

Journal of Pyrotechnics

Issue Number 3, Summer 1996

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CAUTION

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

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

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Publication Frequency

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

Subscriptions

Subscriptions as such do not exist for the *Journal of Pyrotechnics*. 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.

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

Editorial Policy

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

Electric Spark Sensitivity of Reductive Element–Oxidizer Mixtures

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ABSTRACT

Electric spark sensitivities were determined for mixtures of a reductive element and an oxidizer using three types of testers. One tester is a simplified electric spark tester which distinguishes high-sensitivity energetic materials from medium- or low-sensitivity materials. The other two testers determine the 50% ignition energies; one, for high-sensitivity materials, and the other for medium-sensitivity materials.

Typically the reductive elements give the following order of decreasing sensitivity when mixed with oxidizers: $Zr > P > B > Al > Mg > S > Si$. Without any other oxidizer present, Zr and P are high-sensitivity materials in air. The other elements do not ignite without oxidizer present in the apparatus used. The results from the simplified tester agree with results from the tester for high-sensitivity materials; however, some do not agree with those obtained from the tester for medium-sensitivity materials. This is partly attributed to the difference in the way the samples are confined in the apparatus. Correlations were also examined between the results of

the electric spark tester and results from both the drop ball test and the friction test.

Keywords: reductive element, fuel, oxidizer, electric spark sensitivity

1. Introduction

In fireworks, mixtures of a reductive element and an oxidizer have been used for producing pyrotechnic effects such as light, color, smoke and propulsion.^[1] Mixtures of reductive elements and oxidizers are sometimes highly sensitive to impact, friction, heat or electric spark.

One of the authors of this paper has previously developed two electric spark testers, one for medium-sensitivity and the other for high-sensitivity energetic materials.^[2] The two testers have been used for evaluating the electric spark sensitivities of primary explosives, secondary high explosives, pyrotechnic compositions and mixtures of oxidizers and combustible materials.^[3] Recently, Hosoya Kako Company developed a new simplified electric spark tester^[4]

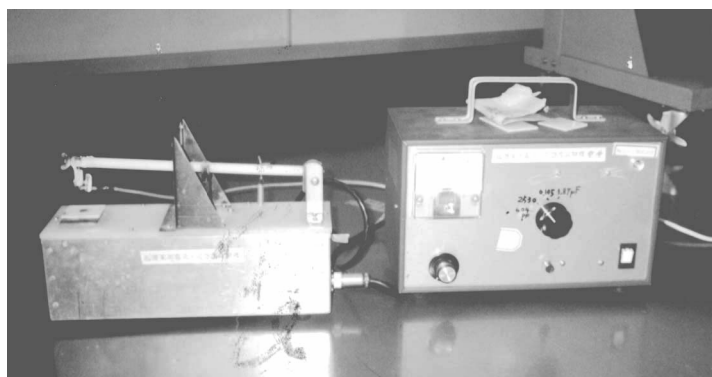


Photo 1. The tester for high-sensitivity materials.

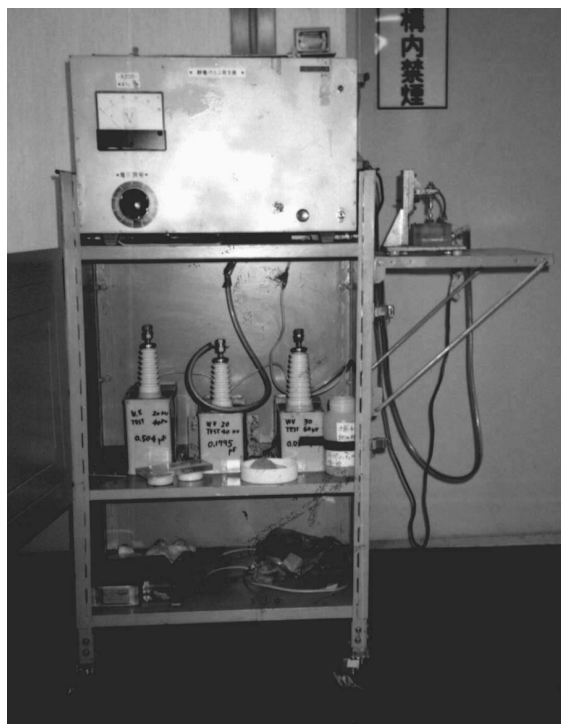


Photo 2. The tester for medium-sensitivity materials.

intended for use by manufacturers of fireworks to assess the safety of materials.

We have collected data on the electric spark sensitivity of mixtures of reductive elements and oxidizers using the three tests mentioned above and have examined the relationships between the results from the different testers. We have also examined the correlations between the BAM

friction sensitivities and the electric spark sensitivities of the mixtures determined with the drop ball. Herein we describe the results of our experiments on the electric spark sensitivity of mixtures of reductive elements and oxidizers.

2. Experimental

2.1 Materials

The reductive elements examined are red phosphorus (P), zirconium (Zr), sulfur (S), magnesium (Mg), aluminum (Al), silicon (Si), and boron (B).

The oxidizers studied are potassium perchlorate (KClO_4), potassium chlorate (KClO_3), potassium nitrate (KNO_3), barium nitrate ($\text{Ba}(\text{NO}_3)_2$), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$), copper(II) oxide (CuO), lead(II) nitrate ($\text{Pb}(\text{NO}_3)_2$), lead(IV) oxide (PbO_2), red lead (Pb_3O_4), iron(III) oxide (Fe_2O_3), calcium peroxide (CaO_2) and barium peroxide (BaO_2). All of the samples are in the form of powder; the elements and oxidizer are manually mixed together on parchment.

2.2 Apparatus

The three testers are shown in Photos 1–3, their electric circuits are shown in Figures 1–3, and the electrode discharge assemblies are shown in Figures 4–6. The simplified tester is used for distinguishing high-sensitivity materials from the medium- and low-sensitivity materials. This tester has fixed output energy (ca. 50 mJ), fixed

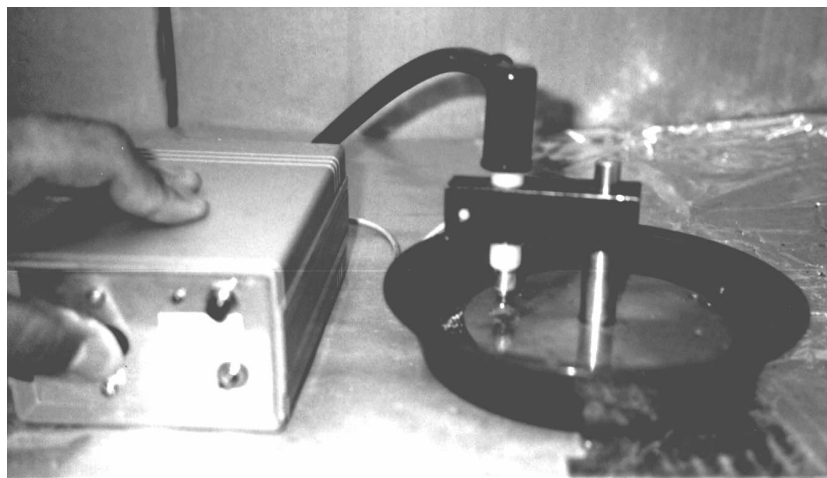


Photo 3. The simplified tester.

bar-plate electrodes, and an open sample holder. The distance between the electrodes is 2 mm. The amount of sample is approximately 5 mg, which is determined by considering the violence of the reaction. This tester can also be used to screen materials before the other two testers are used.

The tester for high-sensitivity materials is used for evaluating the sensitivities of primary explosives, igniter compositions, and highly sensitive pyrotechnic compositions. The tester has variable capacitance energies (8.0×10^{-6} to 8.0×10^{-1} J), movable needle-plate electrodes,

and holds approximately 10 mg of sample in an open well.

The tester for medium-sensitivity materials is used for secondary explosives, propellants, gas generators, intermediately sensitive pyrotechnic compositions, and self-reductive chemicals. The tester has large capacitance energies (1.0×10^{-2} – 82 J), confined fixed-bar electrodes, and can hold a 30 mg sample in a sealed PVC tube. The outside diameter of the tube is 5 mm, and the distance between the electrodes is fixed at 1.5 mm.

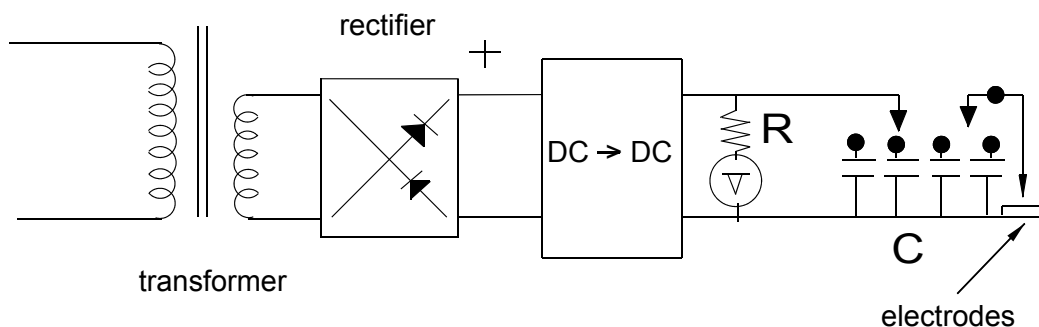


Figure 1. The electric circuit of the tester for high-sensitivity materials.

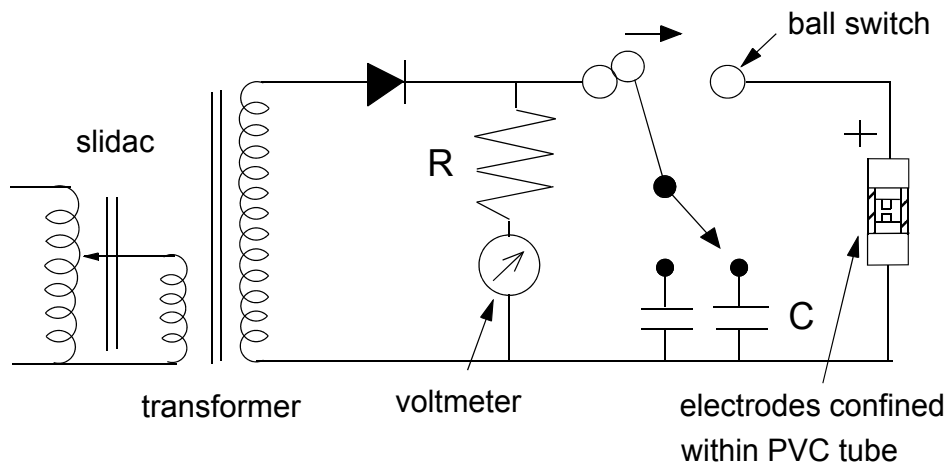


Figure 2. The electric circuit of the tester for medium-sensitivity materials.

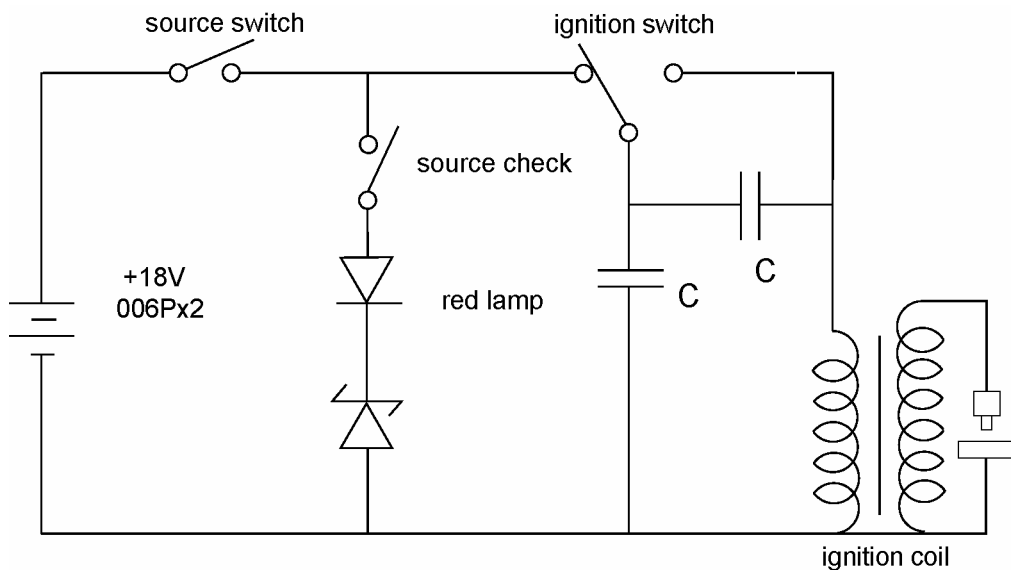


Figure 3. The electric circuit of the simplified tester.

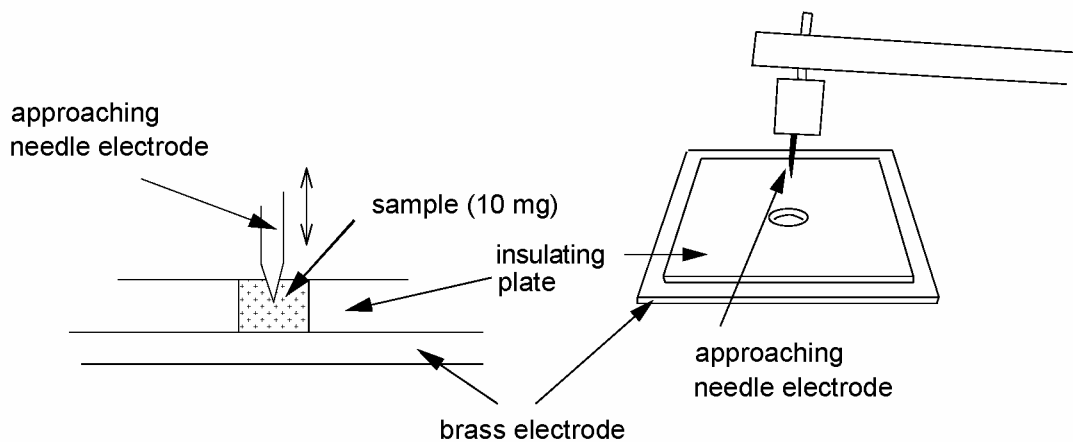


Figure 4. The discharge electrode assembly of the tester for high-sensitivity.

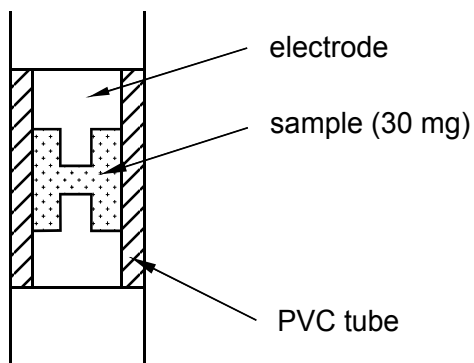


Figure 5. The discharge electrode assembly of the tester for medium-sensitivity.

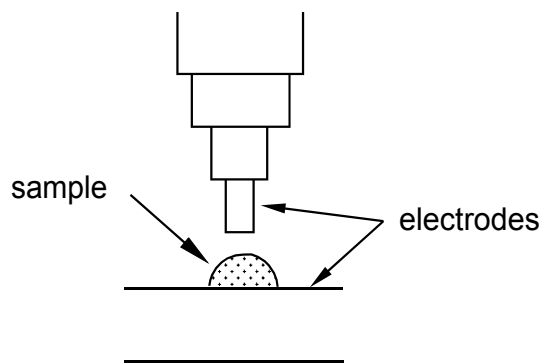


Figure 6. The discharge electrode assembly of the simplified tester.

2.3 Procedure

2.3.1 The Simplified Tester

- (1) Put about 5 mg of sample on the lower electrode plate.
- (2) Set the upper electrode bar above the sample.
- (3) Switch on the power source.
- (4) Push the check button to confirm the source voltage.
- (5) After the count down, push the ignition button to discharge the electrodes.
- (6) Repeat the trial 10 times on a different area of the lower electrode plate.
- (7) After 10 trials, clean both electrodes with sandpaper.
- (8) Noise, flame and smoke are judged as positive results.
- (9) Results are expressed as the number of positive results ("O" in tables; "go" on graphs) out of 10 trials; (negative results are "x" or "no go").
- (10) Qualitative assessment of the relative violence of a reaction in this test is also valuable information.

2.3.2 The Tester for High-Sensitivity Materials

- (1) Weigh 10 mg of sample and put it in the hole of the lower electrode.
- (2) Switch on the power source.
- (3) Set the capacitance dial to an appropriate capacitance.
- (4) Set the voltage dial to an appropriate voltage.
- (5) Push the ignition button.
- (6) Ignition occurs if explosion, combustion or smoke is visible.
- (7) Repeat the test 20 times according to Bruce-ton's up-and-down method.

