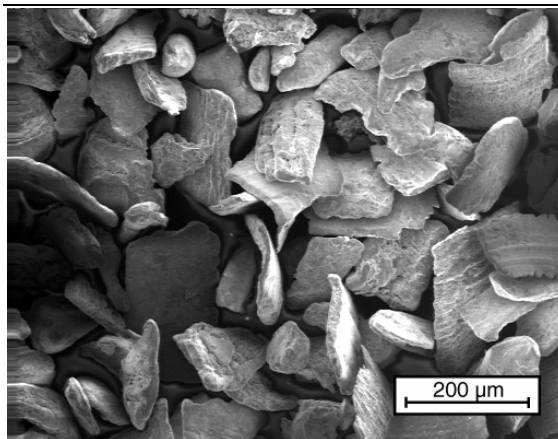


Figure 6. Illustration of titanium metal turnings at two magnifications (100 \times and 300 \times).

Metal powders can be produced in other, less common ways. For example, flaked material can be made by stamping from foil; how-

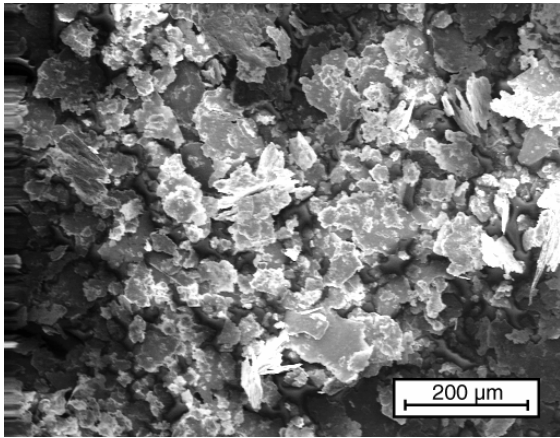


Figure 7. Illustration of flake aluminum powder (100 \times).

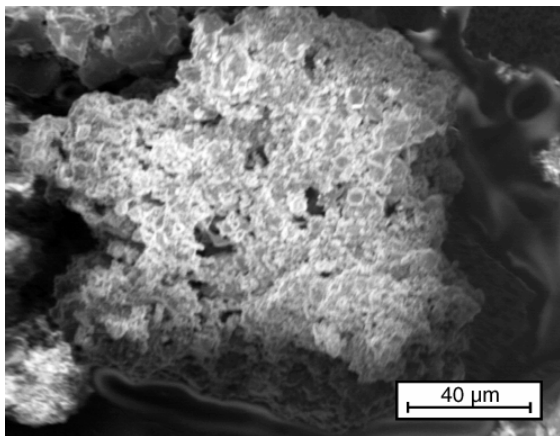
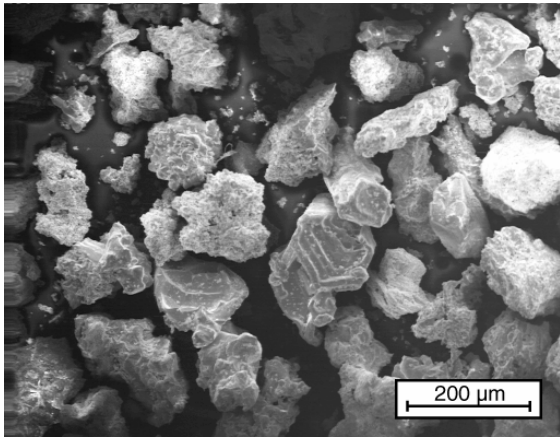


Figure 8. Illustrations of titanium sponge, two magnifications, (100 \times and 500 \times).

ever, this tends to produce materials that are too large and too thick to be of much use in pyrotechnics.

Surface Features

Particle surface features can significantly affect the reactivity of metal fuel particles. Probably the best-known example of this is so-called titanium “sponge”. This is the initial product of normal titanium production, wherein titanium tetrachloride is reacted with magnesium metal. Titanium sponge is quite porous, giving it the appearance vaguely like that of the biological organism for which it is named. While this may not be entirely obvious at low magnification, the structure and porosity becomes more apparent at higher magnifications (see Figure 8). These same features are also easily recognizable as characteristic of the material. Pyrotechnically, it is because of the pores and fine surface structures that titanium sponge ignites easily and can be propelled at very high velocity through the air without being extinguished.

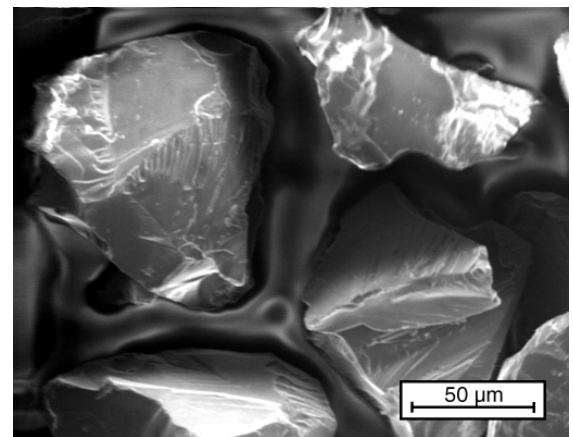
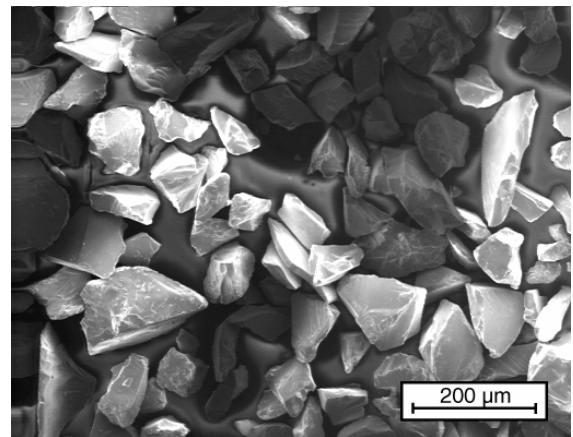


Figure 9. Illustrations of surface features of magnalium, two magnifications (100 \times and 400 \times).

Particle size reduction of especially brittle metals can produce interesting and characteristic surface features. For example, fracture patterns and “whiskers” are seen in Figure 9 of the 50:50 alloy of aluminum and magnesium (often called “magnalium” in pyrotechnics). While these surface features are not thought to significantly affect pyrotechnic reactivity, they certainly help characterize the particles. Similarly, the two examples of surface features mentioned earlier in this article (coarse surface texturing on blown aluminum and tool marks on titanium turnings) are unlikely to have a noticeable affect on pyrotechnic reactivity, but can be diagnostic in terms of establishing a match between materials.

Conclusion

Experience has taught pyrotechnists that particle size, shape and surface features are important controlling factors for ease of ignition (both intentional and accidental) and for burn rate once ignited. Accordingly, knowledge of these attributes is an important first step in designing a pyrotechnic composition or altering the performance of a composition once formulated. From a forensic standard point, these same particle attributes constitute an important part of the basis for establishing a reliable identification of pyrotechnic materials or a match between known and suspect materials. Accordingly, for pyrotechnists it is hoped that this short article provided some information about the physical nature of some of the metal powders being used. For forensic analysts it is hoped that this article has suggested some additional points of comparison that might prove to be useful in their efforts to identify the components of pyrotechnic materials.

Acknowledgements

The authors are grateful for the suggestions of J. Bergman, J. Giacalone, F. Whitehurst, and W. Smith on an earlier draft of this paper.

References

- 1) K. L. and B. J. Kosanke, “Control of Pyrotechnic Burn Rate”, *Proceedings of the 2nd International Symposium on Fireworks*, 1994. Also in *Selected Pyrotechnic Publications of K. L. and B. J. Kosanke, Part 3 (1993 to 1994)*, Journal of Pyrotechnics, 1996.
- 2) *CRC Handbook of Chemistry and Physics*, 75th ed., CRC Press, 1995.
- 3) *Engineering Design Handbook*, “Part III—Properties of Materials Used in Pyrotechnic Compositions”, Army Materials Command, AMP 706–187, 1963.
- 4) F. Whitehurst, “Forensic Testimony: Matches, An Over-Inference of Data? A Giglio Obligation?”, *Journal of Pyrotechnics*, No. 11, 2000.
- 5) W. C. McCrone and J. G. Delly, *The Particle Atlas, An Encyclopedia of Techniques for Small Particle Identification*, Ann Arbor Science Publishers, 1973.
- 6) B. J. & K. L. Kosanke and C. Jennings-White, “Pyrotechnic Spark Generation”, *Proceedings of the 3rd International Symposium on Fireworks*, 1996. Also in *Selected Pyrotechnic Publications of K.L. & B.J. Kosanke, Part 4 (1995 through 1997)*, Journal of Pyrotechnics, 1999.
- 7) K. L. & B. J. Kosanke, “Aluminum Metal Powder in Pyrotechnics”, *Bulletin of the Pyrotechnics Guild International*, No. 85, 1993. Also in *Selected Pyrotechnic Publications of K.L. & B.J. Kosanke, Part 3 (1993 and 1994)*, Journal of Pyrotechnics, 1996.

Forensic Testimony: “Matches”, An Over-Inference of Data? A Giglio Obligation?

Frederic Whitehurst^[1]

Exec. Dir., Forensic Justice Project, 3233 “P” St. N.W., Washington, D.C. 20007, USA

ABSTRACT

The expert witness who over-infers his data through the misuse of adjectives of comparison opens himself up to cross-examination that can and will discredit his work product. This paper uses the example of forensic analysis of black powder explosive to demonstrate that one can not categorically “match” one Black Powder sample to another or very often one complex chemical system to another and that even if this were possible, such “matches” may have limited probative value. The paper also explores the legal obligation of the expert to reveal to the prosecutor, court and trier-of-fact the limitations of the probative value of the evidence where those limitations might be considered to be exculpatory information.

Keywords: Black Powder, forensic analysis, Giglio, sulfur, potassium nitrate, charcoal

The Problem

While reviewing case opinions in criminal matters involving forensic examinations, one is often presented with various adjectives of comparison such as “matches”, “consistent with”, and “identical to”. The expert witness who uses such terms may find counsel elated at seeing these adjectives in forensic reports if legal theories are supported, or disturbed if not. However, one way or the other, there is a wealth of information behind these adjectives of comparison, which may go unexplored. If the basis for use of such terms of comparison is brought up during trial, counsel may find himself either defending new ground during trial or scoring im-

portant points in discrediting proffered expert testimony. One should be drawn to question whether these words are an indication that data has been over-inferred by the expert offering them. One is also drawn to ask, whether the information behind these words should have been presented as possible exculpatory information to unsuspecting prosecutors before trial (following Giglio^[2]). Comparison adjectives left dangling alone to describe the results of comparisons may not properly educate the trier-of-fact to the true significance of the data. And more importantly, the true significance of the data may not be known by the forensic scientist. For example, Jonakait^[3] tells us, “The conclusions of forensic science are often based on skimpy, nonexistent, or shoddy research. Forensic scientists do not give juries a thorough presentation of information about scientific technique.”