- (8) Confirm the voltage decreased to zero.
- (9) Clean the electrodes with sandpaper and cloth after every run.
- (10) Treat the resultant data by Bruce-ton's method.

2.3.3 The Tester for Medium-Sensitive Materials

- (1) Select appropriate condensers and connect them.
- (2) Put 30 mg of sample into the PVC tube set on the lower electrode.
- (3) Switch on the power source.
- (4) Adjust the voltage to the appropriate level using the voltage dial.
- (5) Push the ignition button to discharge a spark at the sample.
- (6) Ignition is judged to occur if the PVC tube ruptures, if noise is heard, or if the sample disappears.
- (7) Conduct 20 trials according to Bruce-ton's method.
- (8) Allow the discharge bar to contact the ball switch to discharge any residual electricity.
- (9) Clean the electrodes with sandpaper and tissue paper after every trial.
- (10) Treat the resultant data by Bruce-ton's method.

3. Results

3.1 The Simplified Tester

Examples of the treatment of data from the simplified tester are shown in Table 1. The final results from the tester are listed in Table 2. The E_{50} value is the 50% ignition energy determined by the testers for high- and medium-sensitivity materials.

Table 1. Examples of the Treatment of the Data by the Simplified Tester.

Sample	Run										Ignition /10	Observation
	1	2	3	4	5	6	7	8	9	10		
P/KClO ₄	○	○	○	○	○	○	○	○	○	○	10/10	Explosion
Al/KClO ₄	○	○	×	○	×	○	○	×	○	○	7/10	Flash
S/KNO ₃	×	×	×	×	×	×	×	×	×	×	0/10	No reaction

Table 2. Results from the Simplified Tester and E₅₀ Values from the Other Testers.

Sample	Ignition /10	Observation	Sensitivity	E ₅₀ (J)	Type of Tester
Zr	10/10	combustion	high	7.6×10 ⁻⁵	High
Zr/KClO ₄	10/10	flash, smoke	high	2.6×10 ⁻⁴	High
Zr/CaO ₂	0/10		not high	3.2×10 ⁻¹	Medium
Si	0/10		not high	82<	Medium
Si/BaO ₂	0/10		not high	2.1×10 ⁻¹	Medium
Si/CaO ₂	0/10		not high	29	Medium
B	0/10		not high	82<	Medium
B/KNO ₃	0/10		not high	1.1	Medium
B/Pb(NO ₃) ₂	0/10		not high	4.9×10 ⁻²	Medium
B/CaO ₂	0/10		not high	3.8	Medium
B/KClO ₃	0/10		not high	3.7×10 ⁻²	Medium
S	0/10		not high	82<	Medium
S/BaO ₂	0/10		not high	9.3×10 ⁻¹	Medium
S/Ba(NO ₃) ₂	0/10		not high	9	Medium
S/KClO ₃	0/10		not high	1.4	Medium
Mg	0/10		not high	82<	Medium
Mg/KClO ₄	0/10		not high	6.4×10 ⁻¹	Medium
Mg/CaO ₂	0/10		not high	1.4	Medium
Mg/CuO	0/10		not high	8.3×10 ⁻¹	Medium
Al	0/10		not high	82<	Medium
Al/KClO ₄	7/10	flash, smoke	high	1.8×10 ⁻¹	Medium
Al/BaO ₂	1/10	fire	high	1.9×10 ⁻²	High
Al/Ba(NO ₃) ₂	0/10		not high	7.4×10 ⁻¹	Medium
Al/CaO ₂	0/10		not high	1.2×10 ⁻¹	Medium
Al/KClO ₃	2/10	flash	high	4.9×10 ⁻¹	High
P	10/10	combustion, smoke	high	5.6×10 ⁻³	High
P/KClO ₄	10/10	fire, smoke	high	2.7×10 ⁻²	High
P/KNO ₃	10/10	fire, smoke	high	2.8×10 ⁻²	High
P/BaO ₂	10/10	fire, smoke, flash	high	2.9×10 ⁻¹	High
P/Ba(NO ₃) ₂	10/10	flash, fire	high	5.6×10 ⁻¹	High
P/Pb(NO ₃) ₂	8/10	fire, smoke	high	2.5×10 ⁻²	High
P/CaO ₂	10/10	flash	high	2.2×10 ⁻¹	High
P/KClO ₃	10/10	sound, fire, smoke	high	9.1×10 ⁻³	High
P/CuO	10/10	fire, smoke	high	7.8×10 ⁻³	High
P/Pb ₃ O ₄	10/10	fire, smoke	high	2.6×10 ⁻²	High
P/PbO ₂	10/10	fire, smoke	high	1.8×10 ⁻²	High

* Columns headed Ignition, Observation and Sensitivity show results from the simplified tester.

** Columns headed E₅₀(J) and Type of Tester list results from the other two testers.

3.2 Testers for High- and Medium-Sensitivity Materials

The data from both of these testers is treated in the same fashion. An example is shown in

Table 3. Figure 7 shows a plot of the sensitivities of the reductive element and the element-oxidizer mixtures determined by the two testers.

Table 3. An Example of Data Treatment for Red Phosphorus.

Sample: red phosphorus	Capacitance: 0.098 μ F
Mass: 5 mg	Increment of logV: 0.1
Tester: high-sensitivity	Observation: combustion

Data from the up-and-down method: 20 trials (O = go X = no go)

logV		O	X
2.75	O	1	0
2.65	O O X X	3	1
2.55	O O X X O X	4	3
2.45	O O X X X X	2	4
2.35	X X	0	2
		10	10

Data treatment

logV	V(v)	E(J)	n(O)	i	i · n	i ² · n
2.75	560	0.015	1	0	0	0
2.65	450	0.010	3	1	3	3
2.55	355	0.006	4	2	8	16
2.45	280	0.004	2	3	6	18
2.35	220	0.002	0	4	0	0
			Ns=10		A=7	B=37

Results

logV ₅₀ = 2.53
V ₅₀ = 338.8 (V)
σ_v = 0.14
logE ₅₀ = -2.25
E ₅₀ = 0.0056 (J)
σ_E = 0.27

Table 4. List of the Electric Spark Sensitivities Determined with Testers for High-and Medium-Sensitivity Materials.

Sample	Tester	Mass (mg)	LogE ₅₀	σ _E
P	High	3	-2.25	0.27
P/KClO ₄	High	3	-1.57	0.08
P/KNO ₃	High	3	-1.55	0.06
P/BaO ₂	High	3	-0.54	0.44
P/Ba(NO ₃) ₂	High	3	-0.26	0.07
P/Pb(NO ₃) ₂	High	3	-0.61	0.16
P/CaO ₂	High	3	-0.66	0.43
P/KClO ₃	High	3	-2.04	0.15
P/CuO	High	3	-2.11	0.15
P/Pb ₃ O ₄	High	3	-1.59	0.09
P/PbO ₂	High	3	-1.75	0.43
Zr	High	10	-4.12	0.23
Zr/KClO ₄	High	10	-3.58	0.1
Zr/KNO ₃	High	10	-3.79	0.08
Zr/BaO ₂	High	5	-4.26	0.35
Zr/Ba(NO ₃) ₂	High	5	-2.54	0.23
Zr/Pb(NO ₃) ₂	High	5	-3.42	0.22
Zr/CaO ₂	Medium	5	-0.49	0.14
Zr/KClO ₃	High	5	-1.96	0.33
Zr/CuO	High	5	-3.88	0.06
Zr/Pb ₃ O ₄	High	5	-4.62	0.35
Zr/PbO ₂	High	5	-3.84	0.14
B	Medium	30	>1.9	—
B/KClO ₄	Medium	30	-1.3	0.08
B/KNO ₃	Medium	30	0.06	0.19
B/BaO ₂	High	5	-2.48	0.37
B/Ba(NO ₃) ₂	Medium	30	1.42	0.18
B/Pb(NO ₃) ₂	Medium	30	-1.31	0.19
B/CaO ₂	Medium	30	0.58	0.18
B/KClO ₃	Medium	30	-1.43	0.15
B/CuO	High	5	-1.59	0.09
B/Pb ₃ O ₄	Medium	30	1.33	0.15
B/PbO ₂	High	5	-3.62	0.15
Al	Medium	30	>1.9	—
Al/KClO ₄	Medium	10	-0.76	0.15
Al/KNO ₃	Medium	10	0.25	0.16
Al/BaO ₂	High	3	-1.73	0.11
Al/Ba(NO ₃) ₂	Medium	30	-0.13	0.21
Al/Pb(NO ₃) ₂	Medium	30	1.28	0.3

Table 4. List of the Electric Spark Sensitivities Determined with Testers for High-and Medium-Sensitivity Materials. (Continued)

Sample	Tester	Mass (mg)	LogE ₅₀	σ _E
Al/CaO ₂	Medium	10	-0.93	0.33
Al/KClO ₃	High	5	-0.31	0.16
Al/CuO	Medium	10	-0.83	0.18
Al/Pb ₃ O ₄	Medium	20	-0.31	0.15
Al/PbO ₂	Medium	20	-0.81	0.15
Mg	Medium	30	>1.9	—
Mg/KClO ₄	Medium	10	-0.19	0.04
Mg/KNO ₃	Medium	10	0.67	0.14
Mg/BaO ₂	Medium	20	0.97	0.3
Mg/Ba(NO ₃) ₂	Medium	20	0.57	0.28
Mg/Pb(NO ₃) ₂	Medium	30	0.39	0.16
Mg/CaO ₂	Medium	30	0.15	0.08
Mg/KClO ₃	Medium	30	-1.37	0.16
Mg/CuO	Medium	30	-0.08	0.23
Mg/Pb ₃ O ₄	Medium	30	1.68	0.08
Mg/PbO ₂	Medium	30	-0.08	0.27
Si	Medium	30	>1.9	—
Si/KClO ₄	Medium	30	1.14	0.14
Si/KNO ₃	Medium	30	1.05	0.07
Si/BaO ₂	Medium	30	-0.68	0.3
Si/Ba(NO ₃) ₂	Medium	30	1.25	0.15
Si/Pb(NO ₃) ₂	Medium	30	1.72	0.09
Si/CaO ₂	Medium	30	1.46	0.14
Si/KClO ₃	Medium	30	1.36	0.27
Si/CuO	Medium	30	1.58	0.33
Si/Pb ₃ O ₄	Medium	30	>1.9	—
Si/PbO ₂	Medium	30	1.9	—
S	Medium	30	>1.9	—
S/KClO ₄	Medium	30	1.26	0.29
S/KNO ₃	Medium	30	1.24	0.08
S/BaO ₂	Medium	30	-0.03	0.14
S/Ba(NO ₃) ₂	Medium	30	0.95	0.22
S/Pb(NO ₃) ₂	Medium	30	1.09	0.08
S/CaO ₂	Medium	30	1.07	0.31
S/KClO ₃	Medium	30	0.15	0.15
S/CuO	Medium	30	1.69	0.09
S/Pb ₃ O ₄	Medium	30	1.67	0.08
S/PbO ₂	Medium	30	1.54	0.22

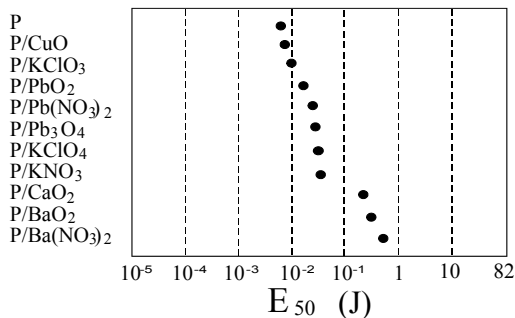


Figure 7(A). Plot of sensitivities of red phosphorus and red phosphorus-oxidizer mixtures.

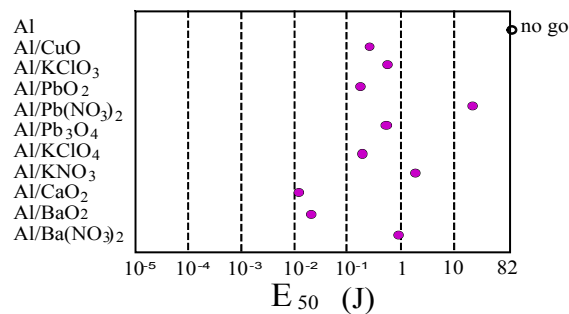


Figure 7(D). Plot of sensitivities of aluminum and aluminum-oxidizer mixtures.

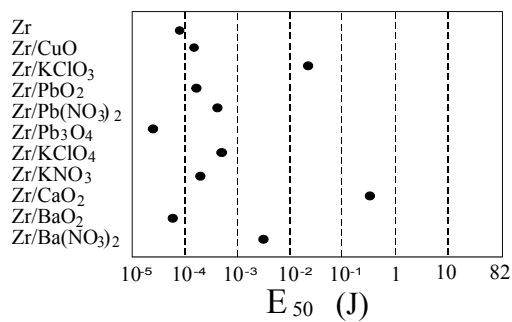


Figure 7(B). Plot of sensitivities of zirconium and zirconium-oxidizer mixtures.

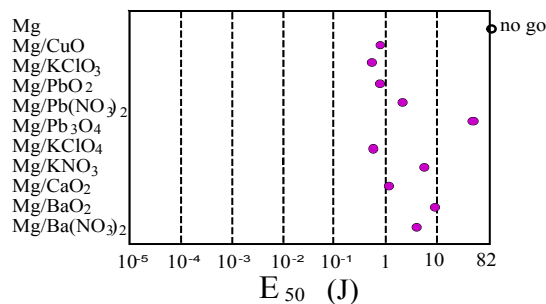


Figure 7(E). Plot of sensitivities of magnesium and magnesium-oxidizer mixtures.

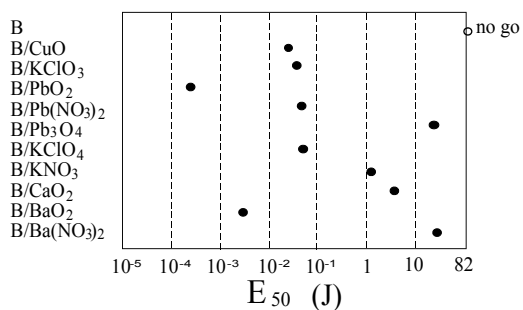


Figure 7(C). Plot of sensitivities of boron and boron-oxidizer mixtures.

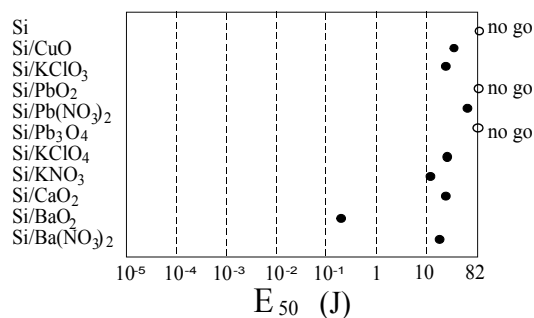


Figure 7(F). Plot of sensitivities of silicon and silicon-oxidizer mixtures.

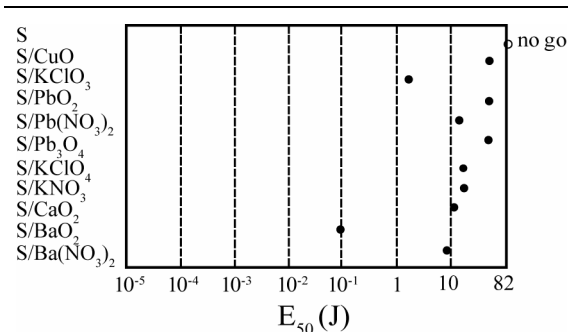


Figure 7(G). Plot of sensitivities of sulfur and sulfur-oxidizer mixtures.

4. Discussion

4.1 Electric Spark Sensitivities of the Reductive Elements Alone

Only zirconium and red phosphorus powders ignite in the tester for high-sensitivity materials in the absence of added oxidizer. The other reductive elements (Al, B, Mg, Si and S) were not ignited in air at room temperature by an 82 J electric spark in the tester for medium-sensitivity materials.

The spark sensitivity of red phosphorus decreases when the element is mixed with any of the oxidizers, which suggests the oxidizers act as inert diluents for red phosphorus. In the case of Zr, only Pb₃O₄ and BaO₂ activate it for ignition; the other oxidizers deactivate Zr. The other reductive elements are all activated when mixed with the oxidizers.

4.2 Electric Spark Sensitivities of Element-Oxidizer Mixtures by the Two Conventional Testers

Among the mixtures examined, most Zr mixtures show the highest sensitivities. Therefore, the Zr-KClO₄ composition with a value of $\log E_{50} = -3.6$ is used as an igniter instead of trinitrate, the E_{50} value of which is -4.4 in the same tester.

The sensitivities of the red phosphorus-oxidizer mixtures are the next highest. The range of sensitivities of these mixtures is rather small: from 0.01 to 1.0 J. In these mixtures, CaO₂, BaO₂, and Ba(NO₃)₂ seem to act as ignition retardants.

In all the mixtures of elements other than Zr and P, oxidizers act as promoters for the spark

ignition of the elements. BaO₂ is the most effective for increasing the sensitivities of many elements but was ineffective for Mg. The most effective oxidizer for increasing the sensitivity of Mg was KClO₃.

Among Al, B, Mg, S and Si mixtures with the oxidizers, B gave the highest sensitivity with BaO₂, then Al with BaO₂, Mg with KClO₃, Si with BaO₂, and S with BaO₂. On the average, the order of decreasing sensitivity of these elements when mixed with oxidizers is: Zr > P > B > Al > Mg > S > Si.

4.3 Deviation in Test Results

The average standard deviations (σ) in the values of $\log E_{50}$ from the electric spark tests are 0.18 for medium-sensitivity materials and 0.20 for high-sensitivity materials. These deviations are similar to those found in the visual small gap test, the shock ignitability test, the small drop ball test, the drop hammer test, and the BAM friction test.^[6-8]

4.4 Comparison of the Results of the Simplified Tester and the Two Conventional Testers

Data from the three testers are plotted in Figure 8.

The materials identified as high-sensitivity by the tester for high-sensitivity were also all identified as high-sensitivity materials by the simplified tester. Most of the materials classified as not highly sensitive by the simplified tester were placed in the medium-sensitivity category by the tester for medium-sensitivity materials.

The output energy of the simplified tester is fixed at ca. 50 mJ. The correlations shown in Figure 8 are reasonable.

However some mixtures do not ignite in the simplified tester even though they have an E_{50} value lower than 0.8 J as determined in the tester for medium-sensitivity materials. It has recently been shown that the values of E_{50} measured by the tester for high-sensitivity materials are larger than those measured by the tester for medium-sensitivity materials as listed in Table 5.^[3]

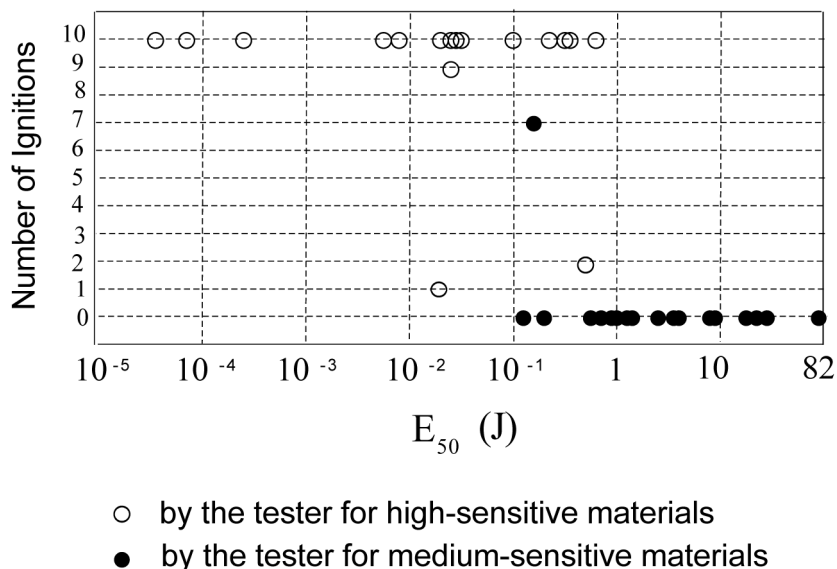


Figure 8. Plot of the number of ignitions in the simplified tester against E_{50} from the two conventional testers.

Table 5. Comparison of Values of E_{50} as Measured by Two Testers.

Materials	Log E_{50}		Difference
	high	medium	
Pb(N ₃) ₂ /dextrin	-0.95	-1.64	0.96
tetrazene/starch(50/50)	-0.65	-1.75	1.07

The difference in the results from the two testers may be partly explained by the different ways the sample is contained. The sample in the simplified tester is put on a plate, and the sample in the high-sensitivity tester is placed in an open well. Part of the discharge energy escapes into the surroundings. Therefore the efficiency of the spark discharge in the two testers may be lower than in the tester for medium-sensitivity materials, in which the sample is confined in a PVC tube with the upper and lower electrodes inserted in it. The confinement may also accelerate the rise in pressure, the accumulation of heat, and the ignition of the sample.

4.5 Correlations of Electric Spark Sensitivities with Impact and Friction Sensitivities

Among the different drop weight tests, the direct impact drop ball test gives the lowest E_{50} values for material with the same energy ratings. The correlation between the results of the electric spark test and the drop ball test is shown in Figure 9.^[6] The values of E_{50} from the drop test and the spark test are similar for medium-sensitivity materials such as RDX, HMX and black powder, and also for some high-sensitivity materials such as red phosphorus-oxidizer mixtures. This indicates that the efficiency of the added energy is nearly the same for these materials in both tests. For high-sensitivity materials such as pure Pb(N₃)₂, trichinate and Zr-KClO₄, the energy efficiency is much lower for the drop ball test than for the spark test.

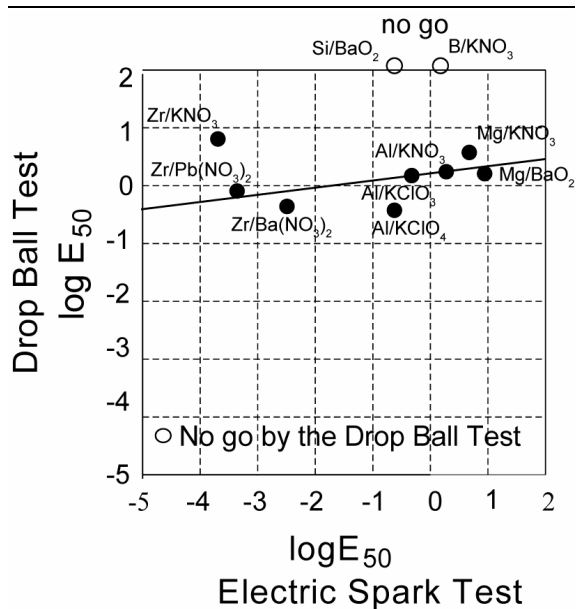


Figure 9. Correlation between values from the electric spark test and the direct drop ball test.

Correlation in the data from the electric spark test and the BAM friction test^[7] are shown in Figure 10. The results are similar to those from drop ball and electric spark test.

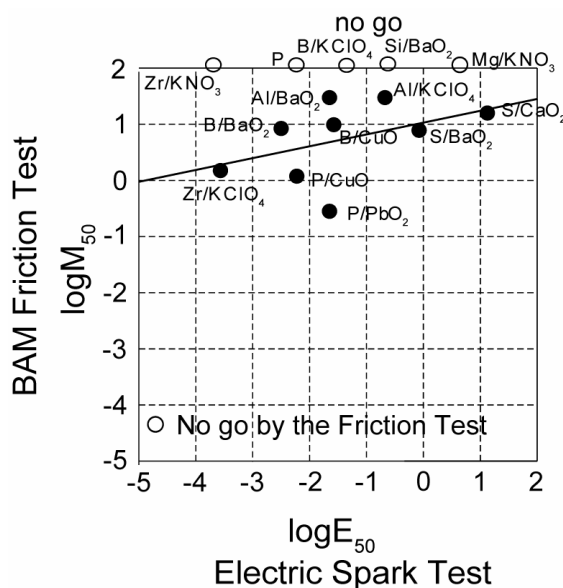


Figure 10. Correlation between values from the electric spark test and the friction test.

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Health Effects from Theatrical Pyrotechnics

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ABSTRACT

Theatrical pyrotechnics are potentially capable of creating ear-damaging sound, eye-damaging light, and airborne toxic chemicals. While damage to the ears and eyes can be dramatic and obvious, potential health problems from inhalation of the smoke are not so easily addressed. The problem is further complicated by the variety of locations in which pyrotechnics are used. A few examples are theaters, theme parks, outdoor arenas, and both indoor and outdoor movie and TV filming locations.

For these reasons, this article will consider the hazards of chemicals used in consumer fireworks, specialized indoor theatrical effects and professional outdoor effects. The article also will include material that is well-known to pyrotechnicians since readers from the theatrical and entertainment industries may find this background information helpful.

Keywords: theater, pyrotechnics, entertainment, health, toxicity, safety, smoke

Introduction

My interest in pyrotechnics began in earnest in January of 1987 when I spoke at the "Health and Safety Conference on Personal Protection and Pyrotechnic Training" hosted by the Yale School of Drama's Department of Technical Design and Production. My talk on potentially toxic and irritating emissions from pyrotechnic products was met with skepticism until the demonstration of indoor effects at the end of the conference. Then a steady crescendo of coughing from the audience made the point effortlessly.

Pyrotechnic Hazards

When indoor and outdoor pyrotechnic effects are used in close proximity to performers and shooters, there is no question that the chemicals in the smoke can be harmful. What is not clear is whether these chemicals are present in significant quantities in theatrical venues to affect health. This issue is not likely to be settled soon since I am unaware of any studies of performers exposed to indoor and outdoor pyrotechnics currently underway.

The only studies I could find from the past were two very limited ones done in 1981 and 1982, both of which are discussed in a National Institute for Occupational Safety and Health (NIOSH) health hazard evaluation report related to pyrotechnics used at the MGM Grand Hotel and Casino in Las Vegas.^[1a]

The MGM Grand Hotel Studies

In 1981, the Nevada Department of Occupational Safety and Health (DOSH) responded to worker complaints about smoke from pyrotechnics used in the show, Jubilee, in the Ziegfeld Showroom of the MGM Grand Hotel in Las Vegas. DOSH tested the air and found that the airborne particulates in the smoke consisted of several chemicals some of which were alkaline. There were no industrial standards that applied to any of these chemicals. DOSH then could only apply the Occupational Safety and Health Administration (OSHA) nuisance dust standard to their findings. This standard allows workers to be exposed to 15 milligrams per cubic meter (mg/m^3) of ordinary-sized nuisance dust particles, and to $5 \text{ mg}/\text{m}^3$ of respirable dust (particles under 10 microns in diameter).

The NIOSH researchers point out that this $15 \text{ mg}/\text{m}^3$ standard is not sufficiently protective,

especially for substances that are alkaline.^[1b] In addition, the majority of the particulates from pyrotechnics are likely to be very small and should be regulated by the respirable dust standard. However, DOSH researchers sampled without characterizing particle size, the total dust standard was not exceeded, and DOSH could take no further action.

Then in 1982, NIOSH received a request from a local union to evaluate complaints of respiratory difficulties, sinus problems, eye irritation, and nausea among the approximately 150 stagehands, wardrobe attendants, and performers at the same show. Arrangements were made for a NIOSH physician to interview a self-selected group of 16 workers. Based on the information obtained during these interviews and from contacts with the workers' private physicians following the interviews, an Interim Report was sent to all concerned parties. The report suggested that the cases of respiratory problems and bronchitis found among the workers indicated that a health hazard did exist in the show.

NIOSH proposed further study including air sampling, but MGM refused to allow NIOSH to make a site visit. (NIOSH is not a regulatory agency and needs the employer's permission to enter the workplace.) In addition, the manufacturers of the pyrotechnic materials would only supply NIOSH with the "general composition of the various types of mixtures used and the expected decomposition products"^[1c] because their products were considered trade secrets. From the limited available data, NIOSH concluded in their Final Report that:

There is a health hazard due to the alkaline dust produced by the pyrotechnics in the "Jubilee" show. There is also a possibility that the potassium sulfate which is probably present in the smoke is at least in part responsible for the bronchitis. A 10% incidence of respiratory problems, some being a bronchitis, is excessively high. This represents a minimum incidence although all of the more serious cases may be included in this sample. The rashes mentioned by wardrobe attendants and performers may also be due in part to the alkaline dust.^[1d]

The report caused MGM to modify pyrotechnic use during the show and to allow the use of respirators by some of the stage hands. A

NIOSH follow-up telephone survey of the workers previously interviewed confirmed that the changes MGM made improved conditions.

What Is in the Smoke?

It is difficult to determine the chemical composition of pyrotechnic emissions. Books on pyrotechnic chemistry have examples of neatly balanced chemical reactions that are predicted to occur when you mix part-A with part-B and ignite. In practice, the reactions are not this simple. Pyrotechnic ingredients are not pure chemicals. In addition, most theatrical pyrotechnic products are highly modified and adulterated to produce colored smoke, flash, "flutter," or other special effects.

For example, the NIOSH researchers in the MGM Grand study showed that the solid decomposition products seen as smoke or found settled on surfaces as a fine gray dust consisted of a complex mixture of aluminum and titanium oxides, strontium carbonate, carbon, strontium chloride, potassium chloride, potassium sulfate, strontium hydroxide and potassium carbonate. Clearly, the metals involved in the reaction formed many different combinations with oxygen, carbon, and chlorine. The presence of strontium suggests the mixture was modified for effect.

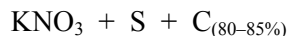
When asked about the gasses released by the pyrotechnic mixture used at the MGM Grand, the pyrotechnic manufacturer referred NIOSH to studies of high quality commercial black powder which showed that primarily nontoxic gases like nitrogen and carbon dioxide were produced on combustion.

However, the composition of the dust from the MGM effects and the MSDSs indicate that they were certainly not anything like simple black powder. It is more likely that the MGM effects produced sulfur oxides, nitrogen oxides, carbon monoxide, hydrogen sulfide, and more.

What Are Pyrotechnics Made of?

The oldest pyrotechnic material probably is gunpowder, a variety of what is known as *black powder* or *blasting powder*. In these products, all the substances necessary for the reaction are premixed together and ready for ignition. In general, they are:

potassium nitrate + sulfur + charcoal



If this reaction were ideal, the resulting "smoke" solids would be potassium compounds and the gases released would be primarily nitrogen and carbon dioxide. However, most gunpowder and black powder explosions also produce hydrogen sulfide, sulfur oxides, carbon monoxide, and methane.^[2]

Powder for theatrical gunfire also can be modified for effect. Adding more carbon produces more visible gunsmoke that simultaneously creates more carbon monoxide and respirable particulates. If aluminum and/or magnesium metals in powdered form are added, the resulting powder also produces aluminum and magnesium compounds.

Modification for Effects and Color

Other types of indoor and outdoor pyrotechnics can be modified by the addition of many substances. "Sparkling" effects are produced when particles of various metals or alloys are added. Color may be produced when compounds containing certain metals are added. Table 1

contains a partial list of the chemicals that will allow various pyrotechnic mixtures to create colored flame or flash effects.

Colored smokes can be produced by adding an organic chemical dye to a pyrotechnic mixture that volatilizes the dye but does not decompose it. The complex organic dyes used for smoke are of low acute toxicity, but some, especially the anthraquinones, are probably carcinogens.

The National Toxicology Program (NTP) has slated six natural and synthetic anthraquinone dyes and intermediates for study to determine if the entire class is suspect.^[3] Four have been studied and found to cause cancer: 1-amino-2,4-dibromoanthraquinone (CAS 81-49-2),^[3] 2-aminoanthraquinone (CAS 117-79-3)^[4a] and 1-amino-2-methylanthraquinone (CAS 82-28-0),^[4b] and Disperse Blue 1 which is 1,4,5,8-tetraaminoanthraquinone (CAS 2475-45-8).^[5] And this year, NTP proposed listing 1,8-dihydroxyanthraquinone (CAS 117-10-2) in the ninth report as "reasonably anticipated to be a human carcinogen."^[6]

Another smoke dye that is not an anthraquinone also may be a carcinogen. It has several names including CI Solvent Yellow 33, Quinoline yellow, and D&C Yellow No. 11 and has showed some evidence of carcinogenic effects in both sexes of rats.^[7]

Some dyes are also likely to partially break down to release toxic chemicals such as aniline during the reaction or during metabolism in the body if inhaled. Some of these dyes and other smoke colorants are listed in Table 2.

Table 1. Flash and Flame Colorants.

Red	Strontium compounds (e.g., nitrate, carbonate, sulfate)
Orange	Calcium compounds (e.g., carbonate, sulfate)
Yellow	Cryolite (sodium aluminum fluoride), sodium compounds (e.g., nitrate, oxalate, sulfate)
Green	Barium compounds (e.g., nitrate, carbonate, sulfate, chlorate), borax
Blue	Copper compounds (e.g., carbonate, chloride, oxide, oxychloride) cupric acetoarsenite*
Violet	Potassium nitrate, lithium chloride

* also called Paris Green (used in some foreign and commercial fireworks)

Table 2. Smoke Colorants.