This paper will address the adjective “matches” as an example pointing out the very wide door of opportunity it opens for future probing during examination. The adjectives, if not properly supported by empirical data, can offer counsel the opportunity to point out to the trier-of-fact what may be a flawed opinion, possibly even a “forensic scam” being perpetrated upon the court through the hiding of exculpatory information. This paper will also explore the legal or Giglio obligation of the prosecution’s forensic scientists to reveal the empirical data (or lack thereof) and their total understanding of that data to full view.

The world of man-made products is composed of complex materials constructed with many components, each with its own manufacturing signature. When the forensic expert testifies that two complex materials “match”, coun-

Table 1. Guaranteed Composition in Weight Percent.

Component	Industrial	Refined
KCl (potassium chloride)	99.5	99.9
Na (sodium)	0.18 max	0.0150 max
Br (bromine)	0.09 max	0.0600 max
SO ₄ (sulfate)	0.001 max	0.0010 max
Ca (calcium)	0.0075	
Ca + Mg (calcium+magnesium)	0.0180	0.0030 max
Pb (lead)	0.0003	0.0003 max
Fe (iron)	0.0005	0.0005 max
Cu, Ni (copper, nickel)	0.0001	0.0005 max
Cu, Mo, V, Ti (copper, molybdenum, vanadium, titanium)	0.00004	0.00001 max

sel is encouraged to ask of what the materials are composed, which of the components match, how the expert has determined this, what components were not and/or cannot be detected with the analyst's tools, and the implications of not being able to determine if these components matched or not. As an initial example we will look at a very simple and very old man-made material, Black Powder, an explosive.

Black Powder

Though the origins of Black Powder are debated, it was the major explosive used in warfare, firearms and industries such as mining until the late 1800's. The black grains of material, which are composed of potassium or sodium nitrate, sulfur and charcoal, have been produced by a number of methods in different countries for hundreds of years. At first glance Black Powder appears to be a simple material of three components. However a closer, "hard look" reveals a fascinatingly complex material of many, many possible subcomponents and physical characteristics. The expert witness who opines that two Black Powders "match" then can be asked to explain what about the materials is it that matches, and what is the significance of that match. Let us explore the world of information behind the word "match" when it is applied to two Black Powder samples.

We may ask first who manufactures the components of Black Powder. This knowledge allows us to check proffered expert opinions against actual manufacturers' understanding of their own products. We can easily determine the manufacturers of a material and ask a number of questions. How is potassium nitrate manufactured? How is sulfur manufactured? How is charcoal manufactured? What are the raw products that go into the manufacture of these materials, and what chemical and physical signatures do they carry with them to the final Black Powder mixture? What possible minor impurities are found in these components that might change the types of Black Powder in minor but important ways? Who manufactures Black Powder itself? How much of the material is manufactured? What are the physical characteristics of Black Powder? What grades of Black Powder are manufactured? The expert who is prepared under oath to render the *bare* opinion that Black Powder specimens "match" should surely have considered these questions at length and have ready answers, data and the scientific literature to support his opinion.

Potassium Nitrate

A quick trip to the chemistry library to look into the *Encyclopedia of Chemical Technology*^[4a] tells us "Potassium nitrate, which was essential in the manufacture of black gunpowder, was produced centuries ago by the Chinese.... The process involved leaching soil in

which nitrogen from urine had combined with mineral potassium. By the time of the Napoleonic wars, potassium nitrate was a strategic chemical and was still obtained in the same manner, primarily from India.” One can certainly imagine that if potassium nitrate were still manufactured in this manner it would carry a lot of impurities out of the soil with it. However we are not to be treated to such a simple answer.

We find from the same reference^[4b] that “Most of the potassium nitrate, KNO_3 , produced commercially in the United States is based on the reaction of potassium chloride and nitric acid.” So here we have two other materials the origins and purity of which we must consider. Table 1 lists the composition of potassium chloride:^[4c]

One can see that with all of these materials in the potassium chloride used in the manufacture of potassium nitrate, their occurrence in the potassium nitrate, derived in part from the potassium chloride, is possible. Indeed, reference to the certificate of analysis on a bottle of a Fisher™ Certified Reagent grade potassium nitrate from lot number 745536, found in the laboratory in which the author works, notes the following impurities:

Component	Guaranteed Composition (wt %)
Fe (iron)	.0001%
Heavy metals (as lead)	.0001%
SO_4 (sulfate)	.001%
Na (sodium)	.005%
Insoluble matter	.001%
Cl (chlorine total)	.002%
PO_4 (phosphate)	.0001%
Ca + Mg (calcium + magnesium)	.002%

As small as the percentages are, they are still measurable and have obviously been measured in the assay of this reagent grade material. Counsel should note that Black Powder is made from technical or industrial grade potassium nitrate, which may very well have higher levels

of impurities than the more refined reagent grade potassium nitrate. Counsel also should not have to accept the opinion that the materials are not present in sufficient quantity to measure and are therefore not important to establishing a match. That kind of statement should be backed up with empirical data, data that indicates that minor components do not change *significantly* between batches or grades of Black Powder. What does “significantly” mean? That is another question for the expert to answer.

Sulfur

In the *Encyclopedia of Chemical Technology*^[5a] we read, “Sulfur has been known since antiquity... One contemporary use was developed in 500 BC, when the Chinese used sulfur as an ingredient of gunpowder.” And further we read,^[5b] “Sulfur occurs in a number of different allotropic modifications, that is, in various molecular aggregations which differ in solubility, specific gravity, crystalline form, etc. Like many other substances, sulfur also exhibits dynamic allotropy, i.e. the various allotropes exist together in equilibrium in definite proportions, depending on the temperature and pressure...The particular allotropes that may be present in a given sample of sulfur depend to a large extent upon its previous thermal history, the amount and type of foreign substance present, and the length of time that has passed for equilibrium to be attained.”

These are statements full of the wonderful potential for exploration. One must ask what type of sulfur did the manufacturer use in his product. Whereas the commercial manufacturer of Black Powder may be limited to the use of a particular type of sulfur in the United States (that typically being a low acidity sulfur commonly referred to as sulfur flour), what limits can one place upon the foreign and homemade Black Powder manufacturers? There is also mention of impurities. What impurities exist in sulfur? An expert in a particular type of material might reasonably be expected to have considered this question in the past just as he might have been expected to consider the impurities in potassium nitrate. After all, if an expert is going to say that the chemical composition of two materials such as Black Powder match, then he

can reasonably be expected to have some understanding of what those chemical compositions are. And then we can ask what allotropes are present in the sulfur that is in the Black Powder. Interestingly the *Encyclopedia*^[5c] notes the many grades of sulfur as follows: amorphous sulfur, bright sulfur, brimstone, broken rock sulfur, colloidal sulfur, crude sulfur, dark sulfur, dusting sulfur, elemental sulfur, flour sulfur, flowable sulfur, flowers of sulfur, Frasch sulfur, insoluble sulfur, lac sulfur, liquid sulfur, molten sulfur, native sulfur, precipitated sulfur, prilled sulfur, recovered sulfur, refined sulfur, roll sulfur, rubbermaker's sulfur, run-of-mine sulfur, screened commercial sulfur, slated sulfur, specialty sulfurs and wetttable sulfur. Now who would imagine that sulfur could come in so many grades? Dare we ask if the different grades might have different impurity signatures? Any expert who professes to know that two Black Powder samples "match" without describing those characteristics that match might be inclined to have asked and to have answered that question. Or possibly the "match" did not include consideration of trace impurities.

Charcoal

The most impressive complex component of Black Powder is charcoal. It is this component that contains the greatest wealth of opportunity for examination, both legal and scientific. The *Handbook of Charcoal Making*^[6a] defines charcoal as "The residue of solid non-agglomerating organic matter, of vegetable or animal origin, that results from carbonization by heat in the absence of air at a temperature above 300 °C."

The definitions also include those of charcoal's components as follows:^[6b]

- 1) Content of Volatiles: If charcoal is heated to 900 °C under confined conditions, it will lose weight because hydrocarbons and nitrogen are driven out. This weight loss is extremely important to industrial charcoal consumers when defining the utilization properties.
- 2) Ash content: The ash is composed of the natural minerals contained in almost any organic matter and contami-

nations. The quantity is related to the composition of the raw material mix, e.g. wood branches with a high proportion of bark will give high ash containing charcoal. Charcoal ashes are distinguished by their solubility in water and by chemical analysis.

- 3) Sulphur and phosphorus content: The low sum of these substances normally found in charcoals makes them especially attractive for use in blast iron furnaces and for metallurgical purposes.
- 4) Pyrolysis Oil: The oil varies very much with the type of raw material. It contains more than one hundred different substances, which once made it a valuable feedstock for the chemical industry.

With these definitions we realize that charcoal could be considered the most complex component of Black Powder.

An important field of research in Black Powder charcoals has been conducted by military laboratories in attempts to better define the power of this explosive.^[7] Black powder is used as an initiating charge, providing rapid and efficient ignition, and as a propellant for some military projectiles. If the Black Powder is not well characterized and does not perform consistently, then high explosive rounds may fall on friendly lines or may not hit intended targets. The work of Ronald Sassé et al. for the U.S. Department of Defense is particularly instructive in characterizing Black Powder. In Sassé's papers^[8-10] we see a treasure of information that can be explored by counsel. Charcoal used in Black Powder originates from different vegetable sources. These sources invariably originate from different areas and therefore nutrient environments. Each batch of charcoal is consequently very likely different. Even the manufacturer who uses the same type of tree for his charcoal utilizes trees that originate from different sources. These sources imprint their own nutrient and growth signature on the charcoal product and, if batches of charcoal are blended, such blends may create their own signatures.

Expert testimony that is offered that Black Powder samples “match” should raise questions concerning the chemical and physical characterization of the charcoals found in the Black Powder. Remembering that charcoal particles will have different contents of organic and inorganic chemicals as well as different shapes and structures, counsel can ask for the data that totally defines these characteristics. If they have not been defined then a dangling “match” must be better defined.