Orange	CI Pigment Orange 7 [15530]* a monoazo dye CI Solvent Orange 86 [58050],* an anthraquinone dye (also used in emergency orange smoke flares)
Green	CI Solvent Green 3 [61565],* an anthraquinone dye
Red	CI Disperse Red 9 [60505], an anthraquinone dye Safranin: any of nine Basic dyes in the phenylsafranin class [50200-50375]*
Violet	1, 4-diamino-2, 3-dihydroanthraquinone (an anthraquinone related to CI Disperse Violet 1) Iodine in various compounds (probably not used today except by some stage magicians for small effects)
Yellow	CI Vat Yellow 4 [59100]* CI Solvent Yellow 33 [47000]* also called "Quinoline yellow" and D&C Yellow 11 CI Basic Yellow 2 [41000]* also called "auramine" Arsenic disulfide (realgar — used in some foreign and commercial fireworks)
White	Phosphorus, inorganic chloride such as ammonium chloride or zinc chloride.

* These dyes are identified by their Color Index (CI) names and [constitution numbers]. This internationally accepted method of classification enables readers to look up the dye's chemical structure.

Pyrotechnic Chemical Classes and Their Emissions

Hundreds of chemicals can be used in indoor and outdoor pyrotechnics. Each chemical has one or more functions in the chemical reactions that occur on combustion. Most common pyrotechnic mixtures consist of an oxidizer, a fuel, a source of carbon, and various additives such as chlorine donors to enhance color and other chemicals to modify appearance or sound. Pyrotechnic chemicals can be grouped by these basic functions as follows.

Oxidizers

Oxidizing agents are usually metal nitrates, oxides, peroxides, chlorates, perchlorates, and chromates. Almost any metal in the periodic table can be present in oxidizers (see Metals below). Reaction may produce metal oxide fumes, metal chlorides, and compounds related to decomposition of nitrate, chlorate, and other radicals.

Fuels (electron donors)

The reaction is fueled by electrons donated from finely divided metals such as powdered aluminum, iron, magnesium, titanium, tungsten, zinc, and zirconium, or nonmetals such as bo-

ron, sulfur, phosphorus, and silicon. Reaction may produce metal oxide fumes, phosphoric acid, sulfur oxides, and silica.

An important subclass of fuels are **Carbon Suppliers**. These may be sugars, starches, epoxy and polyester resins, naphthalene, anthracene, and many solvents. Often carbon suppliers are overlooked as sources of toxic emissions other than carbon monoxide and carbon dioxide. Yet highly toxic substances are emitted by all natural and synthetic carbon-containing substances. It matters little if you burn coal, oil, wood, incense, hamburger, or tobacco. Just because we like the smell of incense or burning autumn leaves does not make their smoke healthier.

In fact, studies show that traditional open burning of leaves in the fall generates dangerously large quantities of carbon monoxide, particulates, and at least seven proven carcinogens. This leaf-burning pollution severely increases breathing problems in a majority of asthmatics in the fall.^[8] Similarly, burning naphthalene and anthracene to produce black smoke in outdoor movie scenes releases cancer-causing benzene and polycyclic aromatic hydrocarbons.

Carbon-containing pyrotechnic effects also produce these toxic emissions. In fact, the greater the amount of excess fuel in the formula and the lower the temperature at which it burns the

greater the production of polycyclic aromatic hydrocarbons and other toxic chemicals. Theoretical effects are particularly likely to be modified in this way.

If the carbon suppliers are solvents that also contain chlorine, they will emit additional toxic substances (see chlorine suppliers below).

Additives

Chlorine (and other halogen) suppliers include chlorinated rubber or plastics such as polyvinylidene chloride (Saran) or polyvinylchloride (PVC), inorganic metal chlorides, chlorates, or perchlorates, dechlorane (Mirex), hexachlorobenzene, carbon tetrachloride, perchloroethylene, and many other chlorinated hydrocarbons. Sometimes other halogens are used such as fluorine in the form of fluoride, bromine, or iodine compounds. Most of these chemicals are very toxic, some are carcinogens, and some (e.g., Mirex and hexachlorobenzene) also are EPA-registered pesticides. Reaction converts them into many hazardous halogen-containing compounds that may include hydrochloric acid, hydrofluoric acid, and phosgene.

Metals. Metals or metallic compounds have many functions including as oxidizers (see above), fuel (see above), flash, or smoke colorants to affect light intensity, sparkle, or for other effects. Some very toxic metals commonly used in fireworks include lead, arsenic, barium, boron, antimony, manganese, mercury, chromium, and copper. After combustion, these metals can be found in the smoke as a fume or settled out on surfaces as a fine dust. Even when metals are in amounts too small to cause toxic reactions, they may cause serious allergies. Some metals, especially chromium, are well-known sensitizers.

Silica. Silicon (Si), used as a fuel, will convert to silica (silicon dioxide — SiO_2) during combustion. It is likely to be emitted in the rather toxic fume form (see Table 3).

Silicon dioxide is also added to some pyrotechnic mixtures in amounts usually ranging from 0.1 to 1.5 percent. Any dust containing more than one percent crystalline silica warrants concern. A pyrotechnic formula containing one percent silica is likely to produce solid emissions containing more than one percent silica

Table 3. Threshold Limit Values* of Various Forms of Silica.

SUBSTANCE	TLV-TWA* (1996 values) milligrams/meter ³
silicon — Si	10
amorphous silica — SiO_2	
diatomaceous earth	10
silica fume	2
crystalline silica — SiO_2	
quartz	0.1
tridymite & cristobalite	0.05

* Threshold Limit Values (TLVs) are workplace air quality standards set by the American Conference of Governmental Industrial Hygienists, 1330 Kemper Meadow Drive, Cincinnati, OH 45240. TLVs are designed to protect the majority of healthy adult workers from adverse effects. The TLV-TWA is a time weighted average of airborne concentrations averaged over the eight hour work day.

since the silica will persist while other substances will decompose or become gaseous.

While it is likely that amorphous silica in the pyrotechnic formula would be emitted still in the amorphous form after combustion, I have not been able to find any actual confirmation of this assumption. This is clearly an important question to answer because the different forms of silica vary greatly in toxicity.

Other Chemicals include explosive chemicals such as TNT (trinitrotoluene) and nitroglycerin, thiocyanates of mercury, antimony, and other metals, various amines such as hexamethylene tetraamine and triethanolamine, and an EPA-registered pesticide called cryolite (sodium aluminum fluoride).

Flash Paper is nitrocellulose which burns with a flash on ignition. Colorants also may be added. The decomposition products of flash paper include toxic and irritating oxides of nitrogen. Used in small amounts it is not very hazardous. For larger amounts such as those used in flitter, fountains, waterfalls, and flamepots, the emissions could be significant.

Organic Pigments and Dyes used to color the smoke may also be present (Table 2). These usually are carbon-containing substances and their hazards are similar to those listed above under Fuels (carbon suppliers).

Health Effects Related to Pyrotechnic Smoke

The only sure way to assess the health effects of a particular pyrotechnic "smoke" is to analyze it and research the health effects associated with each component. Ethically, this should be done before exposing performers, but it is not likely to happen. However, some generalizations can be made about potential health effects.

1. Respiratory and eye irritation can occur from exposure to pyrotechnic smoke. Many of the solid particulates and gases are irritating and some are outright corrosive such as many of the chlorine-, nitrogen-, and sulfur-containing acid gases.
2. Acute and chronic allergic responses of the respiratory system, eyes, and skin can occur from exposure to pyrotechnic smoke. Many of the solids and gases are sensitizing, including those containing chromium compounds and the sulfur oxides. The dyes used to color smoke also may be sensitizers.
3. Acute and chronic systemic toxicity are associated with exposure to small amounts of lead, arsenic, barium, mercury, antimony, and some other metals. Chronic toxicity affecting the nervous system can be caused by some metals including lead, mercury, and manganese.
4. Cancer is associated with many of the metals, chlorine compounds, and organic chemical dyes.
5. Long-term lung problems are associated with the inhalation of fine dusts of silica, aluminum oxide, and other inert compounds.

Hazard Assessment

The first step in determining the hazards of a particular effect is to identify its ingredients. Unfortunately, most pyrotechnics are considered trade secrets, and product labels and the manufacturer's material safety data sheet (MSDS) will not list the ingredients. The MSDS also is supposed to list the hazardous decomposition products, but most do not. Those MSDSs that do list them may be reporting only a theoretical guess.

Another unique problem with both MSDSs and the pyrotechnic literature is that chemicals may be identified by traditional names that hark back to medieval alchemy. For example, mercurous chloride may be called *calomel*, mercuric sulfide may be called *quicksilver vermilion*, ammonium chloride may be called *sal ammoniac*, and arsenic disulfide may be called *realgar*. While the words can be looked up in chemical dictionaries, performers and other theater workers usually do not have ready access to these references and can be misled by this outdated terminology.

Most MSDSs do list highly toxic metals present in the mixture even if they do not identify the exact compounds in which they are present. This, at least, gives users the opportunity to reject highly toxic products.

Precautions for Pyrotechnic Use

1. Evaluate MSDSs and reject effects containing especially dangerous substances such as highly toxic metals (lead, mercury, etc.) and known carcinogens. Assume the smoke and gases released by all pyrotechnics are toxic since they almost assuredly are.
2. Inform performers at audition about the nature of the effects that will be used. Inform the public at the ticket office that pyrotechnic effects will be used on-stage that produce light, sound, and smoke.
3. Assume that exposure is most significant near the effect shortly after combustion. Make provisions for reducing workers' exposure by blocking performers far away from effects and by allowing other personnel to wear respiratory protection.

4. Set up ventilation fans and systems to remove the smoke from the stage and adjacent areas quickly and to keep smoke from entering the house and exposing the audience. Prevailing winds and terrain must be considered when planning outdoor effects.
5. Inform and train all potentially exposed personnel about pyrotechnic hazards and provide them access to the MSDSs as required by law.^[11]
6. Make provisions for medical evaluation and treatment of any cast or crew member who requests it and keep accurate records of any possibly related illness as required by law.^[11] Provide workers with access to their medical records as required by law.^[11]

The Most Important Precaution

Unfortunately, the “macho” approach to pyrotechnics is still alive and well. Complaints from performers and other personnel often are not taken seriously. This author is personally aware of situations in which performers complaining about special effects exposures have been derided, fired, and even blacklisted.

Instead, the potential hazards of pyrotechnics must be accepted as a legitimate concern. The most effective method of preventing health effects from pyrotechnic exposure is to obtain a commitment from special effects directors, company managers, and primary employers that the health of the cast and crew must come before any artistic or financial consideration.

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- Note: the study reported was a National Toxicology Program study that found “some evidence” of carcinogenic activity. The NTP uses five categories of evidence in animal studies:
- Two categories for positive results (“clear evidence” and “some evidence”); one category for uncertain findings (“equivocal evidence”); one category for no observable effects (“no evidence”); and one category for studies that cannot be evaluated due to major flaws (“inadequate study”).
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Suggested Reading

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Observations on the Perceived Burst Size of Spherical Aerial Shells

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ABSTRACT

This paper examines the effects of visual perspective on the observed size of shell bursts. The National Fire Protection Association (NFPA) codes specify minimum distances from the shell firing positions to the spectator boundaries in the United States. This paper addresses observed burst size and elevation as a function of mortar placement and spectator viewing positions, using shell burst radius and height information gathered by other researchers.

Keywords: aerial shell, burst size, display, perception, mortar placement, NFPA, spectators

Introduction

This paper grew from a debate the authors were having concerning the merits of large caliber shells in fireworks displays. It seemed obvious to us that there were distinct qualitative advantages with larger shells, such as effect duration, effect complexity, and break symmetry. It was not obvious, however, that there existed much quantitative difference in observed size for spectators (or sponsors) gathered near the fallout zone boundary, particularly when mortar placement follows the NFPA 1123 guidelines^[1].

The human eye is capable of seeing light and movement nearly 90 degrees in all directions from the center of its gaze. The greatest detail, color perception, and conscious attention are generally associated with the central 25–40 degrees (diameter) of vision called the central visual field.^[2,3] Bursts nearing or exceeding these angles would require conscious effort to take in the whole burst, and would contribute to the perception of a burst “filling the sky.” Other-

wise, two shells having the same burst angle, regardless of the actual size of the burst, would appear to have the same size. This is particularly true if smoke is present, and the observer cannot use stereo visual cues to correct for size and distance.

For example, which break would “appear larger” (assuming identical effects and manufacturers); a 10-inch shell fired 700 feet from the spectators and bursting at 1070 feet, or a 5-inch shell fired 350 feet from the spectators bursting at 700 feet? In this case it happens that the 5-inch shell actually bursts approximately 780 feet from the eye of the closest observers, and the 10-inch shell bursts approximately 1280 feet away, 500 feet further. To an observer near the fallout zone boundary, the additional distance results in the two bursts looking nearly identical in size.

In this paper, typical burst sizes of several shells launched from various NFPA-compliant locations have been translated into their apparent sizes at the observer. The term Apparent Angular Diameter (AAD) is used to denote the observed size of a shell burst. It is defined to be the angle subtended by the edge of the (spherical) shell burst, at the observer. Comparisons of the calculated AAD values for several bursts will be used to analyze observed burst sizes for several mortar placements and observer locations.

For all calculations and tables, the conversion factors used were: 1 inch = 25.4 mm; and 1 m = 3.28 feet.

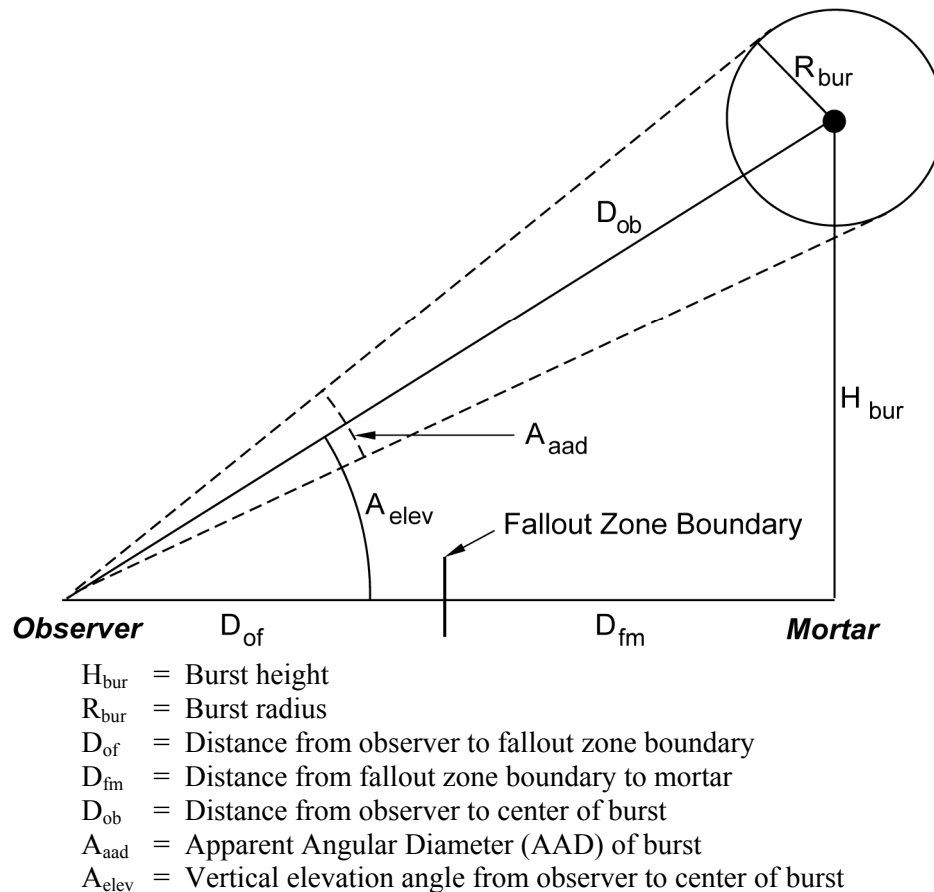


Figure 1. Model used to determine AAD for various shell sizes, mortar placements, and observer locations.

Data Model

A simple trigonometric model was used to perform the AAD calculations. The parameters driving the model are the measured burst height (H_{bur}) and radius (R_{bur}) derived from previously published experimental results, the distance from the fallout zone to the mortar (D_{fm}) (which is constrained to at least the minimum NFPA distances based on shell caliber), and the spectator distance from the fallout zone (D_{of}).