Black Powder, The Product

Black powder utilized in the United States originates from a number of sources. The largest of those sources is Goex, Inc.^[11] The GOEX Black Powder plant in Moosic, Pennsylvania, started producing Black Powder in 1912. Kosanke^[12] advises that there are also sources of Chinese, German, Russian, Brazilian, Scottish and homemade Black Powders in the United States at this time as well as Black Powder that originates from military surplus. A simple review of the GOEX sales brochure notes that Black Powder comes as superfine black sporting powder, military powder, fireworks powder, blasting powder and commercial powder. Each of those headings has subclasses. Under superfine black sporting powder one finds cannon, Fg, FFg, FFFg, FFFFg, and cartridge powders. Under military Black Powder one finds type Mil-P-223P powder further subdivided into class 1 through class 8 propellant composition, type JAN-P-663A subdivided into type I fuse and type II fuse powders, and type JAN-P-362 powders. Under fireworks powder one finds 1Fa through 7Fa, meal D, fine meal and extra fine meal. Under Blaster Powder one finds 1FBB, through 4FBB powder. Under commercial fuse powder one finds powders with speeds of 85, 108, 111, 116, 124, 126, 132, 140 and 165 seconds/yard.

As the reader can see, these powders, though all composed of potassium or sodium nitrate, sulfur, and charcoal may have different characteristics. For instance, no two Black Powder granules, which have the appearance of blackened coarse grains of sand, are exactly alike in size and shape. Sassé and Rose can therefore tell us that there is a size distribution of these

powder particles in any one product type.^[13] According to information the author received from a representative of GOEX, because of this size distribution, particles of one size may be found in more than one type of Black Powder. For example, particles of a particular size that are found in FFg may also be found in FFFg powder. Therefore while noting that particles from two different sources of different types of Black Powder match in size, the expert must also honestly put forth the information that other sources of different types of Black Powder are not excluded as possible sources. It would also be helpful to let counsel and the trier-of-fact know just how many other sources of a particular type of Black Powder there were. This may be impossible as the Black Powder particles fracture in the can.^[14] Another problem with Black Powder size comparison may very well be in comparing uninitiated Black Powder with Black Powder particles found in residue from exploded improvised explosives devices. If powder can fracture in the can, one can be certain that it will fracture when subjected to explosive forces.

Though quantities of Black Powder that exist in the United States are not known accurately, one can get an estimate from looking at Black Powder usage as well as the published scientific literature on Black Powder. Jon Uithol, of the National Muzzle Loading Rifle Association^[14] advises that there are three to seven million muzzle loading state hunting licenses issued per year in the U.S. These firearms utilize Black Powder or substitutes such as PyrodexTM^[15] and Clean ShotTM.^[16] Black powder is sold in units as small as one pound. This would indicate that millions of pounds of Black Powder presently exist in this country as purchased product. Rose notes about Black Powder “the civilian consumption alone must be more than a thousand metric tons annually”.^[17]

A Range of Choices

The Federal Judicial Center’s *Reference Manual on Scientific Evidence*^[18] asks the question “Have alternative explanations been ruled out?” explaining, “Alternative explanations and confounding factors should be examined and ruled out to avoid reaching an erroneous con-

clusion. However, it is never possible to rule out every alternative explanation.” Another source^[19] describes Judge Weinstein in *Agent Orange*^[20] recognizing that unless research seeking to establish causation for one agent also takes into account other factors that may explain the plaintiff’s injuries, the finding may improperly overestimate causation. Because the evidence presented failed to take into account factors other than Agent Orange dioxin that could have caused the veteran’s illnesses, it was not scientifically valid, and Judge Weinstein properly excluded the evidence as legally unreliable.” This is very much on point here. Complex materials and their components are manufactured in many forms with many uses, and with upper and lower limits of acceptance of physical and chemical characteristics. Those limits translate into products having different chemical and physical characteristics even though produced on the same production lines for identical purposes. When those limits are very tight, differences are difficult if not impossible to detect with modern analytical tools. The result of this is that alternative explanations cannot always be ruled out no matter how thorough the analysis is. In the case of Black Powder, the manufacturers’ upper and lower limits must be carefully controlled so that the powder initiates only upon command and not spontaneously, resulting in unplanned damage and/or death. The range of differences in Black Powder do exist, however, and preclude absolute matches.^[21] The analyst is compelled to determine the limits of ranges and if possible to determine if suspect materials fit within those ranges and therefore could have originated from the same sources. Ultimately, however, the scientist reaches the point at which available technology cannot assist in the further characterization of materials. At that point the legal system must determine if the scientist should be compelled to report that failure and its in light of what alternative explanations for the data cannot be ruled out. Apparently Judge Weinstein would suggest that alternative explanations that cannot be ruled out should be presented as evidence.

Giglio v. United States

One would assume that a prosecutor would want to know the weaknesses of opinions presented by forensic experts if for no other reason than to avoid problematic revelations during testimony on cross examination. But does the forensic scientist have a duty to present his total understanding of data or just that part that gives strength to the prosecutor’s theory of guilt?

One approach to the reporting of limitations of scientific protocols is that established under *Giglio*. It is strange that a forensic scientist would even have to consider the law in dealing with the completeness of his reports. One would hope that there would be no taint of bias and that the scientific opinions would be rendered objectively. However as noted in the British case *Regina v. Judith Theresa Ward*,^[22] “the disclosure of scientific evidence was woefully deficient. Three senior RARDE scientists took the law into their own hands and concealed from the prosecution, the defense and the court, matters that might have changed the course of the trial.” Forensic scientists do at times take the law into their own hands and become partisan. Therefore guidance in the reporting of the significance of forensic evidence might be necessary.

We are taught in “The Prosecutor’s Duty of Disclose: From *Brady* to *Agurs* and Beyond”^[23] that *Giglio* and progeny establish that “Generally a prosecutor ‘should know’ of a piece of evidence if it is in his possession or in the possession of any agency involved in the prosecution.” Other agencies can include other prosecutors in the office,^[24] law enforcement officers,^[25] and any other investigative agencies involved in criminal prosecution.^[26] This would naturally include government forensic laboratories. And in footnote 130 of this article, quoting *U.S. v. McCord*,^[27] “The prosecution involves all agencies of the federal government involved in any way in the prosecution of criminal litigation.” *Giglio* and progeny establish that failure to present exculpatory information is not excused as a result of the prosecutor having no personal knowledge of such information while members of the agency assisting in the prosecution do have such knowledge. What does this say for forensic scientists who present their

findings as “matches” without describing the underlying meaning of the adjective? Do these scientists have an obligation to present the underlying meaning of the data that establishes the match? If the matches are not absolute should the level of uncertainty be exposed to the prosecutor? If the level of uncertainty is unknown should that also be reported to the prosecutor? If forensic scientists are not willing to report the significance of their data objectively, then how can the prosecutor decide if *Brady* material and *Giglio* obligations exist as a result of scientific investigations?

What obligation does the prosecutor have to provide possibly exculpatory forensic information? *Agurs*^[28a] teaches that:

Although there is, of course, no duty to provide defense counsel with unlimited discovery of everything known by the prosecutor, if the subject matter of such a request is material, or indeed if a substantial basis for claiming materiality exists, it is reasonable to require the prosecutor to respond either by furnishing the information or by submitting the problem to the trial judge. When the prosecutor receives a specific and relevant request, the failure to make any response is seldom, if ever, excusable.

But how does defense make specific requests about complex scientific information that may be exculpatory in nature, or may prove or be favorable to establishing innocence. The “matching” of complex forensic samples is generally not a skill that is employed outside the government’s own laboratories. How can defense counsel even know to ask about the morphological structure of the charcoal in Black Powder samples, or the volatile organic compounds, or the pyrolysis oils, or the impurity content of potassium nitrate, or the size distribution characteristics of particular types of Black Powder? Generally, neither prosecution nor defense counsel have appropriate backgrounds to delve into or understand this type of information.

Agurs^[28b] identified this situation in describing the prosecution’s failure to disclose allegedly favorable evidence that the defense had not specifically requested. This failure could be

inexcusable under *Giglio*, and yet the prosecutor, defense and court never pick up on the failure when forensic evidence is concealed. One can imagine testimony that established that two Black Powder samples “matched” and yet the “match” was only in qualitative content of potassium nitrate, sulfur and charcoal. A trier-of-fact could wrongly infer from this testimony that both Black Powder samples had unique characteristics that set them apart from all the other hundreds of thousands, possibly millions, of pounds of Black Powder in existence in the United States. Without explaining the meaning and limitations of “match” and without the prosecutor or defense counsel being able to see through the problem, the trier-of-fact might not be able to place the proper weight on evidence and injustice might result.

What evidence would be considered exculpatory? It would not take a great leap of faith to believe that if Black Powder were found at a crime scene and at a defendant’s residence that the defendant would argue that there are thousands of tons of Black Powder available and in the hands of the American public and that the Black Powder found at the crime scene did not originate from the defendant’s Black Powder. The expert who opined simply that the two Black Powder samples “matched” could very well mislead the trier-of-fact into believing that the two samples of Black Powder originated from the same source. That expert would be concealing evidence that very well could be considered to be exculpatory. One can also imagine the trier-of-fact who has been led by the expert to believe that two Black Powder samples “match” most likely originated from the same source. Under these circumstances, any information that revealed the limited weight of that evidence could be considered favorable to the defense. Such evidence, if unsuccessfully concealed, might even lead jurors to question the credibility of the proffered expert. Imagine the trier-of-fact who has been led to believe through the “dangling adjective of comparison” that two samples originated from the same source. Imagine now the effect on that same trier-of-fact when she learns that there are thousands if not millions of possible sources of the same material, that the analyst can not, in reality, determine if the two materials are

chemically and physically identical, and that the analyst did not present that information in his report or in his testimony.

Solutions

Counsel should look behind the adjectives of comparison, demanding to know what they mean. Forensic scientists should report their full understanding of the meaning of the comparison adjectives, remembering that the oath is to “Tell the truth, the whole truth, and nothing but the truth.” A list of possibly useful exploratory questions is presented as a guide, using Black Powder as an example:

- 1) Of what is Black Powder composed?
- 2) What analytical techniques were used to determine the composition of these pieces of evidence?
- 3) What information about the components did each of these analytical techniques and instruments present?
- 4) Are each of the materials used in the manufacture of Black Powder pure? How is purity defined or determined?
- 5) If not, then did the instruments measure these impurities?
- 6) If the instruments did not measure the impurities, how can one be sure that the Black Powders “match”?
- 7) What does “match” mean?
- 8) If you did not or cannot measure impurities such as pyrolysis oils and minerals in Black Powder particles, then how can you say that the particles match without revealing in what specific ways they do match?
- 9) Are all Black Powder particles the same size and shape?
- 10) If they are not the same size, then what is the size distribution of the particles that you analyzed and how did you measure the distribution?
- 11) Was the Black Powder used in an improvised explosives device that exploded?
- 12) Wouldn't such an explosion break apart powder particles?
- 13) If you say that it would not, please present your empirical data and results of your scientific analyses to show that an explosion would not fracture larger Black Powder particles into smaller particles?
- 14) Did you conduct a scanning electron microscope comparison analysis of the morphology, size and shape of the charcoal in the Black Powder particles that you had as evidence?
- 15) Did you determine whether the Black Powder particles that you had were manufactured with charcoal from different types of trees?
- 16) If you did not, why didn't you before you simply said that the two powder samples matched?
- 17) Do you know what types of trees are used for the charcoal used in the manufacture of Black Powder particles? If you do, then would you name them?
- 18) Did you look for these different types of wood charcoal? How do you recognize the different charcoals?
- 19) Did you measure the density and hardness characteristics of the Black Powder particles, which you say “match?” If not, why not? If so, can you provide the data and explain how you conducted that measurement?
- 20) If you believe that the Black Powder particles “match” and yet you have not measured all the characteristics of the particles, can you explain what is the basis for your saying that the particles match?
- 21) Can you explain why even though you were not able and/or did not measure some very important characteristics of the Black Powder particles, you still wrote a laboratory report that said the Black Powder particles matched and did not further explain the significance of the “match?”

Summary

Adjectives of comparison such as “match”, “consistent with” and “identical to” can be misleading to triers-of-fact and can be used to prove almost anything. The expert witness who opines that two materials match opens the door very possibly to cross-examination that could be easily used to discredit the witness. Cross-examination can delve into the physical characteristics and chemical components of the matching materials, the instrumental data from analyses of the materials and into the basic scientific foundation for the opinion rendered.

We are left with a question as to whether *Giglio* obligations of the prosecutor require that the prosecutor’s experts reveal the basis for their use of comparison adjectives in their reports to the prosecutor. These revelations would seem to be necessary in order that the prosecutor be able to decide if information held by members of his team was favorable to the defense. Such information would normally be found in scientific reports from other disciplines and should not be left out of forensic reports.

References and Notes

- 1) Executive Director, Forensic Justice Project, Washington, D.C.; Former Supervisory Special Agent, Federal Bureau of Investigation, assigned to FBI laboratory, Washington, D.C., 1986–998; B.S., Chemistry, 1974, East Carolina University; Ph.D., Chemistry, 1980, Duke University; J.D., 1996, Georgetown University School of Law.
- 2) “*Giglio v. United States*”, Vol. 405 U.S., 1970, p 150.
- 3) Randolph N. Jonakait, “Stories, Forensic Science, and Improved Verdicts”, *Cardozo L. Rev.* Vol. 13, 1991, pp 343, 349.
- 4) W.B. Dancy, “Potassium Compounds”, *Encyclopedia of Chemical Technology*, Vol. 18, John Wiley & Sons. 1982; [a] p 920; [b] p 939; [c] p 930.
- 5) D. W. Bixby, H.L. Fike, J.E. Shelton and T.K. Wiewiorowski, “Sulfur”, *Encyclopedia of Chemical Technology*, Vol. 22, John Wiley & Sons, 1982; [a] p 78; [b] p 79; [c] p 97.
- 6) Walter Emrich, *Handbook of Charcoal Making*, D. Reidel Publishing Co., 1985; [a] p 13; [b] pp 14, 17.
- 7) R. Sassé, H. Homes, D. Hansen, W. Aungst, O. Doali, and R. Bowman, “Evaluation of Black Powder Produced by the Indiana Army Ammunition Plant”, Vol. 11 *Proc. Int. Pyro. Semin.* Technical Report, Ballistic Research Laboratory, Aberdeen Proving Ground, MD, 1986, p 489.
- 8) S. Wise, R.A. Sassé, and H.E. Homes, *Organic Substitutes for Charcoal in ‘Black Powder’ Type Pyrotechnic Formulations*, Technical Report, Ballistic Research Lab, Army Armament Research and Development Center, Aberdeen Proving Ground, MD, 1984.
- 9) R. A. Sassé, *Characterization of Maple Charcoal Used to Make Black Powder*, Ballistic Research Lab, Army Armament Research Development Center, Aberdeen Proving Ground, MD, 1983.
- 10) R. A. Sassé, “Characterization of Charcoal Used to Make Black Powder”, *Proc. Int. Pyrotechnic Sem.*, Vol. 9, 1984, p 471.
- 11) GOEX, Inc., P.O. Box 659, Doyline, LA, 71023-0659, USA; (318) 382-9300.
- 12) Kenneth Kosanke, Editor of *Journal of Pyrotechnics*, 1775 Blair Road, Whitewater, CO, 81527 USA, (970) 245-0692.
- 13) R. Sassé and J.E. Rose, “Comparison of Spherical and Ellipsoidal Form Functions for Evaluating Black Powder”, *Proc. Int. Pyrotechnic Sem.*, Vol. 13, 1988, p 679.
- 14) John Uithol, Executive Vice President, National Muzzle Loading Rifle Association, Friendship, IN, USA; (812) 667-5131, advised the author in a private communication that some Black Powder rifle enthusiasts wish greater reproducibility of results in shooting. They therefore sieve purchased Black Powder to achieve a more uniform particle size distribution. The sieving is required not only because of the size distribution, which originates with the

purchased product, but also because of fracture in the can over time with jarring and dropping.

- 15) Hodgdon Powder Co. Inc., P.O. Box 2932, Shawnee Mission, KS, 66201, USA; (913) 362-9455.
- 16) Clean Shot Technology, Inc., P.O. Box 100, Whitewater, CO, 81527, USA; (970) 262-0100.
- 17) J.E. Rose, "Black Powder – A Modern Commentary – 1979", *Proc. Symp. Explos. Pyrotech.* Vol. 10, 1979, p 6a-1.
- 18) Federal Judicial Center, *Reference Manual on Scientific Evidence*, West Publishing Co., 1993, p 163.
- 19) "Confronting the New Challenges of Scientific Evidence", *Harv. L. Rev.*, Vol. 108, 1995, pp 1481–1539.
- 20) "In re Agent Orange", Vol. 611 F. Supp. p 1223 (E.D.N.Y. 1985), aff'd, Vol. 818 F.2d p 187 (2d Cir. 1987), cert. denied, Vol. 487 U.S. p 1234, 1988.
- 21) L. Freedman and R. Sassé, "The Thermodynamics of Real and Unreal Black Powder", *Proc. Int. Pyrotechnic. Sem.*, Vol. 9, 1984, pp 177–178. [Describes the manifes-

tations of the variability of Black Powders. Interestingly the authors note that "Good analyses of Black Powder are rare; analyses of the charcoals used are even rarer."]

- 22) "Regina v. Judith Theresa Ward" was heard in the Royal Courts of Justice in the Court of Appeal, Criminal Division on June 4, 1992 before Lord Justices Glidewell, Nolan and Steyn. The case is notorious for its exposure of inappropriate forensic practices by government scientists.
- 23) "The Prosecutor's Duty of Disclose: From Brady to Agurs and Beyond", *J. Crim. L. & Criminology*, Vol. 69, 1978, p 197.
- 24) "Giglio v. United States", Vol. 405 U.S., 1972, p 150.
- 25) "Barbee v. Warden, Maryland Penitentiary", Vol. 331 F.2d (4th Cir. 1964) p 842.
- 26) "United States v. Eley", Vol. 335 F. Supp. (N.D.Ga. 1972) p 353.
- 27) "United States v. McCord", Vol. 509 F.2d (D.C. Cir. 1974) p 334.
- 28) "United States v. Agurs", Vol. 427 U.S., 1976; [a] p 97; [b] p 106.

Events Calendar

Pyrotechnics

5th Int. Symp. on Special Topics in Chemical Propulsion Combustion of Energetic Mat.

June 19–22, 2000, Stresa, Italy

Contact: Prof. Kenneth K. Kuo, Co-Chair.
140 Research Building East, Bigler Road
Pennsylvania State University
University Park, PA 16802, USA

Phone: +814-863-6270

FAX: +814-863-3203

email: kkkper@entr.psu.edu

web: www.me.psu.edu/kup/5-isicp

Int. Workshop on Unsteady Combustion & Interior Ballistics

June 26–30, 2000, St. Petersburg, Russia

Contact: Prof. Valery Babuk

email: kav_ml@bstu.spb.su

web: www.intlpyro.org/Ministry for
Education of Russia.html

31st Int. Annual Conf. of ICT “Energetic Materials – Analysis, Diag. and Testing”

June 27–29, 2000, 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)721-4640-111

email: mw@ict.fhg.de

web: www.ict.fhg.de

27th Int. Pyrotechnics Seminar

July 16–21, 2000, Grand Junction, CO, USA

Contact: Alita Raoch, IPS 2000 Coordinator

Los Alamos, NM 87545, USA

Phone: +505-665-6277

FAX: +505-665-3407

email: alita@lanl.gov

web: www.ipsusa.org

Chemistry of Pyrotechnics & Explosives

July 23–28, 2000, Chestertown, MD, USA

Advanced Pyrotechnic Seminar: Explosives & Propellants—The Past, Present & Future

Jul. 30–Aug 4, 2000, Chestertown, MD, USA

Contact: John Conkling

PO Box 213

Chestertown, MD 21620, USA

Phone: +410-778-6825

FAX: +410-778-5013

email: John.Conkling@washcoll.edu

28th Int. Symp. on Combustion

July 28–Aug. 4, 2000, Edinburgh, Scotland

Contact: Clansman Monarch

1a Hill Street

Edinburgh, EH2 3JP, UK

Phone: +44 (0) 131-226-5222

FAX: +44 (0) 131-624-7277

email: events@clansman.com

2nd Int. Symp. on Safety Science & Technology

Aug. 10–13, 2000, Beijing China

Contact: Prof. Changgen Feng

Mech. & Engr. Deptl, Brijing Inst. of Techn.