The model used to perform the AAD calculation is illustrated in Figure 1. The effects of mortar placement and observer location on perceived burst size were demonstrated by varying D_{fm} and D_{of} for various shell sizes.

AAD is found by determining the solid angle (at the observer) encompassing the edges of the sphere. Since we are assuming spherical bursts, this analysis can be reduced to determin-

ing the angle between two lines originating at the observer, and tangent to the circle. Elevation is determined as a function of burst height, and distance to the observer.

The relevant trigonometric relations associated with this model are:

$$D_{ob} = \sqrt{(D_{of} + D_{fm})^2 + H_{bur}^2}$$

$$A_{elev} = \tan^{-1} \frac{H_{bur}}{(D_{of} + D_{fm})}$$

$$A_{aad} = 2 \sin^{-1} \frac{R_{bur}}{D_{ob}}$$

The AAD of the shell burst is dependent not only on the observer's distance from the mortar, but also the height achieved by the shell. Large caliber shells, while having larger bursts, also attain greater heights. Near the fallout zone

boundary, the larger H_{bur} value is a significant factor affecting the perceived size.

The closer a burst is to the observer (as measured by D_{ob}), the smaller it needs to be to result in any given AAD. It also follows that bursts which are further away must be correspondingly larger to be perceived as equivalent.

The NFPA distances used for the mortar placements are shown in Table 1. These are derived from the NFPA guidelines for a fallout radius of 70 feet per inch (0.84 m/mm) of shell diameter.

The burst height and radius data used for this paper are shown in Table 2. The height and burst radius data have come from private communication^[4] as well as previous publications by Kosankes and Schwertly^[5] (height), and Kosankes^[6] (radius). The fitted data published by Wharton^[7] confirms that the burst height data used can be considered typical for these shell sizes.

Table 1. NFPA Fallout Distances for Shell Sizes Used in This Paper.

Shell Size in inches (mm)	NFPA Fallout Distance in	
	feet	(m)
3 (76)	210	(64)
4 (103)	280	(85)
5 (127)	350	(107)
6 (152)	420	(128)
8 (203)	560	(171)
10 (254)	700	(213)
12 (305)	840	(256)

Table 2. Typical Values for Burst Height and Radius for Various Shell Sizes.

Shell Size inches (mm)	Typical Burst Height (H_{bur})		Typical Burst Radius (R_{bur})	
	feet	(m)	feet	(m)
3 (76)	400	(122)	130	(40)
4 (103)	560	(171)	170	(52)
5 (127)	700	(213)	210	(64)
6 (152)	785	(239)	250	(76)
8 (203)	950	(290)	410	(125)
10 (254)	1070	(326)	430	(131)
12 (305)	1175	(358)	450	(137)

Three shell launching configurations were used in the analysis. The first configuration, which is typical at hand-fired displays, is to have all shells grouped in the same general area, with the separation distance consistent with the largest shell in the group. In this case 8-inch shells are considered the largest that would be hand-fired. Figure 2 illustrates the burst patterns relative to the fallout zone boundary for this configuration as viewed from the side. The negative distances shown in Figures 2–4 indicate placement within the shooting area.

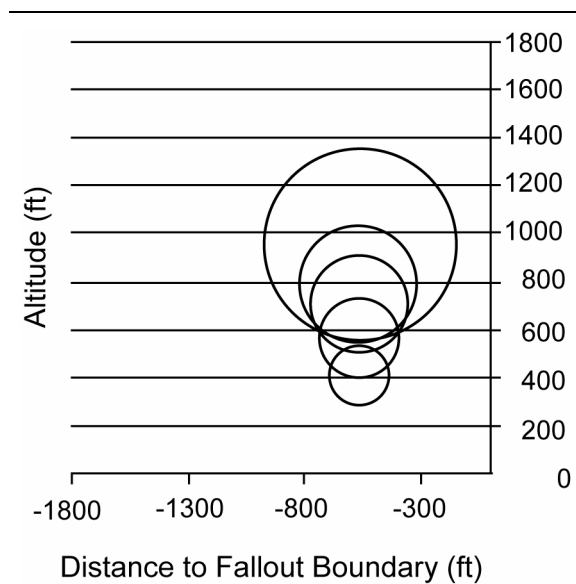


Figure 2. Burst profile for configuration 1.

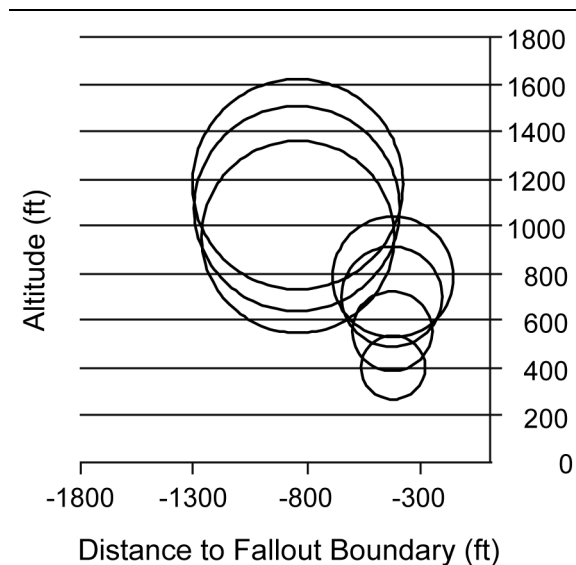


Figure 3. Burst profile for configuration 2.

The second configuration, typical at many displays, is to group all the small caliber shells up to 6-inch at one firing location 420 feet away, and all larger caliber shells at the location appropriate for the largest, in our example, 840 feet away for 12-inch shells. Figure 3 illustrates the profiles for this configuration.

In the third configuration, all mortars are simply distributed according to the NFPA guidelines. This results in 3-inch shells being placed 210 feet from the fallout zone boundary, 4-inch shells placed at 280 feet, and so on through 12-inch shells being placed 840 feet from the fallout zone boundary. Generally, arrangements like this would only be practical for electrically fired shows, where shoot crews would not need to be present among the various mortars. Figure 4 illustrates the burst profile for this configuration. All configurations assume the shells are launched from vertical mortars.

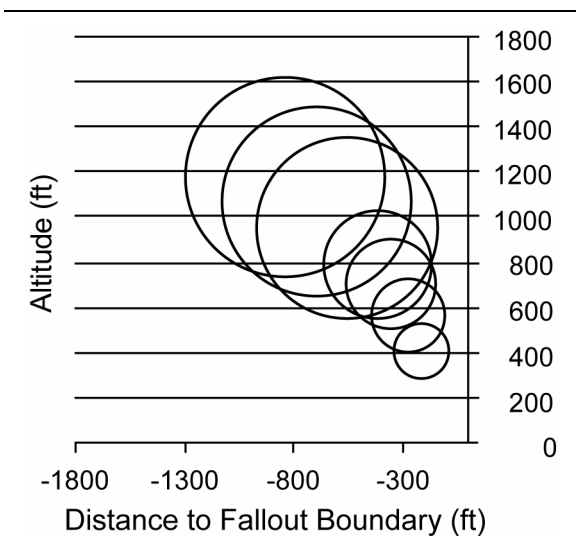


Figure 4. Burst profile for configuration 3.

A summary of the mortar placements for the three configurations relative to the fallout zone boundary is shown in Table 3.

Table 3. Summary for the Three Shell Launching Configurations Used for the AAD Calculations.

	Mortar Distance to Fallout Boundary (ft)						
	Shell Size (Inches)						
	3	4	5	6	8	10	12
Config. 1	560	560	560	560	560	—	—
Config. 2	420	420	420	420	840	840	840
Config. 3	210	280	350	420	560	700	840

Results

One of the main observations resulting from this investigation is that the largest caliber shells do not always result in the largest observed burst pattern, especially when the observer location is near the fallout zone boundary. This may be somewhat counter-intuitive, but at such close ranges, the effects of burst height and placement of the mortar relative to the observer are both significant contributors to the AAD.

Figure 5 shows the apparent angular diameters calculated for four shell sizes, fired at their NFPA distance from the fallout zone boundary. The diagram illustrates AAD results from the fallout zone boundary through 1 mile (1610 m) away. Even though the 12-inch shell has the largest actual burst radius of all the shells used (see Table 2), it does not have the largest apparent burst size near the fallout zone (compared to an 8-inch shell for example). This is due to the fact that a 12-inch shell needs to be fired further away from the spectators than an 8-inch shell, and it achieves a greater altitude before bursting. Both of these effects contribute to a significantly greater D_{ob} , resulting in a reduced AAD. Near the fallout zone boundary, there is virtually no observed AAD difference between a 3-inch shell burst and a 5-inch shell burst, and both of these are only within a few degrees of the observed 12-inch AAD. As observer distance is increased, the sizes of the shell bursts become more distinct.

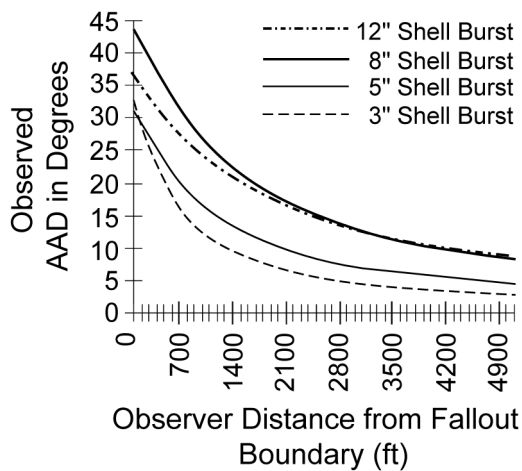


Figure 5. AAD drop-off as a function of observer distance from the fallout zone (mortars placed per configuration 3).

The AAD of the burst was not the only physical parameter that varied with observer distance. The elevation of the burst also changed. Elevation is the angle from the horizon to the center of the burst. An elevation of 0 degrees means that the center of the burst occurred on the horizon (as in a ground break), and an elevation of 90 degrees means that the burst would break directly overhead (as if one were standing directly under the burst).

The following figures illustrate the elevation and azimuth profile for each burst. Elevation is an absolute measurement from the horizon, and the azimuth is relative to the center of the burst.

The burst profile for an observer standing at the fallout zone boundary, with the mortars placed per configuration 1, is shown in Figure 6. In this example, the burst coverage appears as expected, with the smaller shells having a smaller burst diameter and appearing lower in the sky.

Figure 7 shows the burst profile for an observer standing in the same location, but seeing shells fired from mortars placed per configuration 2. The smaller shells have an AAD approaching the larger ones, and also appear to be higher in the sky.

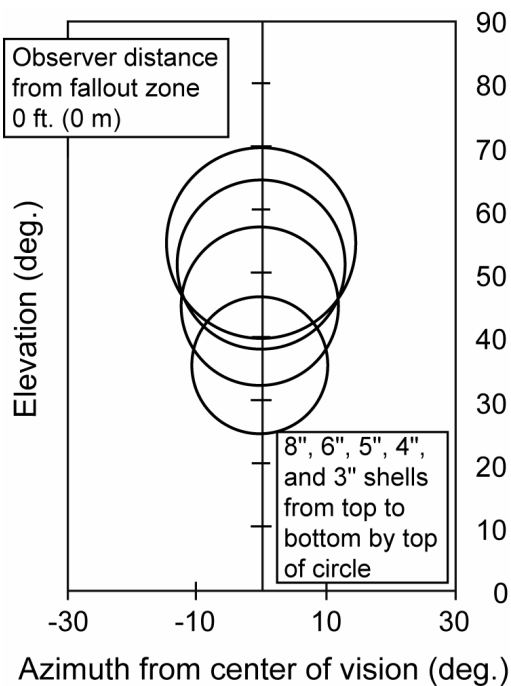


Figure 6. Burst coverage for Configuration 1 viewed 0 feet from the fallout zone boundary.

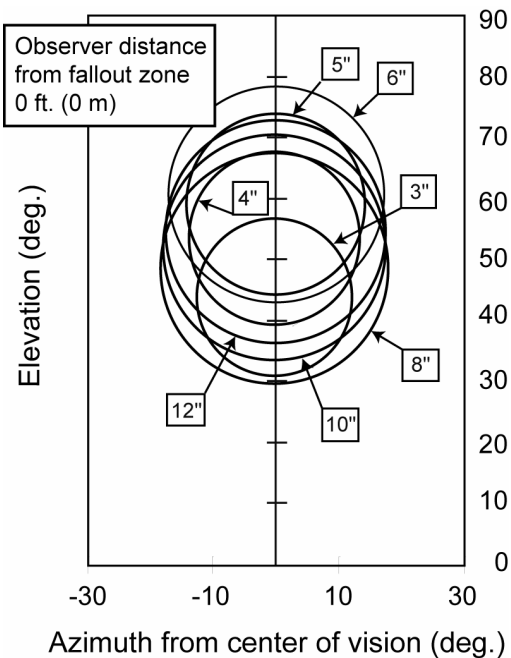


Figure 7. Burst coverage for configuration 2 viewed 0 feet from the fallout zone boundary.

Finally, the burst profile for configuration 3 is shown in Figure 8. Here there are significant differences in the observed bursts versus the first configuration.

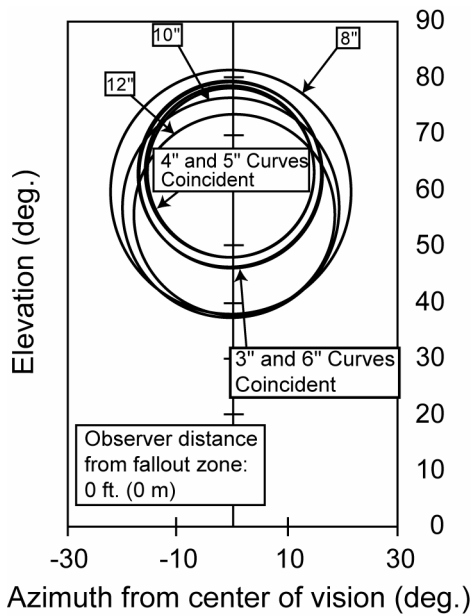


Figure 8. Burst coverage for Configuration 3 viewed 0 feet from the fallout zone boundary.

When viewed from the fallout boundary, it is virtually impossible to distinguish the burst sizes of the 3-inch shells and 6-inch shells. The same effect is also apparent with the 4-inch and 5-inch shells. Another interesting result is that the 8-inch shell burst appears larger than either the 10-inch or 12-inch shell bursts.

The 12-inch burst with an AAD of 36.3° is only 3.7° larger than the 6-inch burst AAD of 32.6° . It also appears smaller than the 8-inch burst having an AAD of 43.7° .

It is, therefore, easy to see how observers anticipating the large break of a 12-inch shell might be disappointed when viewing the display from near the fallout zone boundary. What may not be appreciated up close is the visual effect

at greater distances. Figures 9 and 10 show the burst profiles for configuration 3 at distances of 500 and 2000 feet from the fallout zone boundary. As observer distance is increased, the actual differences in burst radius and height become more apparent.

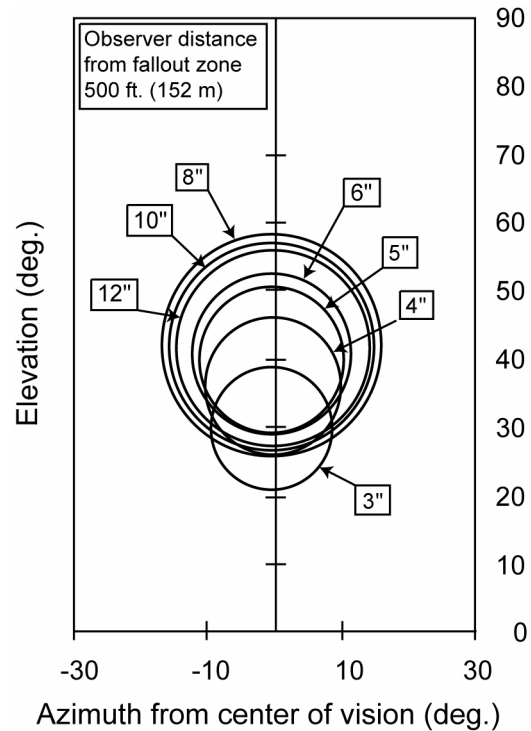


Figure 9. Burst coverage for configuration 3 viewed 500 feet from the fallout zone boundary.

When viewed from 2000 feet and beyond, all configurations have essentially the same appearance, because the observer's distance from the fallout zone (D_{of}) dominates the distance from the observer to the shell burst (D_{ob}) and therefore the observed burst size.

A summary of the elevations and apparent angular diameters for the three configurations is shown in Table 4. For each configuration (for D_{of} values of 0, 500, and 2000 feet), both the calculated AAD and elevation is shown.