PO Box 327

Beijing 100081, China

Phone: +86-10-6891-2764

FAX: +96-10-6891-1849

email: Cgfeng@public.east.cn.net

2nd Int. Disposal Conference

Nov. 9–11, 2000, Linköping, Sweden

Contact: Stig Johansson

Johan Skyttes väg 18, SE 554

Jönköping, Sweden

FAX: +46-3616-3734

email: listh@sto.foa.se

web: www.intlpyro.org/swedish.htm

5th Int. Symp. & Exhib. on Sophisticated Car Occupant Safety Systems “Airbag 2000+”

Dec. 4–6, 2000, 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)721-4640-111

email: mw@ict.fhg.de

web: www.ict.fhg.de

Explosives

Computational Mech. Assoc. Courses–2000

Explosive Effects and Applications

(May 16–19)

Fundamentals of Shaped Charges

(June 12–16)

Chemistry of Explosives

(Aug. 28–Sep. 1)

Shaped Charges in the Exploration and Production of Oil & Gas Resources

(Oct. 16–20)

Introduction to Explosives

(Oct. 29–Nov. 3)

Contact: Computational Mechanics Associates

PO Box 11314,

Baltimore, MD 21239-0314, USA

Phone: +410-532-3260

FAX: +410-532-3261

Year 2000 Blasting Technology Course

June 12–16, 2000, Ottawa, ONT, Canada

Contact: Dept. Engineering

Queen’s Univ., Goodwin Hall

Kingston, Ont., Canada K7L 3N6

Phone: +1-613-533-2198

FAX: +1-613-533-6597

web: mine.queensu.ca/conted/blast2000

29th US DoD Explosives Safety Seminar

July 18–20, 2000, New Orleans, LA, USA

Contact: Brent Knoblett

Phone: +1-703-325-1375

FAX: +1-703-325-6227

email: Brent.Knoblett@HQDA.Army.mil

web: www.hqda.army.mil/ddesb/esb.html

Munich Conference on Explosives and Blasting Technique

Sep. 6–8, 2000, Munich Germany

Contact:

Phone: +49-9081-22444

27th ISEE Conference on Explosives and Blasting Technique

Jan. 28–31, 2001, Orlando, FL, USA

Contact: Lynn Mangol

Phone: +1-440-349-4004

12th Int. Symp. on Chemical Problems Connected with the Stability of Explosives

May 14–18, 2001, Sweden

Contact: Stig Johansson

Johan Skyttes väg 18, SE 55448

Jönköping, Sweden

Phone/FAX: +46-3616-3734

email: listh@sto.foa.se

Fireworks

Benson & Hedges Pyrotechnic Competition

Montreal 2000

- June 17 Panzera (Opening)
- June 25 Marutamaya Ogatsu Fwks. (Japan)
- July 2 Pirotecnia Minhota (Portugal)
- July 9 Ipon S.R.L. (Italy)
- July 12 Rozzi's Famous Fwks. (USA)
- July 16 Syd Howard Fwks. Int'l (Australia)
- July 19 Caballer (Spain)
- July 23 Weco Pyrotehn. Fabrik (Germany)

July 26 BEM Fireworks Recruit (Canada)

July 28 Panzera (Closing)

Toronto 2000

June 17 Pyro Spectacular (South Africa)

June 24 Pirotecnia Minhota (Portugal)

June 28 A.P.E. Pirotecnica (Italy)

July 1 Foti's Int'l Fwks (Australia)

July 5 Antonio Caballer (Spain)

July 8 Grand Finale

Vancouver 2000

July 29 A.P.E. Pirotecnica (Italy)

Aug. 2 Foti's Int'l Fwks (Australia)

Aug. 5 Antonio Caballer (Spain)

Aug. 11 Grand Finale

Pyrotechnics Guild International Conv.

Aug. 5–11, 2000, Fargo, ND, USA

Contact: Ed Vanasek, Sec. Treas.

18021 Baseline Avenue

Jordan, MN 55352, USA

Phone: +952-492-2061

e-mail: edvanasek@aol.com

web: www.pgi.org

High Power Rocketry

LDRS 2000

July 1–4, 2000, Orangeburg, SC, USA

Contact: see web site

www.tripoli.org/launchpad/LDRS2000.html

Model Rocketry

NARAM 2000

July 20–Aug. 4, 2000 – SE Colorado, USA

Contact: — see web site for details:

web: www.naram2000.org

For launch information visit the NAR Web site: www.nar.org

Study on Various Polyesters as Binders for Pyrotechnic Composition

J.P. Agrawal*, S.N. Singh, D.B. Sarwade, V.A. Mujumdar & NT Agawane
High Energy Materials Research Laboratory, Sutarwadi, Pune 411 021, India

ABSTRACT

Two tracer compositions were formulated based on magnesium, strontium nitrate and sodium nitrate with unsaturated non-halo and halo polyesters as binders. They were characterized for mechanical properties, thermal behaviour, burning rate, luminous output, and impact, friction and spark sensitivities. The data show that the composition with chloropolyester as binder is better for tracer compositions.

Keywords: polyester, halopolyester, binder, tracer composition

Introduction

Polymeric binders play multiple roles in pyrotechnic compositions and, in general, contribute towards better mechanical strength^[1,2] and moisture-absorption resistance, which leads to improved shelf-life.^[3,4] They also contribute significantly to the performance of tracer compositions by increasing the reaction rates. A literature survey reveals that a number of synthetic binders such as polyesters, epoxies, silicones, thiokols, have been studied in place of natural binders in search of more luminous efficiency.^[5] The use of halogenated resins as binders in various tracer compositions has recently been reported,^[6] and it has been concluded that the polyester resins give higher luminosity, while fluorinated polymers contribute to the combustion exothermicity leading to faster burn rates.

The literature on binders for tracer compositions indicates that polyester resins are promising,^[7] but a comparative account of non-halo and halo polyesters has not yet been reported. This study was therefore undertaken with a view

to make the comparison. This article reports the data generated on pyrotechnic compositions based on magnesium, strontium nitrate and sodium nitrate with unsaturated non-halo and halo polyesters as binders.

Experimental

Materials

Chemicals conforming to the following specifications were used for the study.

- i) Magnesium [Mg] (Grade V) conforming to Commonwealth Specification (CS) 5035A having an average particle size of 63 μm with a purity of 98%.
- ii) Strontium nitrate [$\text{Sr}(\text{NO}_3)_2$] conforming to Joint Services Specification (JSS) 1052 (1964) passing Indian Standard (IS) 125 μm sieve, purity of 97% with moisture content 1% (maximum) and insoluble matter in water 0.25 % (maximum).
- iii) Sodium nitrate [NaNO_3] conforming to JSS 1095 (1968) passing IS 125 μm sieve, purity of 97% with moisture content 1% (maximum) and total impurities 1% (maximum).
- iv) Polyvinyl chloride [Caliplast 370] conforming to Indian/Military Explosives (IND/ME) 741(a) (1977) passing IS 75 μm sieve, with bulk density 0.4 g/cm^3 (minimum) and volatile matter 0.5% (maximum).
- v) Tetrachlorophthalic-anhydride- and phthalic-anhydride based unsaturated polyesters were synthesized in the High Energy Materials Research Laboratory by a process given elsewhere.^[8]

Preparation of Tracer Composition:

- i) **Chemical Composition:** The composition formulation in percent and the amount for a 200 g batch is as follows:

Ingredient	%	g
Magnesium	53	106
Strontium nitrate	22	44
Sodium nitrate	13	26
Polyvinyl chloride	2	4
Resin (binder)	10	20

- ii) **Drying of ingredients:** Oxidizers [$\text{Sr}(\text{NO}_3)_2$ and NaNO_3] were ground, sieved and dried in an electric oven at 100 ± 2 °C for 8 hours. The ingredients were again sieved through IS 125 μm sieve. Polyvinyl chloride (PVC) was dried in a water-jacketed oven at 60 ± 2 °C for three hours and sieved through IS 300 μm sieve.
- iii) **Coating of Mg Powder:** The coating of Mg with polyester resin was done as given below. Either Polyester resin or chloropolyester resin (20 g) was premixed with catalyst (2%) and accelerator (1%). Mg powder Grade V (106 g) was placed in a bowl and coated with polymeric binder. Premixed ingredients as stated above were added to coated Mg and hand mixed for half an hour. The whole mixture was then passed through IS 600 μm sieve five times to get a homogeneous composition. The composition was finally dried/cured for 18 hours by spreading in aluminium trays.

Characterization

Mechanical Properties:

The compositions were consolidated into pellets of 20 mm diameter and 20 mm height under the load of 3 tons with a dwell time of 15 seconds. The compression strength and percent compression of the pellet were recorded using Instron UTM (Model-1185) as per the American Society for Testing and Materials (ASTM) method.^[9]

Thermal Characterization:

- i) The heat of combustion was determined by PARR Bomb Calorimeter (300 ml volume) by igniting 1 g of the sample in air as per the ASTM method.^[10]
- ii) Differential Thermal Analysis (DTA) was carried out using an apparatus fabricated in this laboratory; the details are described elsewhere.^[11] Five milligrams of pyrotechnic composition were placed in an open platinum cup and heated simultaneously with an equal amount of reference sample (calcined alumina) in another cup. The temperature difference between the test and reference sample was measured as a function of temperature. To calculate the activation energy of the ignition process of the pyrotechnic composition, DTA runs were recorded at five different heating rates (i.e., 5, 10, 15, 18 and 20 °C/min). The peak maxima (T_m) thus obtained at different heating rates for various pyrotechnic compositions are given in Table 2. The energy of activation of ignition was determined using the Ozawa^[12] and the Kissinger^[13] methods. In the Ozawa method, a curve was plotted between the logarithm of the heating rates (β) versus the reciprocal of the peak maxima temperature (i.e., $\log \beta$ vs. $1/T_m$), which gave a straight line, and the energy of activation (E) was calculated from its slope;

$$\text{Slope} = 0.4567/1.987 \times E$$

In the Kissinger method, the energy of activation was calculated by plotting the curve between $\ln \beta/T_m^2$ vs. $1/T_m$, which is also a straight line. The activation energy was then calculated from the slope, similar to the Ozawa method.

Burning Rate and Luminous Output:

The compositions were pressed in paper-lined steel tubes of 20 mm diameter and 30 mm length, under 15 tons of dead load with a dwell time of 15 seconds. The tracer compositions were electrically ignited, and their luminous outputs and burning times were measured using a photometer, (Photometer, Model 550 from M/s EG & G, Massachusetts, USA).

Table 1. Mechanical Properties, Burn Rate and Luminosity of NHP and CP Based Tracer Compositions.

Composition based on	Compression strength (MPa)	Compression (%)	Linear Burn Rate (mm/s)	Mass Burn Rate (g/s)	Luminosity (cd × 10 ⁴)	Efficiency [(cd·s/g) × 10 ⁴]
NHP	32.0	5.8	4.7	3.48	6.329	1.81
CP	41.23	6.7	4.3	3.19	3.692	1.167

Sensitivity:

- i) **Impact sensitivity** was determined by the fall-hammer method using a 2 kg weight on 20 mg samples, and the height for 50% explosion was recorded.^[14]
- ii) **Friction Sensitivity** was determined on the Julius Peter apparatus using 10 mg samples, and the minimum weight, for which five samples did not ignite, was recorded.^[15]
- iii) **Spark sensitivity** was determined by placing 10 mg samples between two electrodes that were spaced at a distance of 2 to 2.5 mm. The energy of the spark was varied from 15 mJ to 5 J, and the ignition or non-ignition of the samples was recorded.

Results and Discussion

The data on mechanical properties (Table 1) indicate that the tracer composition based on chloropolyester (CP) has higher compression strength and percent compression than the one

based on non-halo polyester (NHP). This is attributed to greater tensile strength of CP compared to NHP^[16,17] and is reflected in the compression strength of the tracer composition.

Differential thermal analysis data reveals that the T_i and T_m are less for the CP-based composition than the NHP-based composition at all the heating rates. This may be due to the involvement of chloropolyester in the ignition process of the composition. It is consistent with the activation energy of the CP-based composition being less than that of the NHP-based composition (Table 2). Further, heat of combustion data on show that both the compositions release approximately the same amount of heat (Table 3).

The impact, friction, and spark sensitivity data (Table 3) suggest that both compositions are reasonably safe with respect to impact, friction and electrostatic charge. However, the CP-based composition is more sensitive to impact and friction as compared to the NHP-based composition. This is because chloropolyesters are generally rigid as compared to their coun-

Table 2. Peak Inception Temperature (T_i), Peak Maxima Temperature (T_m) and Activation Energy of NHP and CP Based Tracer Compositions.

Composition Based on		Heating Rate (°C/min)					Activation Energy (kcal/mol)	
		5	10	15	18	20	Ozawa Method	Kissinger Method
NHP	T_i	436	442	451	462	457	34.27	33.1
	T_m	453	458	463	476	479		
CP	T_i	424	429	445	443	447	31.0	29.8
	T_m	442	446	458	465	469		

Table 3. Sensitivity and Heat of Combustion of NHP and CP Based Tracer Compositions.

Composition based on	Friction Sensitivity (kg) (does not ignite until)	Impact Sensitivity (cm) (height for 50% Explosion/ignition)	Spark Sensitivity (J) (does not ignite until)	Heat of Combustion (cal/g)
NHP	28.8	162.5	3.5	2029
CP	24.0	127.0	3.5	1982

terpart non-halo polyesters.^[16,17] As a result, they behave like grit particles in pyrotechnic compositions leading to increases in their impact and friction sensitivity. Similar behaviour is observed in differential thermal analysis.

The data on luminosity and luminous efficiency (Table 1) indicate that the NHP-based composition gives more luminous output. But, as a practical matter, flares filled with NHP-based compositions do not ignite easily, probably due to the higher activation energy of NHP. Further, the CP-based composition intensifies the red colour of the flame, presumably due to the presence of chlorine atoms, which aid in the formation of the red-colour-emitting species.

Conclusions

Tracer compositions are required to give bright red light for better visibility of the tracer both during day and night; therefore, chlorinated binders are preferred, as chloro groups enhance the red colour of the flame. Moreover, the CP-based tracer composition has better mechanical properties than the NHP-based composition. As the tracer compositions have to burn under spin and mechanical stresses, compositions with higher mechanical strength are preferred. While the NHP-based tracer composition gives higher luminous output, it is difficult to ignite, and hence the composition may fail to burn.

On balance, the more intense red colour of the CP-based composition, coupled with its greater mechanical strength, make it the better choice for tracer use.

References

- 1) J. C. Cackett, *Monograph on Pyrotechnic Compositions*, RARDE, 1965, p 34.
- 2) A. A. Shidlovskiy, *Principles of Pyrotechnics*, 1964, p 324.
- 3) J. C. Cackett, *Monograph on Pyrotechnic Compositions*, RARDE, 1965, p 111.
- 4) F. R. Taylor and D. E. Jackson, "Use of Organic Coating to Improve the Storage-ability and Safety of Pyrotechnic Composition", *Proc. 12th International Pyrotechnic Seminar*, 1987, p 325.
- 5) P. Bieran and M. Bremseau, "Study of Various Polymers as Candidate Binders in Pyrotechnic Compositions", *Proc. 14th International Pyrotechnic Seminar*, 1989, p 45.
- 6) S. N. Singh et al., *Study of Magnesium Strontium Nitrate Tracer Compositions with Different Binders*, ERDL Report No. 17/93.
- 7) B. Paul, "Studies on Properties and Applications of B/KNO₃", *Proc. 3rd International Pyrotechnic Seminar*, 1972, p 253.
- 8) J. P. Agrawal and K. S. Kulkarni, "Kinetics of NG Migration through Halo and Non-Halo Saturated Polyesters", *Polym. Intl., U.K.*, Vol. 35, 1994, p 257.
- 9) American Society for Testing and Materials, D698, 1993.
- 10) Annual Book of ASTM Standards, D240 - 1987 & K. G. Julius Peters, Stronstrasse, 39, 1000 Berlin 21, "Instrument Manual".

- | | |
|--|---|
| <p>11) J. P. Agrawal, J. S. Chhabra, J. Athar and H. Singh, "Comparative Study of Various Oxidants for HTPB Prepolymer", <i>Plastics, Rubbers & Composites Processing and Applications, UK</i>, Vol. 20, 1993, p 305.</p> <p>12) T. Ozawa, "A New Method of Analyzing Thermogravimetric Data", <i>Bull. Chem. Soc. Japan</i>, Vol. 38, 1965, p 1881.</p> <p>13) H. E. Kissinger, "Reaction Kinetics in Differential Thermal Analysis", <i>Anal. Chem.</i>, Vol. 29 (1957) p 1702.</p> <p>14) J. E. Sinclair, "The Effect of Explosive Mixture on Impact Sensitivity", Naval Post-Graduate School, Technical Report 16, 1957.</p> | <p>15) K. G. Julius Peters; "Instruction Manual for Friction Sensitivity Apparatus", Stron-strasse 39, 1000 Berlin 21, 1981, pp 12, 34, 41, and 471.</p> <p>16) J. P. Agrawal and K. S. Kulkarni, "Comparative Study of Unsaturated Halo and Non-Halo Polyesters and Inhibition of Double-Base Propellants", <i>J. Appl. Polym. Sci.</i>, Vol. 50, 1993, p 1655.</p> <p>17) R. C. Nametz, "Self Extinguishing Polyester Resins", <i>Ind. Eng. Chem.</i>, Vol. 39, 1967, p 99.</p> |
|--|---|
-

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 of Event

Contact information — including, if possible, name of contact person, 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>

Communications

Brief technical articles, comments on prior articles and book reviews

Shell Altitude vs. Mortar Length

Ron Dixon

Four-D Enterprises, Inc.
10510 El Comal Dr., San Diego, CA 92124

Introduction

During the mid 1980's, I was the President and General Manager of San Diego Fireworks, Inc. At many of our Pyrotechnic Safety and Training Seminars, I was asked about the correlation between mortar length and altitude attained by aerial shells. Further, I have overheard many theories relating to a "vacuum" created within a mortar, if that mortar is longer than some optimum length. Others have made statements indicating that exceptionally long mortars would project shells well beyond "normal" altitudes for given sizes of shells.

Upon reaching saturation of these various theories, our staff decided to perform some basic tests to see if any of these theories had merit.

Prior to making the determination to conduct this field test, we had the opportunity to view videotape produced by a Japanese firm. This videotape showed shells being fired from a thick-walled glass mortar. Our observations indicated that there was a considerable amount of gas generated by the lift charge and that the vast majority of this gas was produced well after the shell had left the open end of the mortar during launch.

Although our methods were not purely scientific, in that we did not use precise measurement instruments, we did use devices that were recognized in the industry as acceptable and would be able to determine if the theories were in fact accurate or erroneous. We were not looking for precise data, but data sufficient to determine if these theories warranted further investigation.

Approach

The decision was made to purchase a ten-foot length of mortar tube material. The material selected was three-inch i.d. HDPE, a currently approved mortar material by the California State Fire Marshal (CSFM) for use in the public display fireworks industry. This section of tube was fitted with a three-inch o.d. wooden plug that also met the CSFM regulations.

This mortar was used to launch three-inch aerial shells supplied by a manufacturer that we had determined, from past experience, provided consistent quality shells and that demonstrated the most repeatable lift times, when tested for choreography purposes annually. Further, we wanted to be sure to use shells from the exact same production lot, in order to minimize any variations in the product used. We selected a full case of three-inch shells manufactured by Yung-Feng Fireworks. The variety was a Green Chrysanthemum.

The shells were fired using a Daveyfire SA2000 B Electric match that had the head inserted into the lifting charge of each shell. The wire leads from the match were routed through a 1/8-inch hole placed in the base of the mortar, just above the wooden plug. This routing was done to eliminate any potential interference with the launching of the aerial shell. We determined that the gas loss from the 1/8-inch hole was insignificant.

Following each firing, the mortar was cleaned to remove any remaining shell lift bag debris. It was then shortened by six inches. The mortar was again loaded, placed upon a firm plate of steel to minimize recoil, and attached securely to a steel post set vertically in the earth. This was done to assure vertical stability during repetitive firings. This process was repeated until the mortar length reached 12 inches (one foot).

Altitude Measurement

In order to measure—simply, but reasonably accurately—the altitude attained by the shells, we used a commercially available protractor manufactured by Estes Rocket Company, for determining the altitudes of model rockets. The Estes product name was the “Altitrak Altitude Finder” part number 2232.

This device can be calibrated for use at one of three different distances from the launch site to the measurement site. The device is calibrated for use at 75, 150 or 300 meters from the launch site to the measurement site. The three different distances are for three different ranges of altitudes produced by their products. It is recommended that the user select the distance from the launch point to the measurement point that most closely equates to the expected altitude of the device being measured.

The device is aimed at the product being launched and a trigger is pulled back, which releases the measurement pendulum. The product is tracked to the point at which it reaches its apex and the trigger is then released, which captures the position of the pendulum. The altitude is determined by reading the appropriate scale on the pre-calibrated quarter rings on the device. We selected the range of 150 meters from point of launch to point of measurement.