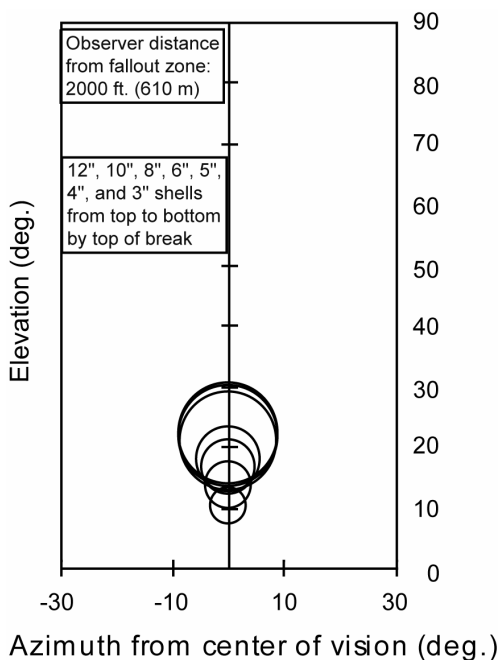


Figure 10. Burst coverage for configuration 3 viewed 2000 feet from the fallout zone boundary.

The greatest effects of varied mortar placement can be observed within 500 feet of the fallout zone boundary. Some inversion (larger actual bursts having smaller perceived size) of the AAD values for the larger shells can be seen at observer distances of 500 feet and below, especially for the NFPA-based mortar placement in configuration 3.

Conclusion

Understanding perspective when designing shoot site layouts can lead to greater control of what the spectators see, and may contribute to more efficient use of materials. For example, if one were providing a display for a small party, where the spectators can be considered grouped rather narrowly along the fallout zone boundary, there may be no quantitative advantage to shooting 5-inch and 6-inch shells versus 3-inch and 4-inch shells, as they will appear nearly the same size when viewed. Such consideration

may result in reduced display cost, or an increased number of shells to be presented.

In another possible extrapolation, if the majority of the spectators are to be within 2000 feet of the fallout zone boundary, there may be little advantage to presenting anything larger than an 8-inch shell. Unless many observers are a great distance away (or one wishes to present the display to an entire metro area) the addition of the larger effects may not be fully appreciated.

To achieve the largest overall vertical spread in the sky, one should collocate all mortars at the further firing positions (such as 560 feet away, as in configuration 1) and use a variety of shell sizes. Locating all mortars at their respective NFPA distances maximizes the perceived size of each burst, but also puts them at nearly the same elevation. The resulting effect can be bursts "stepping on" other bursts, with little variety in elevation. Collocating all mortars would result in a more "layered" effect.

Clearly, the visual impact of aerial shells depends not only on the size of the shell itself, but also observer location and mortar placement. In some situations, smaller, less costly shells can produce bursts of equal or larger perceived diameter than larger shells fired at the greater distances necessitated by the NFPA table of distances.

If these parameters are carefully considered, an impressive and effective display can be staged even if large fallout zones are not available or budget is limited. Careful attention to the effects of perspective can also help the pyrotechnician plan the shooting site to maximize the artistic effects he or she is trying to achieve.

While a purely quantitative analysis might indicate that smaller shells fired closer to the fallout zone boundary might be a more effective way to maximize the perceived burst size, there are other reasons to use large shells. There is a clear qualitative difference between large and small shells of similar effect. There is something majestic and beautiful about the slow-motion opening and complexity presented by large shells, which smaller shells cannot match.

Table 4. Summary of AAD and Elevation Values for All Three Mortar Placement Scenarios at 0, 500, and 2000 feet from the Fallout Zone Boundary.

		Shell Sizes, AAD, and Elevation (all values in degrees)													
		3-inch		4-inch		5-inch		6-inch		8-inch		10-inch		12-inch	
Feet		AAD	Elev	AAD	Elev	AAD	Elev	AAD	Elev	AAD	Elev	AAD	Elev	AAD	Elev
Config. 1	0	21.8	35.5	24.8	45.0	27.1	51.3	30.1	54.5	43.7	59.5				
	500	13.2	20.7	16.3	27.8	19.0	33.4	21.9	36.5	33.5	41.9				
	2000	5.8	8.9	7.4	12.3	9.1	15.3	10.7	17.0	17.3	20.4				
Config. 2	0	25.9	43.6	28.1	53.1	29.8	59.0	32.6	61.9	37.7	48.5	36.9	51.9	36.3	54.4
	500	14.9	23.5	18.2	31.3	20.9	37.3	23.9	40.5	28.9	35.3	29.0	38.6	29.3	41.2
	2000	6.1	9.4	7.8	13.0	9.6	16.1	11.3	18.0	15.7	18.5	16.3	20.6	16.8	22.5
Config. 3	0	33.4	62.3	31.5	63.4	31.1	63.4	32.6	61.9	43.7	59.5	39.3	56.8	36.3	54.4
	500	18.4	29.4	20.4	35.7	22.0	39.5	23.9	40.5	33.5	41.9	31.0	41.7	29.3	41.2
	2000	6.6	10.3	8.3	13.8	9.8	16.6	11.3	18.0	17.3	20.4	17.0	21.6	16.8	22.5

Where economics, shooting location, and audience distribution allow, ten-inch, twelve-inch, and larger shells certainly have their place. However if they are to be fully appreciated by spectators and customers, the closest viewing positions are not necessarily the best.

Overall, a pyrotechnician is responsible for applying all applicable factors when planning a display to ensure satisfaction, safety, and value to the customer. Manufacturers should also be able to make use of perspective to optimize their product for maximum visual performance.

While characterizing the visual perspective effects of fireworks displays is only one aspect of the art and science of pyrotechnics, a practical understanding of it can be an invaluable tool to the fireworks manufacturer, show planner, and display operator.

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Aerial Shell Drift Effects:

(A) The Effect of Long Mortars

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(B) The Effect of Capsule-Shaped Shells

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ABSTRACT

Aerial shell drift is defined as the difference between the ballistically predicted trajectory of a shell and its actual trajectory. It had been speculated that longer length mortars and capsule-shaped shells might experience significantly different drift than normal length mortars and spherical shells. It was found that while longer mortars propelled 6-inch (155 mm) aerial shells to greater heights, the average shell drift was unaffected. Further it was found that 6-inch (155 mm) capsule-shaped shells probably drifted slightly more than spherical shells.

Keywords: aerial shell drift, mortar length, shell shape.

Introduction

Knowing the initial conditions (mortar tilt and azimuth, wind speed and direction, and shell parameters), the flight path of aerial shells can be calculated using ballistics models^[1]. While

such calculations are fairly good at predicting the average path of a large number of identical shells, they are rather poor at predicting the actual path of an individual aerial shell. In large measure this results from aerodynamic forces acting on the shells along their trajectory; for example, the Magnus force resulting from the shell tumbling along its path^[2]. For a dud aerial shell, shell drift is defined as the difference between the ballistically predicted and actual points of fall of the aerial shell.

Aerial shell drift was originally studied for the purpose of helping determine the adequacy of spectator separation distances during fireworks displays. Based on initial tests, the average drift distance for dud spherical aerial shells was established to be approximately 32 feet per inch of shell size (0.38 m/mm)^[2]. If there are conditions that produce significantly different average drift distances, that could be justification for suggesting different spectator separation distances for those conditions.

During various discussions of the initial reports of shell drift, it was speculated that mortar

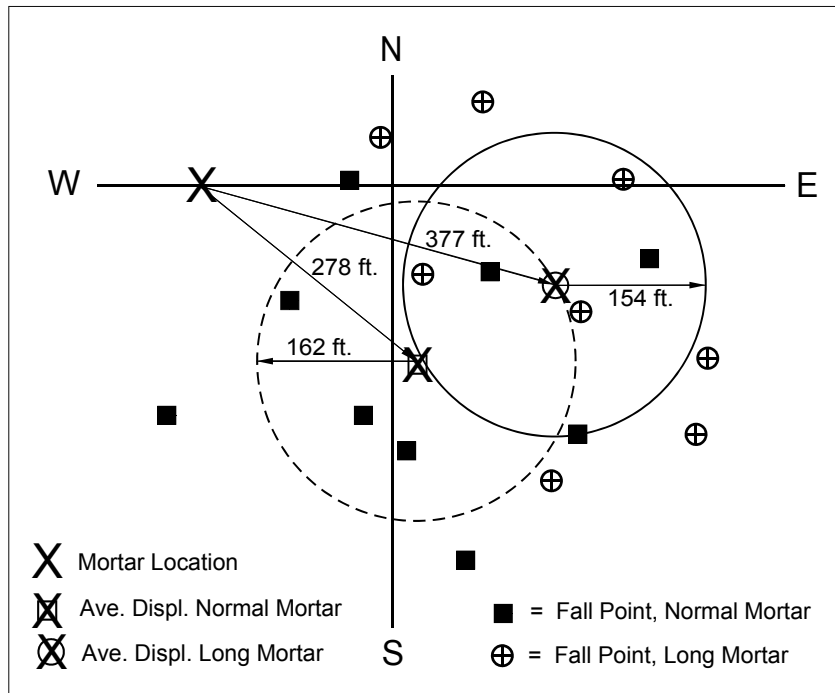


Figure 1. The location of points of fall for the shells fired from the long and normal length mortars.

length might affect the results. For example, using longer mortars might result in increased average aerial shell drift, because the shell would have a higher initial velocity, causing a greater magnus force and allowing more time for it to act on the shell. On the other hand, a longer mortar might result in reduced average shell drift, because the longer mortar might allow less divergence of the shell (a result of the shell being smaller than the mortar ID). This possibility is supported by some observations that the use of long mortars facilitates the precise placement of shell bursts during choreographed displays. Assuming this is true, reduced shell drift may be part of the explanation.

Some results discussed in reference 2 for an unusual shell shape (a cylinder with one concave and one convex end) apparently had a drift distance less than that for spheres. Accordingly, it seemed possible that capsule-shaped shells (roughly a cylinder with two convex ends) might

also have a drift distance less than spheres. The two brief studies reported in this article were conducted to determine whether either mortar length or the modified shell shape significantly affected drift distance of dud shells.

(A) The Effect of Long Mortars

Nine pairs of identical aerial shells were fired to determine whether there was an effect of mortar length on shell drift. The shell pairs were nominally 6-inch (155 mm) Sunny International shells. The lift charges were temporarily removed from the shells and water was injected into the time fuses to prevent them from burning. The mortars used were 6.08 inch (154 mm) internal diameter steel pipe with internal lengths of 29 and 65 inches (0.75 and 1.65 m). Both mortars were placed vertically in a field at approximately 600 feet (180 m) above sea level.

Table 1a. Data from Normal Length Mortar Shell Drift Tests.

Shell Number	Time of Flight (sec.)	Point of Fall (Orig. Coord. Sys.)		Point of Fall (Shifted Coord. Sys.)		Drift Distance (feet)
		North (ft.)	East (ft.)	North (ft.)	East (ft.)	
1	12.2	-5	-43	167	-69	181
2	14.3	-225	189	-63	163	175
3	(a)	-339	75	-177	49	184
4	13.7	-66	262	96	236	255
5	12.1	-78	100	84	74	112
6	(a)	-104	-104	58	-130	142
7	14.5	-241	15	-78	-11	79
8	(a)	-208	-229	-46	-255	259
9	(a)	-207	-29	-45	-55	71
Average	13.4	-162	26	≅ 0	≅ 0	162
Std. Dev.	1.1					68

(a) Time of flight not determined, usually because shell was lost sight of.

For conversion to SI units, 1 foot = 0.30 m.

Table 1b. Data from Long Mortar Shell Drift Tests.

Shell Number	Time of Flight (sec.)	Point of Fall (Orig. Coord. Sys.)		Point of Fall (Shifted Coord. Sys.)		Drift Distance (feet)
		North (ft.)	East (ft.)	North (ft.)	East (ft.)	
1	16.1	76	92	166	-74	182
2	15.6	-80	31	10	-135	135
3	17.9	44	-12	134	-178	223
4	15.4	-156	321	-66	155	168
5	14.7	-267	162	-177	-4	177
6	(b)	(b)	(b)			
7	15.9	6	235	96	69	118
8	(a)	-114	192	-24	26	35
9	(a)	-225	309	-135	143	197
Average	15.9	-90	166	≅ 0	≅ 0	154
Std. Dev.	1.1					58

(a) Time of flight not determined, usually because shell was lost sight of.

(b) This shell burst in the air, because one of its time fuses functioned even after having been wetted.

For conversion to SI units, 1 foot = 0.30 m.

For these tests, it would have been preferred to have essentially calm wind conditions. However, the tests were conducted as part of another project that had a serious time constraint, and which resulted in having to perform the tests on a day when surface wind averaged 25 mph (40 km/h). The test protocol followed was the same as used in all previous tests, which approximately corrects for the effects of wind (and minor mortar orientation errors), and is reported

in reference 2. In essence, the shells are fired into the air, and their points of fall determined in a coordinate system with the mortars at a known location. (In this case the mortars were located at North 0 and East -200 feet). A new coordinate system is established at the point of average displacement (center of gravity) of the collection of points of fall from the mortar. Then shell drift is measured within this new coordinate system. It is the shift of the coordi-

nate system that is believed to approximately correct for wind effects and mortar positioning errors (in the case of these measurements, care was taken to assure that the mortars were vertical to within less than 0.5 degree). In these tests, to minimize the effect of any changes in wind speed or direction between the firing of shells from the long and normal length mortars, both shells of each pair were fired within seconds of each other. The data from these tests are presented in Tables 1a and 1b, and in Figure 1. Also shown in Figure 1 are the average displacements of the points of fall of the shells from the long and normal length mortars, and the average drift distances about these average displacements.

As expected, the average times of flight for the shells from the long mortar are longer (by 2.5 seconds), indicating that these shells were propelled to a greater height before falling back to earth. This allowed the wind to act for a longer time on those shells, causing their average point of fall to be shifted further down wind. That average displacements of the two sets of points of fall do not lie on the same line from the mortars, must be partly due to statistical effects, but may also be due in part to different wind direction as a function of altitude.

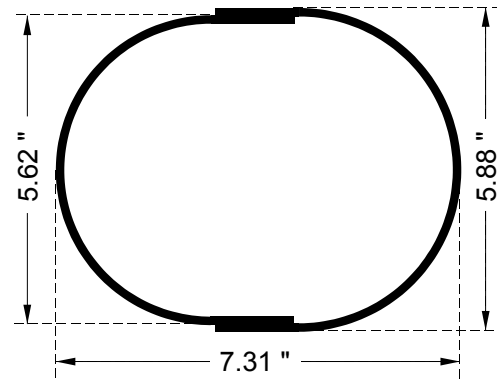


Figure 2. Illustration of the capsule-shaped aerial shell casings.

The average shell drifts for the paired sets of shells were found to be 162 feet (49 m) and 154 feet (47 m) for the normal and long mortars, respectively. The one-sigma Standard Errors are ± 23 feet (7.0 m) and ± 19 feet (5.8 m). Thus the two drift distances are the same, to within the limits of statistical certainty.

Table 2. Data from Capsule-Shaped Shell Tests.

Shell Number	Time of Flight (sec.)	Point of Fall (Orig. Coord. Sys.)		Point of Fall (Shifted Coord. Sys.)		Drift Distance (feet)
		North (ft.)	East (ft.)	North (ft.)	East (ft.)	
1	12.3	-13	-240	31	-189	192
2	13.4	-229	61	-185	112	216
3	13.3	-241	-66	-197	-15	197
4	13.6	-147	-237	-102	-186	213
5	13.4	287	-10	331	41	334
6	13.3	202	-220	246	-169	299
7	14.5	-114	-90	-70	-39	80
8	14.6	-167	299	-123	350	371
9	13.9	87	212	131	263	294
10	12.3	-106	-219	-62	-168	179
Average	13.5	-44	-51	$\cong 0$	$\cong 0$	237
Std. Dev.	0.7					82

For conversion to SI units, 1 foot = 0.30 m.

(B) The Effect of Capsule-Shaped Shells

Ten 6-inch (155 mm) capsule-shaped aerial shells were fired to determine whether this configuration resulted in shell drifts that were noticeably different from typical spherical shells of the same size. A cross sectional view of the capsule-shaped shell casing is illustrated in Figure 2. The shells had a maximum diameter of 5.88 inches (149 mm), a length of 7.31 inches (186 mm), and were filled to a weight of 2.5 pounds (mass of 1.13 kg) using a mixture of dry dog food and small pebbles. The shells were fired from a steel mortar with an internal diameter of 6.05 inches (154 mm) and a length of 29 inches (0.75 m). The mortar was positioned vertically. In each case, a propelling charge of 1.75 ounce (50 g) of 4FA Black Powder was used. This is about one ounce (28 g) less than typical for a 6-inch (155 mm) spherical shell, and was done in an attempt to correct for the fact that these shells fit more tightly in the mortar. They were about one-quarter inch (6 mm) larger in diameter than typical spherical shells. The success of this adjustment can be judged by comparing the flight times reported in Tables 1a and 2.

These tests were conducted at an elevation of approximately 4600 feet (1400 m) above sea level and with a surface wind of less than 2 mph (3.2 km/h). Again, the standard test protocol was used^[2]. The test results are presented in Table 2.

The average drift distance for the 6-inch (155 mm) capsule-shaped pulp molded shells was 237 feet (72 m) with a 1-sigma standard er-

ror of ± 26 feet (7.9 m). Past measurements of 6-inch (155 mm) shells under similar conditions gave a drift distance of 145 feet with a 1-sigma standard error of 31 feet (9.5 m). Based on a linear fit to drift data for various sized shells, a drift distance of approximately 192 feet (59 m) would be expected.^[2] Accordingly, it seems that the capsule-shaped shells do not drift less than spherical shells, and it is likely they drift somewhat more.

Conclusion

Based on the brief studies reported above, it seems clear that mortar length does not have a major effect on spherical aerial shell drift. Further, it seems clear that capsule-shaped shells do not drift significantly less than spherical shells and probably drift slightly more. Accordingly, it would seem there is no reason to consider modified separation distances for either case.

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Ammonium Perchlorate Composite Basics

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ABSTRACT

This article addresses the theory and design of ammonium perchlorate/hydroxyl-terminated polybutadiene (AP/HTPB) composite propellant rocket motors. A discussion of the operating principles of solid motors, including motor dynamics, the combustion process of AP composite propellants, and basic nozzle theory is presented. Several grain geometries and thrust profiles are illustrated, and requirements for various casing, nozzle and adhesive materials are compared. The propellant system itself, consisting of oxidizer, binder and fuels, plasticizers, bonding agents and burn rate modifiers, is described.

Keywords: composite propellant, ammonium perchlorate, AP, specific impulse, grain geometry, HTPB, hydroxyl-terminated polybutadiene, nozzle expansion ratio, chamber pressure

Introduction

Propellants function to impart motion to an object through the conversion of potential energy into useful or kinetic energy. Two ingredients, a fuel and an oxidizer, neither of which will burn satisfactorily without the presence of the other, are necessary in a propellant system. Two main classes of propellants are recognized on the basis of physical character: liquid propellants and solid propellants. Most solid propellants belong to one or the other of two types. Homogenous propellants contain both the oxidizer and fuel in the same molecule and may also be referred to as monopropellants. These systems, consisting mostly of nitrocellulose and nitroglycerin in a colloidal mixture, are called double-based propellants. The second type is the heterogeneous or composite propellant, where

the oxidizer is a finely ground inorganic salt and the fuel is plastic in nature, binding the propellant grain structure together. Black powder, the oldest of propellants, falls into this category since it uses potassium or sodium nitrate as the oxidizer and sulfur as both binder, and with charcoal, as a fuel.

Modern composite propellants first emerged in the late 1940's. These incorporate various thermoplastic and thermosetting resins or elastomers with a variety of nitrates or perchlorates as oxidizers. Perhaps the most popular of the composite propellant systems in current use consists of ammonium perchlorate, NH_4ClO_4 , as the oxidizer and usually a copolymer or terpolymer of butadiene with other monomers such as acrylic acid or acrylonitrile as the binder. This article will examine the design and construction of composite propellant rocket motors using hydroxyl terminated polybutadiene (HTPB) and ammonium perchlorate (AP).

Operating Principles of Solid Propellant Rockets

As solid propellants have certain advantages over liquid propellants, composites may be more desirable for some applications than the familiar black powder formulations. All solid propellants possess a high degree of reliability by virtue of design. Once ignited, a solid rocket normally operates according to a preset thrust program, which is primarily determined by the configuration of the propellant grain. The amount of thrust which may be obtained from a given grain design is largely determined by the propellant composition. Composite propellants burn at higher temperatures and pressures than black powder, with a net result that pound for pound, they can deliver about two and one half times the power of a black powder motor.

Propellant Characteristics

Fundamental to the design of any solid propellant rocket is a simple geometric principal: The burning surface of a solid propellant recedes in parallel layers. Because of this, solid motors are self-stabilizing. That is, should small convex or concave irregularities arise on the burning surface, as would happen if an air bubble was trapped in the propellant grain, such irregularities would disappear as burning proceeds. This is significant because as bubbles are encountered, the burning surface of the propellant and consequently the internal pressure of the motor and the burn rate of the propellant are increased. When this exceeds the design parameters of the motor, rapid overpressurization occurs, leading to a catastrophic failure.

The burning rate, r , of a solid propellant is the linear rate of propellant consumption in a direction normal to the burning surface. It typically ranges from 0.1 to 2.0 inches per second and is primarily influenced by the combustion pressure, P_c ; propellant composition; and to a lesser degree by the ambient grain temperature and the velocity of gas flow past the burning surface. Burning rate may be expressed by the following equation:

$$r = aP_c^n \quad \text{Equation 1}$$

The burning rate, r , is in inches per second; the pressure of combustion is in pounds per square inch; and a and n are constants. Propellant composition and pre-ignition temperature are the determinants for the value of the constant a , which ranges between .002 and .05. The pressure or burning rate exponent n is solely a function of the propellant formulation with negligible influence of the bulk temperature. Typical values for the burning rate exponent range from 0.2 to 0.5, but in some cases may vary between 0 and 0.9. The burning rate exponent is of critical importance in maintaining the stable operating pressure of any rocket motor.

During combustion, a rocket functions in a state of dynamic equilibrium. A stable operating pressure is maintained by a delicate balance between the rate at which gas is being generated by the burning propellant and the rate at which it is being expelled through the nozzle. This is affected by an area ratio between the

propellant burning area and the nozzle throat area. This area ratio; K_n , where:

$$K_n = \frac{A_b}{A_t} \quad \text{Equation 2}$$

and the specific formulation of a propellant and its burning rate exponent, will determine the operating pressure of a given motor. The relationship between the K_n and operating pressure of a given motor is expressed by the equation:

$$P = B(K_n)^{\frac{1}{1-n}} \quad \text{Equation 3}$$

where P is the pressure in pounds per square inch, B is a constant for a specific propellant, and n is the same pressure or burning rate exponent as appears in the burn rate equation (Equation 1). Small changes in the value of n can lead to significant changes in the operating pressure of a rocket motor and consequently in the propellant's burn rate which was shown in Equation 1 to be pressure dependent. If n is 0.3, $(1-n)$ is .7 and $1/(1-n)$ is 1.42. A 20% increase in burning area would cause a 30% increase in pressure. But if n should be 0.8, $(1-n)$ is .2, and $1/(1-n)$ would be 5. For such a propellant, that same 20% increase in burning area would cause a 148% increase in pressure. It becomes evident that propellants with high exponents are to be avoided, as small variations in the burning surface such as when bubbles become trapped within the propellant grain or cracks are present in the grain, lead to greatly magnified variations in chamber pressure.

Specific Impulse

The quantity of energy available from a rocket propellant is determined by the chemical nature of the oxidizer and fuel molecules, as well as by the chemical nature of the reaction gas products. This is most conveniently expressed as specific impulse, I_{sp} , which is an effective measure of the performance of various propellant systems compared to one another. The higher the I_{sp} value, the more efficient the propellant. Specific impulse may be considered to be the amount of thrust which is available for each pound per second of propellant burned. It is the reciprocal of the specific consumption of propellant and is expressed in pounds of thrust per pound of propellant used per second. This is

found by dividing the thrust, or total impulse (I_t) by the weight flow rate expressed in pounds.

$$I_{sp} = \frac{I_t}{W_t} \quad \text{Equation 4}$$

The range of specific impulse for most ammonium perchlorate composite propellants may vary from near 170 to approximately 230, with a common figure around 200. In comparison, the I_{sp} of black powder is between 70 and 80, roughly two and one half times less than that of a composite propellant.

The total impulse of a rocket motor describes the total amount of energy stored in that motor. Thus, if it contained two pounds of propellant with an I_{sp} of 210, the total impulse would be:
 $I_t = I_{sp} \times W_t = 210 \text{ sec.} \times 2.0 \text{ lbs} = 420 \text{ lb-sec.}$
Depending on the grain design, this motor would be capable of producing 420 pounds of thrust for 1 second, 105 pounds of thrust for 4 seconds, or any combination of thrust \times time which would come out with a product of 420 lb-sec.

Motor Dynamics

Regardless of the propellant system used or the I_{sp} of a given propellant, the design of a nozzle is a fundamental criterion in the construction of a rocket motor. The rocket nozzle functions to transform the heat energy of combustion into the kinetic energy of a high velocity gas stream with the maximum possible efficiency. Nozzle theory is based upon the laws of thermodynamics, gas dynamics and fluid dynamics. A basic understanding of nozzle function is of paramount importance to the proper design of rocket motors. Derivations and discussion of the fundamental laws pertaining to the conservation of matter and energy, and of the dynamic processes involved, are presented in depth in the proper texts for the interested reader to pursue. The following discussion of combustion process and nozzle theory will provide the basis for general understanding.

Combustion of Composite Propellants

The combustion of composite propellants occurs in different phases, with the oxidizer particles decomposing in the midst of the decomposing fuel matrix. Ammonium perchlorate

itself does not melt, but rather undergoes an exothermic decomposition resembling that of homogenous propellants. Adjacent streams of fuel-rich and oxidizer-rich gasses rise from the surface, and immediate reaction is not possible until mixing by diffusion is complete. The combustion process takes place in three distinct zones, the foam, fizz, and flame zones. At the combustion surface, the gas velocity is relatively small and possesses little kinetic energy. It is in the flame zone that the final reaction occurs and the majority of the heat and gaseous products are evolved. There, the high pressure of the expanding gasses forces the gas particles to the rear, causing a slight decrease in potential energy at the nozzle entrance, but an increase in velocity.

Nozzle Theory

There are three basic types of rocket nozzles: subsonic, sonic, and supersonic. It is the supersonic nozzle which is of interest, consisting of three parts; a convergent section, a throat of specific diameter and therefore area, and a divergent section. Nozzles of this type are often called DeLaval nozzles, after their inventor, and may be thought of as two cones joined at their vertices by a short, straight throat section, with all transitions being smooth so as to avoid disturbances in gas flow.

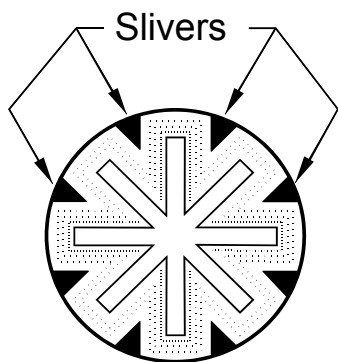
When gas enters the converging portion of the nozzle, the decreasing cross-sectional area causes the flow to speed up. The maximum velocity which can be obtained in the converging portion of the nozzle occurs at the throat, and corresponds at that section to the local sonic velocity. In practice, this will not occur unless the ratio of chamber pressure to throat pressure reaches a certain minimum value, the critical pressure ratio, which corresponds to thirty-two pounds per square inch absolute or twice the ambient atmospheric pressure. Once this chamber pressure has been reached, the velocity of gas at the throat will always correspond to the critical throat velocity regardless of further chamber pressure increases.

Once the exhaust gas has reached sonic velocity, several of its major flow properties change. This may be used to advantage by the addition of a diverging section to the nozzle.

Gas velocity increases into the supersonic range and pressure decreases, as expansion of the exhaust gasses takes place over the entire length of the divergent section. Optimum expansion occurs when the pressure of the exhaust gasses at the exit plane of the nozzle is equal to the ambient pressure. This will be found at a specific cross-sectional area of the nozzle exit, A_e , of a given rocket, which may be related to the throat cross-sectional area as the nozzle area expansion ratio.

$$E = \frac{A_e}{A_t} \quad \text{Equation 5}$$

Thrust is lost when the area ratio varies in either direction from the optimum. There are upper and lower pressure limits for all propellants. Very high chamber pressures, above 6000 psia for most propellants, cause erratic and rapid burning, frequently leading to catastrophic failure of the motor. On the other hand, many propellants will not support combustion at low pressures. This may be advantageous as a safety feature, but must be taken into account when designing the grain geometry so as to minimize the unburned propellant residue or "slivers" at motor burnout. For a particular propellant grain having a fixed surface area exposed to combustion, there exists a maximum effective throat area which will maintain a chamber pressure high enough to support combustion. Most solid rockets employ nozzles which will maintain chamber pressures well above this critical limit.



It is hoped that the preceding discussion provides the basis for an appreciation of the intricacies involved with designing solid pro-

pellant systems. Let us now examine the practical application of theory.

Nozzle Design

The mechanical requirements for nozzle fabrication are quite stringent. The material utilized must exhibit good machinability or ease of fabrication while retaining excellent resistance to erosive change under the most extreme conditions. The throat section is usually made from graphite or some non-ablative material which is surrounded by insulation to keep the outside structural material cool. The inside of the exit cone in large motors is made from such materials as asbestos-phenolic backed by an external structure to contain the nozzle pressure. Fiberglass phenolic laminates and ceramics have all seen application as nozzle materials in small rocket motors, but problems with cost, fabrication, and erosion have limited their use. By far, the most simple and economic solution has been the full diameter graphite nozzle, machined from readily available rod stock which fits snugly into the inside diameter of the motor. The major drawback of this system is that the graphite acts as a heat sink and in larger or long burning motors may cause charring of non-metallic motor casings. This difficulty may be circumvented by suspending a graphite nozzle insert of significantly smaller diameter than the motor case in a high temperature epoxy which provides insulation for the casing. Thermosetting, high-temperature, injection molded plastics combine moderate erosion resistance with the insulating properties needed to protect the motor wall, and are currently enjoying widespread usage. These nozzles are most effectively utilized in the design of neutral burning motors. By taking advantage of the erosive nature of the nozzle in combination with a progressive grain design, a neutral thrust curve may be obtained. Their major disadvantages are the high initial cost of tool and die fabrication.

When designing a rocket nozzle, consideration must be given to the angle of convergence, the angle of divergence, the nozzle area ratio, and the nozzle throat area with its relationship to the propellant burning area, K_n . All of these parameters must be precisely calculated from complex equations in order to optimize motor

performance and efficiency. However, some useful generalizations may be drawn. The convergent cone half-angle, β , varies between 15 and 45 degrees, with 30 degrees being a good compromise and 45 degrees being a more space and material efficient choice. For the divergent cone, a nozzle half-angle, β , between 12 and 18 degrees, has been found experimentally to be optimum, with 15 degrees being a good choice in high thrust motors.

The nozzle area expansion ratio, E , that is the ratio of nozzle exit area to throat area, deserves more attention. Expansion of the exiting gasses is ideal when the external pressure is equal to the nozzle exit pressure, and the motor delivers maximum thrust. An under-expanding nozzle will discharge the exhaust at a pressure greater than the external pressure, because the exit area is too small. Thus, the gas expansion is incomplete within the nozzle and continues outside. The nozzle exit pressure is higher than the atmospheric pressure. An over-expanding nozzle is one in which gasses are expanded to a lower pressure than the external pressure due to it having an exit area which is too large. Separation of the gas jet from the nozzle wall will result, reducing the exhaust velocity, thereby leading to a loss of thrust. The formation of shock waves is also of concern with improperly designed nozzles. It is best to design a nozzle with the optimum expansion ratio or one which under-expands the gas jet slightly. A ratio of 1:3 to 1:4 is appropriate for composite motor systems operating in the 300 to 400 psia range. At higher pressures, the area ratio would increase. This would also be the case for sounding rockets operating at high altitudes where the exhaust gasses must expand further so that they can match the lower atmospheric pressure at the nozzle exit plane. The upper stage nozzles of such vehicles often have exit diameters ranging from five to seven times the throat diameter.