Data Measured

The Table 1 presents the mortar length versus the altitude measured. Figure 1 is a graph of the same data.

Conclusion

Looking at the data and excluding the last data point at the 12-inch mortar length, we find the average altitude was 163.2 meters. The lowest point recorded was 141 meters and the highest point was 186 meters.

We expected some deviation due to other minor characteristics such as shell spin, slight wind drift, and variations inherent in the less than precision method of measurement.

Table 1. Mortar Length vs. Altitude.

Mortar Length (feet)	Altitude (meters)
10.0	141
9.5	157
9.0	186
8.5	142
8.0	169
7.5	147
7.0	167
6.5	171
6.0	178
5.5	159
5.0	175
4.5	166
4.0	156
3.5	164
3.0	170
2.5	172
2.0	155
1.5	163
1.0	74

However, we found that there was no direct correlation between mortar length and attained shell altitude until the mortar was cut to less than 1.5 feet (18 inches) in length. Further, we also found that there is no apparent vacuum created when mortars are excessively long.

Subsequent to our rather crude tests, a formal test was published.^[1] This article presents data that is consistent with the data we recorded. The Kosanke and Schwertly data was gathered using a device called the “Pyro-Meter II”.

The Pyro-Meter uses electronic counters, latching mechanisms, and optical eyes to precisely measure such altitudes. Their data indicated that the average burst height for a 3-inch shell was 124 meters with a maximum altitude of 140 meters and a minimum of 110 meters. We believe variations between the Kosanke and Schwertly data and our data are attributable to the type of shells used (ball versus cylindrical, which affects wind drag) altitude of the test site, humidity (which affects air density), etc. This also assumes the mortar used in their test was at least 1.5 feet in length.

References

- 1) K. L. Kosanke, L. A. Schwertly and B. J. Kosanke, "Report of Aerial Shell Burst Height Measurements" *Pyrotechnics Guild International Bulletin*, No. 68, 1990.

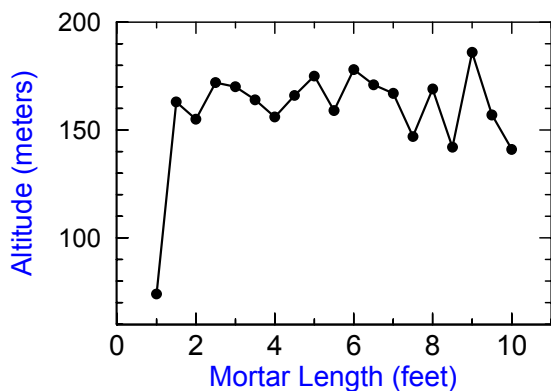


Figure 1. Graph of mortar length versus altitude attained for three-inch shells.

The Effect of Sample Containers on the Ignition Temperature of Sulfur/Chlorate Mixtures

D. Chapman and J. E. Fletcher

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

ABSTRACT

In this communication we report the lowered thermal stability of sulfur/chlorate mixtures in contact with glass surfaces. Ignition temperatures as low as 100 °C were found in glass test tubes and are about 15 °C less than for the same mixture in a cardboard fireworks tube.

Keywords: chlorate, sulfur, thermal stability, ignition temperature, glass

Introduction

In our study^[1] of the thermal stability of sulfur/chlorate mixtures under a number of different conditions we used cardboard fireworks tubes to hold the test samples. Ignition temperatures in the region of 115–120 °C were commonly found, and the variation in the results was attributed to, particle size distribution in the samples.^[2] Tanner^[3] has previously reported ignitions at 82–91 °C when sulfur/chlorate mixtures, in cardboard, were heated by a lamp. Storey^[4] observed low ignition temperatures at about 100 °C and non-ignition exotherms as low as 75 °C for sulfur/chlorate mixtures in unspecified vessels.

In an attempt to investigate the effect of container material on the ignition temperature of sulfur/chlorate mixtures, we have examined glass and stainless steel tubes. In this short paper we report the effect of these tubes on the thermal stability of 2 g sulfur/chlorate mixtures (sulfur 30%) and compare the results with those obtained in cardboard fireworks tubes.

Table 1. The Effect of Container Material on the Ignition Temperature of Loose Sulfur/Chlorate Mixtures (30% Sulfur, 70% Potassium Chlorate).

Containment	Notes	Ignition Temp (°C)	
		Tube 1	Tube 2
Open Pyrex glass tube ‡		110	110
Sealed Pyrex glass tube ‡	Rubber bung in top of tube	107	108
Open steel tube		121	—
Open cardboard tube	Composition contained 30% powdered glass (from a Pyrex test tube)	125	129
Open cardboard tube	control samples	120	121

‡ Glass test tubes taken from “laboratory stock” (i.e., clean, previously used and not pre-treated).

Results and Discussion

The first series of tests (Table 1) indicated that the use of glass test tubes produced lower ignition temperatures than any other container. It is likely that some previous work on sulfur/chlorate could have been carried out in glass vessels and we believe that this may have contributed to the low non-ignition exotherms and ignition temperatures.^[4] Interestingly, the addition of powdered Pyrex glass (not sieved to give a specific fraction) to the composition in the cardboard tube did not result in the reduction in ignition temperature observed when the basic composition was placed in glass tubes.

A second series of tests was carried out using a fresh batch of potassium chlorate (Table 2). The control samples (cardboard tubes) had a lower ignition temperature, which we attribute to a change in the particle size distribution of the potassium chlorate.^[2] In this second series, glass tubes of different histories and types were investigated. In all cases the contact between the glass and the sulfur/chlorate mixture produced a reduction in the ignition temperature. This effect was more pronounced with “new” test tubes and appeared to reduce with freshly washed glass.

Currently we have not found a suitable explanation for the observed effect of glass on the reactivity of sulfur/chlorate mixtures. However, this note has been produced to warn pyrotechnicians of the heightened risk when this mixture is placed in glass containers.

Tanner^[3] heated sulfur/chlorate mixtures using a lamp with the material contained in cardboard salvaged from books of matches. It is likely that the temperature measured in the bulk of the sample (82–91 °C) was lower than that at the surface. Storey^[4] reported exotherms as low as 75 °C for mixtures of sulfur and chlorate. Re-examination of the thermal traces suggests that these were non-ignition exotherms since the subsequent exotherms at about 100 °C or higher were more energetic and therefore more likely to have been ignitions.

Contact with a glass surface is not the sole explanation for low temperature reactions of sulfur/chlorate mixtures. Other contributing factors could include source, acidity and history of the sulfur sample, particle size distribution, heating rate and relative humidity.

References

- 1) D. Chapman, R. K. Wharton, J. E. Fletcher and G. E. Williamson, “Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures. Part 2. Stoichiometric Mixtures”, *Journal of Pyrotechnics*, Issue 7 (1998) pp 51–57.
- 2) D. Chapman, R. K. Wharton, J. E. Fletcher and A. E. Webb, “Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures. Part 3. The Effects of Stoichiometry, Particle Size and Added

Materials”, *Journal of Pyrotechnics*, Issue 11 (2000) pp 16–24.

3) H. G. Tanner, “Instability of Sulfur–Potassium Chlorate Mixture”, *Journal of Chemical Education*, Vol. 36 (1959) p 58.

4) P. D. Storey, “Identification and Assessment of Hazardous Mixtures in Pyrotechnics”, *13th International Pyrotechnics Seminar*, Grand Junction, CO, USA (1988) p 765.

Table 2. The Effect of Pre-Treatment of Glass on Sulfur/Chlorate Ignition Temperature (30% Sulfur).

Tube type	Pre-treatment	Ignition Temp. (°C)	
		Tube 1	Tube 2
Pyrex	None, “new tubes”	101	100
Pyrex	None, “previously used”	110	108
Soda Glass	None, “new tubes”	100	101
Pyrex	New, washed with distilled water	104	104
Soda Glass	New, washed with distilled water	101	102
Pyrex	New, washed DECON 90, rinsed distilled water	111	111
Soda Glass	New, washed DECON 90, rinsed distilled water	113	112
Control samples in cardboard fireworks tubes ignited at 115 °C			

© British Crown copyright, 1999

Journal Sponsors

Journal of Pyrotechnics wishes to thank the following Sponsors for their support.

Individual Sponsors:

Ed Brown

P.O. Box 177
Rockvale, CO 81244, USA
Phone: 719-784-4226
email: edwinde@cs.com

Larry Crump

2001 SE 11th Street
Mineral Wells, TX 76067-6615, USA
Phone: 940-325-1517
Fax: 972-323-2252
email: lcrump1@wf.net
web: www.wf.net/~lcrump1

Gerald Laib

17611 Longview Lane
Olney, MD 20832, USA
Phone: 301-744-4358
FAX: 301-744-4784
email: gerald_laib@yahoo.com

Corporate Sponsors:

AED / Jeroen Louwers

Jeroen Louwers
Bertelindislaan 3
Waalre, 5581 CS, The Netherlands
Phone: 31-40-221-3972
FAX: 31-40-221-3972
email: aed@iae.nl
web: iae.nl/users/aed

Allied Specialty Insurance

David H. Smith
10451 Gulf Blvd.
Treasure Island, FL 33706, USA
Phone: 800-237-3355
FAX: 727-367-1407
email: info@alliedspecialty.com
web: www.alliedspecialty.com

American Fireworks News

Jack Drewes
HC 67 Box 30
Dingmans Ferry, PA 18328-9506, USA
Phone: 570-828-8417
FAX: 570-828-8695
email: afn@98.net
web: www.fireworksnews.com

blacksky Corporation

Scott Bartel
3179 Roosevelt Street
Carlsbad, CA 92008, USA
Phone: 760-730-3701
FAX: 760-730-3704
email: scott@blacksky.com
web: www.blacksky.com

Canadian Explosives Research Laboratory

Ron Vandebek
CANMET, 555 Booth St.
Ottawa, ON K1A 0G1, Canada
Phone: 613-995-1275
FAX: 613-995-1230
email: rvandebe@nrca.gc.ca
web: www.nrca.gc.ca

Daveyfire, Inc.

Alan Broca
500 Ygnacio Valley Rd, Suite 250
Walnut Creek, CA 94596, USA
Phone: 925-926-6414
FAX: 925-926-6439
email: daveyfire@msn.com

Delcor Industries Inc.

Sam Bases, Pres.
19 Standish Ave.
Yonkers, NY 10710, USA
Phone: 914-779-6425
FAX: 914-779-6463
email: delcor@hotmail.com

Dolliff, Inc. / Insurance

John Allen
6465 Wayzata Blvd., Suite 850
St. Louis Park, MN 55426, USA
Phone: 800-338-3531/612-593-7418
FAX: 612-593-7444
email: JAllen@dolliff.com
web: www.dolliff.com

European Pyrotechnic Arts Newsletter

Rob Driessen
Van Hoensbroekstraat 16
Swalmen, NL 6071 CN, The Netherlands
Phone: 31-475-501-711
FAX: 31-475-501-711
email: driessen@cuci.nl

Fire One

Dan Barker
863 Benner Pike
State College, PA 16801, USA
Phone: 814-238-5334
FAX: 814-231-0950
email: info@fireone.com
web: www.fireone.com

Firefox Enterprises Inc.

Brandon Purrington
11612 N. Nelson
Pocatello, ID 83202, USA
Phone: 208-237-1976
FAX: 208-237-1976
email: custserv@firefox-fx.com
web: www.firefox-fx.com

Fireworks Professionals

Anthony Lealand
PO Box 17-522
Christchurch, 8030, New Zealand
Phone: 64-3-384-4445
FAX: 64-3-384-4446
email: anthony@firework.co.nz

Fireworks

John Bennett
68 Ridgewood Gardens, Bexhill-in-Sea
East Sussex, TN40 1TS, England
Phone: 44-1424-733-050
FAX: 44-1424-733-050
email: JFBen@netcomuk.co.uk
web: fireworks.co.uk/fireworks-journal

Fireworks and Stage FX America

Kevin Brueckner
P.O. Box 488
Lakeside, CA 92040-0488, USA
Phone: 619-596-2800
FAX: 619-596-2900
email: go4pyro@aol.com
web: www.fireworksamerica.com

Fireworks Business

Jack Drewes
HC 67 Box 30
Dingmans Ferry, PA 18328-9506, USA
Phone: 717-828-8417
FAX: 717-828-8695
email: afn@98.net
web: www.fireworksnews.com

Fullam's Fireworks, Inc.

Rick Fullam
P.O. Box 1808 CVSR
Moab, UT 84532, USA
Phone: 435-259-2666

Goex, Inc.

Mick Fahringer
PO Box 659
Doyline, LA 71023-0659, USA
Phone: 318-382-9300
FAX: 318-382-9303
email: goexpowder@aol.com
web: www.goexpowder.com

High Power Rocketry

Bruce Kelly
PO Box 970009
Orem, UT 84097-0009, USA
Phone: 801-225-3250
FAX: 801-225-9307
email: 71161.2351@compuserve.com
web: www.tripoli.org

Industrial Solid Propulsion

Gary Rosenfield
1955 S. Palm St. - Ste. 6
Las Vegas, NV 89104, USA
Phone: 702-641-5307
FAX: 702-641-1883
email: garyr@powernet.net
web: aerotech-rocketry.com,
specificimpulse.com,
menceely.net/RCS

Iowa Pyro Supply

Mark Mead
1000 130th St.
Stanwood, IA 52337, USA
Phone: 319-945-6637
FAX: 319-945-0007
email: iowapyro@netins.net
web: www.netins.net/showcase/iowapyrosup

Island Fireworks Co. Inc.

Charles Gardas
N735 825th St.
Hager City, WI 54014, USA
Phone: 715-792-2283
FAX: 715-792-2640
email: islndfwk@presenter.com

Kastner Pyrotechnics & Fireworks Mfg. Co

Jeri Kastner
Rt 3, 938 Logtown Rd.
Mineral Point, WI 53565, USA
Phone: 608-987-4750
FAX: 608-987-4750
email: kastner@mhtc.net

KC's Fireworks Displays

Clive Featherby
P.O. Box 1103
Nambour, QLD, 4560, Australia
Phone: 61-74-468-236
FAX: 61-74-468-456
email: firework@dcc.net.au
web: kcsfireworks.com.au

Lantis Fireworks & Lasers

Ken Lantis
PO Box 491
Draper, UT 84020, USA
Phone: 801-768-2255
FAX: 801-768-2433
email: info@fireworks-lasers.com
web: www.fireworks-lasers.com

Luna Tech, Inc.

Tom DeWille
148 Moon Drive
Owens Cross Roads, AL 35763, USA
Phone: 256-725-4225
FAX: 256-725-4811
email: PyropakUSA@aol.com
web: www.pyropak.com

Marutamaya Ogatsu Fireworks Co., Ltd.

1-35-35 Oshitate Fuchu
Tokyo, 183-0012, Japan
Phone: 81-42-363-6251
FAX: 81-42-363-6252
email: moff@za2.so-net.ne.jp

Mighty Mite Marketing

Charlie Weeth
122 S. 17th St.
LaCrosse, WI 54601-4208, USA
Phone: 608-784-3212
FAX: 608-782-2822
email: chzweeth@pyro-pages.com
web: www.wi.centuryinter.net/chzweeth

Miller Pyrotechnics

Chy Miller
119 North 9th
Sterling, KS 67579, USA
Phone: 316-278-3028
email: millers@awav.net
web: www.oe-pages.com/BIZ/Getrich/pyroman

MP Associates Inc.

P.O. Box 546
Ione, CA 94640, USA
Phone: 209-274-4715
FAX: 209-274-4843

Ontos Pyrotechnics, Inc.

John and Karin Driver
1059 Carter Road
DeLand, FL 32724, USA
Phone: 904-736-8996
FAX: 904-740-0555
email: JWDriver@worldnet.att.net

OXRAL, Inc.

Tom DeWille
P.O. Box 160
Owens Cross Roads, AL 35763, USA
Phone: 256-725-4225
FAX: 256-725-4811
email: oxral@pyropak.com
web: www.oxral.com

Precocious Pyrotechnics

Garry Hanson
4420 278th Ave. N.W.
Belgrade, MN 56312-9616, USA
Phone: 320-346-2201
FAX: 320-346-2403
email: ppinc@midstate.tds.net
web: www.pyro-pro.com

Pyro Shows, Inc.

Lansden Hill
P.O. Box 1406
LaFollette, TN 37766, USA
Phone: 800-662-1331
FAX: 423-562-9171

Pyrodigital Consultants

Ken Nixon
1074 Wranglers Trail
Pebble Beach, CA 93953, USA
Phone: 831-375-9489
FAX: 831-375-5225
email: pyrodig@aol.com
web: www.infinityvisions.com/pyrodigital

PyroLabs, Inc.

Ken Kosanke
1775 Blair Road
Whitewater, CO 81527, USA
Phone: 970-245-0692
FAX: 970-245-0692
email: ken@jpyro.com

Pyrotechnics Guild Int., Inc.

Ed Vanasek, Treas.
18021 Baseline Avenue
Jordan, MN 55352, USA
Phone: 612-492-2061
email: edvanasek@aol.com
web: www.pgi.com

RES Specialty Pyrotechnics

Steve Coman
Route 1, Box 7601
Prior Lake, MN 56011, USA
Phone: 612-873-3113
FAX: 612-873-2859
email: respyro@minn.net

Service Chemical, Inc.

Marvin Schultz
2651 Penn Avenue
Hatfield, PA 19440, USA
Phone: 215-362-0411
FAX: 215-362-2578

**The Show Factory Pty.
Ltd.**

Jack Moeller
Factory 3 / 21 Church Street
Abbotsford, Melbourne,
VIC 3067, Australia
Phone: 61-3-9428-7710
FAX: 61-3-9428-0901
email: pyrohead@onthe.net.au

Skylighter, Inc.

Harry Gilliam
PO Box 480
Round Hill, VA 20142-0480, USA
Phone: 540-554-2228
FAX: 540-554-2849
email: custservice@skylighter.com
web: www.skylighter.com

**Starburst Pyrotechnics &
Fireworks Displays (Pty)**

Bonnie Pon
2nd Floor, Sui Hing Hong
Building - 17 Commissioner St.
Johannesburg
Gauteng 2000, South Africa
Phone: 27-11-838-7704
FAX: 27-11-836-6839
email: starbrst@global.co.za
web: www.artslink.co.za/starburst

Sunset Fireworks Ltd.

Gerald Walker
10476 Sunset Drive
Dittmer, MO 63023, USA
Phone: 636-274-1500
FAX: 636-274-0883
web: www.sunsetfireworks.com

**Sunset Fireworks, Ltd. /
Omaha**

Jack Harvey
2335 South 147th Street
Omaha, NE 68144-2047, USA
Phone: 402-681-5822
FAX: 402-333-9840

**Syd Howard Fireworks
Int'l**

Syd Howard
420 Halcrows Road, Glenorie
Sydney, NSW, 2157, Australia
Phone: 61-29-652-2244
FAX: 61-29-652-1581
email:
mail@sydhowardfireworks.com.au
web:
www.sydhowardfireworks.com.au

Theatre Effects Inc.

Nathan Kahn
642 Frederick St.
Hagerstown, MD 21740, USA
Phone: 301-791-7646
FAX: 301-791-7719
email: nathan@theatrefx.com
web: www.theatrefx.com

Total Pyrotechnics

William McDougall
1728 Cardinal Dr.
Gatlinburg, TN 37738, USA
Phone: 865-430-2653
FAX: 865-453-8254
email: drmc@vic.com

Western Pyrotechnics, Inc.

Rudy Schaffner
2796 Casey Road
Holtville, CA 92250, USA
Phone: 760-356-5426
FAX: 760-356-2051
email: renitad@thegrid.net

Sponsorships

No advertising as such will be printed in the *Journal of Pyrotechnics*. However, a limited number of sponsors will be sought so that the selling price of the Journal can be reduced from the listed cover price. The cost of a corporate sponsorship of the *Journal of Pyrotechnics* is \$70 per issue. In addition to a listing in the Sponsor section of the Journal, you receive two free copies of the sponsored Journal and a brief listing on a flyer inserted under the transparent cover of the Journal.

Additionally, if you so desire, we will provide a link from the Journal of Pyrotechnics Web Site to sponsors' web site, e-mail address or simply a company name, address and phone information listing. If you would like to be a sponsor contact the publisher.

Guide for Authors

Style Guide

The *Journal of Pyrotechnics* has adopted the *ACS Style Guide* [ISBN 0-8412-3462-0]. It is not necessary that authors have a copy; however, a copy can be ordered through a local bookstore.

Manner of Submission

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 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 2000, 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)].

Editing

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.

More Information

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

or
email bonnie@jpyro.com