Throat Diameter

The final parameter which must be considered in nozzle design is the throat area. As has been previously discussed, the propellant characteristics of burn rate, r and pressure exponent, n must be considered when choosing the area of the throat. By substituting Equation 2 into Equ-

ation 3, the relationship of the throat area to the operating pressure and burning area is demonstrated:

$$P = B \left(\frac{A_b}{A_t} \right)^{\frac{1}{1-n}} \quad \text{Equation 6}$$

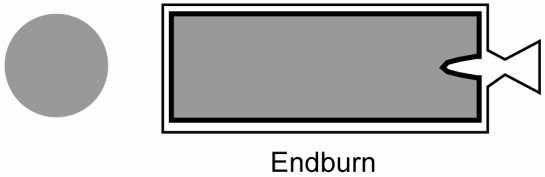
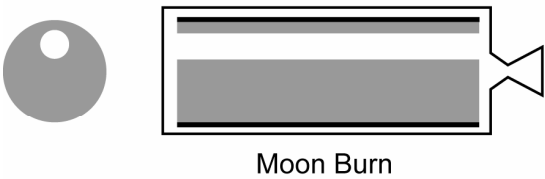
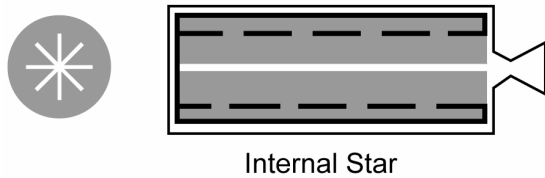
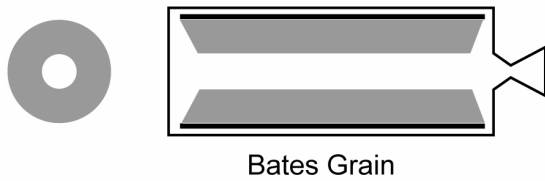
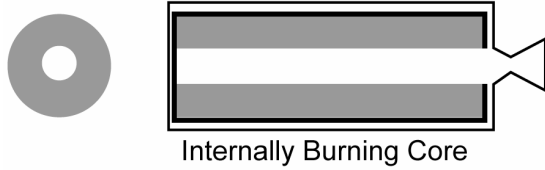
The operating pressure is subject to the weight and strength limitations of the motor casing, while the burning area is a function of grain geometry.

Grain Geometry

All of the many variations of grain geometry fall into three broad classes. Regressive grains have a large initial surface area which decreases as burning progresses. Neutral burning grains will maintain a constant burning area and progressive grains exhibit an increase in burning surface as propellant is consumed. Each of these categories has inherent advantages and disadvantages. For example, a moon burning grain geometry with regressive characteristics would be useful in long burning, relatively slow traveling rockets going to high altitude. The high thrust of this initially progressive geometry would be desired at the beginning of the flight when vehicle weight is high. As the rocket gains altitude, its mass is decreasing as propellant is consumed. At the same time, the frictional resistance or drag decreases as the atmosphere thins, and the grain geometry becomes regressive as it burns out to a sustainer phase. In this way, a subsonic velocity with its lower drag coefficient may be maintained, thus optimizing vehicle altitude. When constant thrust is desired, neutral burning grains are called for. This is characteristic of an end-burning charge consisting of a solid cylindrical section of propellant which is inhibited on all surfaces, except at one end, so that it will burn like a cigarette. The end is often machined into a cone shape to increase the initial surface area. Such charges have a constant burning area (unless the end is coned) and have a very long burning time, with very limited applicability for composite rockets. Hollow rod or rod and tube geometries will also provide neutral burning characteristics while exposing more propellant

Propellant Grain
Cross Sections

Casing
 Inhibitor
 Propellant



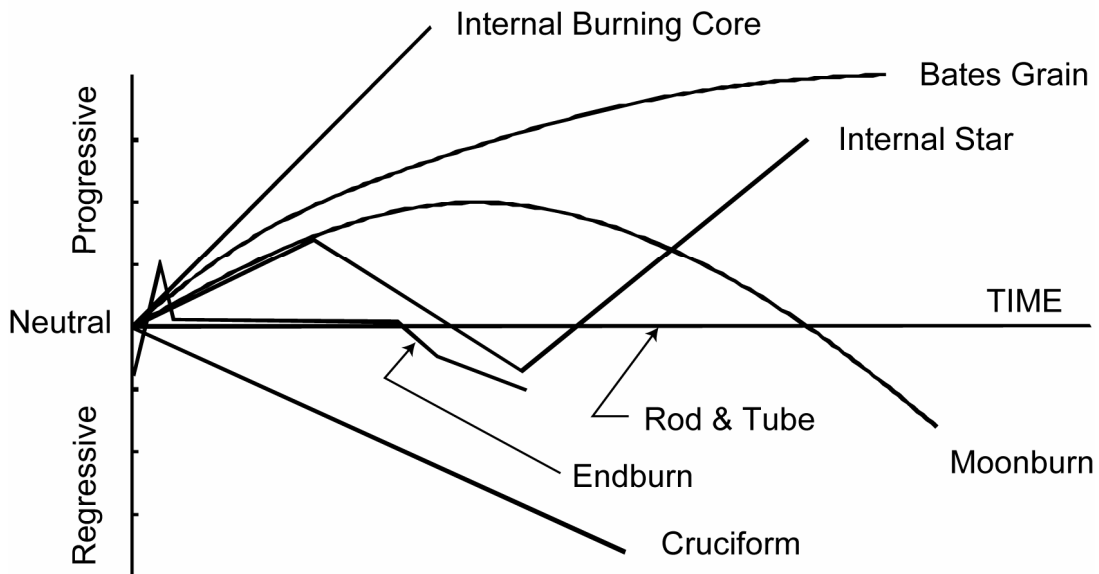
surface area and providing higher thrust levels than are available with end-burning designs.

Progressive burning characteristics are found in internal burning case-bonded charges. An internal burning charge, as its name implies, burns outwardly from the internal perforation. It may have single or multiple ports in a variety of shapes, which provide these motors with high levels of thrust over moderately short burn times. Such motors are useful in boosting large or heavy payloads. These propellant grains may be severely stressed during motor function, particularly at the internal perforation. Moderate tensile strength (100–150 psi) and good elongation (30–70%) are necessary for case-bonded charges.

Thrust programs may be designed so as to combine the characteristics of progressive, neutral or regressive burning in a single motor. For an internal burning star grain shape, the initial surface area can be made nearly equal to the outside or final area of the grain. During burning, the surface will increase slightly, then decrease to a minimum, then increase gradually until the points of the star reach the outer surface. At that point, there will be left semi-lunar sections, or slivers, which will burn out with ever decreasing area.

Progressive–regressive profiles are characteristic of moon burn grains first designed by Bill Wood, which utilize an offset core which is approximately 25% of the grain diameter. Initially, such motors are progressive core-burners up to the point where the expanding core reaches the case wall. Then, the remaining propellant, which is now in the shape of a crescent moon, burns regressively. A “D” shaped grain consisting of a solid rod with a thin slice cut off lengthwise will exhibit a similar thrust profile.

Grain Geometry Burning Characteristics



A working knowledge of the interrelationships already discussed between operating pressure, propellant burn rate, and propellant surface area leads to a second manner in which the thrust program of a given motor may be varied: changing the throat diameter. By using an ablative nozzle material which erodes at a known rate during motor function, the K_n of a motor may be changed in conjunction with the surface area of propellant burning. It is possible to design a neutral burning motor by combining a progressive grain geometry with an ablative nozzle, thus maintaining a relatively constant K_n , burn rate, and operating pressure.

Materials

Motor Casings

The combustion chamber or motor casing functions as a simple pressure vessel. High strength and low weight are of primary concern when choosing a casing material. For large rockets, steel has been a frequent choice. Aluminum is a lighter metal, but the thicker walls necessary to fabricate a casing of the same strength as steel, resulting in no net advantage. Of the metals, titanium is by far the strongest and lightest, but it is very difficult to fabricate and is an expensive alternative.

Smaller composite rocket motor casings are generally made from phenolic paper or cloth, or fiberglass. These materials are exceptionally strong and very light, and possess the added advantage of having a decreased hazard potential from shrapnel in the event of motor deflagration. Fiberglass casings may be manufactured from glass cloth or by filament winding where plastic or more commonly epoxy impregnated fiberglass is wound over a mandrel to form a tube. When the resin is cured, the mandrel is removed to make the casing. When using filament, it is desirable to maintain a 55 to 60 degree angle of winding so as to prevent the formation of micro-porosities extending through the walls of the finished casing. In addition, 6061-T6 aluminum tubing is presently enjoying widespread usage in reloadable motors.

The phenolic based materials are lighter and less expensive than their fiberglass counterparts, as well as being more resistant to the high flame temperatures of composite propellants. They are also much weaker than fiberglass and therefore contraindicated for use in high pressure motors. In some cases, thin wall phenolic tubes are used as rigid liners into which propellant grains may be cast, then machined and loaded into motors.

Although not commonly considered as an appropriate material for composite motor casings, the author has recently developed a one-pound size paper casing motor (29 mm) using specially made high tensile virgin Kraft tubes with ablative ceramic nozzles.

Many motor casings will incorporate a liner as insulation. Most often it is fabricated from the same binder as the propellant and filled with inert materials such as titanium dioxide, silicon dioxide, and/or other high temperature resistant materials. Asbestos free high density gasket material, (1/32") available at automotive supply stores, is an easy to use alternative when desired.

Epoxies

Epoxy compounds have received widespread utilization as the material of choice for sealing bulkhead and nozzle closures of small rocket motors. These materials are well adapted for withstanding the high heat and high pressure environment of motor function. An almost infinite number of formulations are possible based on the specific primary resin, modifying resin, and additives such as reactive diluents, bonding agents, surface active agents, fillers, and curatives.

An excellent and readily available epoxy may be found at local hobby shops which cater to radio control airplane enthusiasts: SIG One Hour Cure Epoxy is a medium viscosity clear epoxy suitable for cementing full diameter nozzles and delays.

When "floating" a nozzle of substantially smaller diameter than the motor casing, a reinforced, filled epoxy is required. These materials are commonly used for potting or encapsulating electronics components and are available in various viscosities and thermal conductivities. Biwax Corporation's Formula 411 works well for this application.

The Propellant System

Oxidizer

The primary use of ammonium perchlorate, NH_4ClO_4 , is as an oxidant in solid propellants. It is also used in explosives, mines, shells, timing devices, and pyrotechnics. It is produced from anhydrous ammonia, aqueous hydrochloric acid, and sodium perchlorate. Ammonium perchlorate is a white crystalline solid with a molecular weight of 117.49 and specific gravity of 1.95. It is slightly soluble in water. Pure ammonium perchlorate is stable below 65.6 °C and undergoes an endothermic reaction at 240 °C, followed by two exothermic steps at 275 and 470 °C. Contamination with metallic salts such as those of copper, chromium, and iron catalyzes the second decomposition step so that it occurs at progressively lower temperatures as the impurity concentration is increased. Ammonium perchlorate is a strong oxidizer which is not explosive unless contaminated. It constitutes an extreme fire hazard in contact with oxidizable substances, organic materials, ammonium compounds, cyanides, sulfur and sulfur compounds, powdered metals, phosphorus and metal salts. Strong acids may react with perchlorates to generate perchloric acid, a dangerous explosive if allowed to contact oxidizable materials. Ammonium perchlorate crystals have piezoelectric properties, and may generate a charge upon stress deformation.

Ammonium perchlorate contains 34% available oxygen, considerably less than that of the sodium or potassium salts. Nevertheless, because of the low weight fraction of solids in their combustion gasses, propellants containing it have overall performance characteristics exceeding that obtainable with either of the other two oxidizers. It also has the advantage of not producing smoke.

Ammonium perchlorate propellants produce hydrogen chloride and other chlorine compounds during combustion. In high humidity or a moist atmosphere, the hydrogen chloride will condense into a dangerous fog of hydrochloric acid. The exhaust gasses of these motors are toxic, as well as being highly corrosive to many materials.

Particle Size

Ammonium perchlorate is produced in three ordinance grades. The fine classified grade is available in 55 and 90 micron sizes, both coated with tricalcium phosphate (TCP) as an anti-caking agent. Regular-Class I is 200 microns and Coarse-Class II is 400 micron in size. The latter two grades are offered with or without the TCP and may be rotary rounded, producing spheroidal grains.

The shape of the grains and particle size of the oxidizer are of critical importance in a propellant formulation, influencing the burning rate, processing properties and the physical properties of the propellant. In general, a decrease in particle size results in an increase in burning rate, with the most significant effect in the submicron range up to about one hundred microns. The effects of crystal size are sometimes so significant that a whole series of propellants can be made with the same composition by merely varying the particle size.

Multi-Modal Propellant Systems

In practice, most composite propellants are multi-modal, consisting of several different sizes of oxidizer in specific ratios. The larger 200 and 400 μ grains are rounded to spheres so as to present the smallest possible surface area per volume of oxidizer. The smaller crystals of ground oxidizer will then fit into the interstices between the larger particles. The net result is a propellant with high solids loading which is not fuel rich and thus maximizes the I_{sp} and mechanical properties of that propellant.

Binder System

Binder

Hydroxyl terminated polybutadiene (HTPB) is a long chained clear liquid rubber polymer. First used as a binder and fuel in solid propellants by Aerojet in 1962, HTPB is chemically a polyurethane because it is cured with isocyanates. Reaction sites for cross linking are provided by hydroxyl (—OH) radicals at several points along each chain, as well as at terminal ends. It is the three dimensional matrix of the cross-linked rubber chains which impart the im-

portant mechanical properties to a propellant. The ability of a propellant to withstand high strain rates is directly related to the low temperature properties of the binder, such as elongation and brittle point. In high solids loaded propellants, a modulus of 400–700 psi with good elongation and tensile properties is required, particularly when case bonding. With a glass transition temperature near or below -100°F , HTPB has excellent characteristics.

Table 1. Physical Data for HTPB.

Boiling point		300 °C
Specific gravity	@25 °C	.90
Viscosity (Brook)	@25 °C	6000
Strain capacity	@-65 °F	25–35%

The actual mechanical properties of a specific propellant are a function of the exact formulation (i.e., by the size distribution and amount of solids, the ratio of binder to curing agent, and the amount of plasticizer).

Curative

As previously mentioned, HTPB is cured by isocyanates. Some require an elevated temperature (oven cure) of $+125^\circ\text{F}$ to activate, while others such as isophorone diisocyanate (IPDI) or PAPI; are active at room temperature. Such curatives are usually present in the range of 8–10% of the rubber content of the propellant, based on calculation of the activity of the particular agent used. These curatives are all toxic compounds, with some more so than others. Among the room temperature curing agents, toluene diisocyanate gives the shortest pot life and is the most toxic. PAPI-901 (Dow Chemicals) and N-100 are two good choices for low toxicity and adequate pot life for room temperature curatives. Care must be taken to ensure that all propellant components are kept dry, as isocyanate groups will react with water, producing a substituted urea and liberating CO_2 in a gas-sing reaction.

Plasticizer

A number of very low viscosity plasticizing agents may be added to a propellant for improved wettability which will allow higher solids loading and consequently improve performance. These agents will improve the mechanical properties of a propellant, retard oxidation and embrittlement to a certain extent, and when used as a significant portion of the binder system (25–30%), will allow for some propellants to be pourable.

❖ Dioctyl adipate (Uniflex DOA, Union-Camp) is a high quality grade of DI-2-ethylhexyl adipate which is used as a diester fluid for synthetic lubricants. This colorless liquid has low acute oral toxicity, but is considered as a high health hazard due to its mutagenic and carcinogenic effects.

❖ Dioctyl azelate (DOZ) is a similar product with a slightly higher molecular weight and lower toxicity.

❖ Isodecyl pelargonate, IPDI, (Emery 2911 Synthetic Lubricant Basestock, Emery Chemicals), is another synthetic oil of even lower viscosity than DOA, which is an excellent plasticizer.

In effect, most any low viscosity type of oil may be used as a plasticizing agent. The advantage of the aforementioned products lies in their wetting ability and ultra low viscosity.

Bonding Agents

Most published propellant formulations will contain a bonding agent. These compounds react with the surface of the ammonium perchlorate crystals (frequently releasing gaseous ammonia) and facilitate actual bonding of the rubber to the crystal. Without such an agent, the oxidizer crystals are simply retained physically within the propellant, captured in effect by a three dimensional matrix of rubber. Without a bonding agent, crystals of oxidizer which are on cut or machined surfaces of a propellant grain will be lost during processing, leaving a fuel rich surface. TEPANOL Dynamar™ Bonding Agent/ Processing Aid HX-878) is one such bonding agent and commonly comprises 0.25% of the entire propellant formulation. Bonding agents greatly improve the mechanical strength

and properties of a propellant, but are not of significance in small rocket motors.

Metallic Fuels

Finely divided metals are added to almost all composite propellant formulations. These fuels provide a variety of benefits and enter into some very complex interactions during combustion. Spheroidal aluminum is perhaps the most commonly used metal in composite propellants, found in various formulations from near 1% up to around 18%. The ballistic performance of aluminumized propellants is greatly increased, raising the I_{sp} in the range of up to 10% when compared to the same formulation without metal. It must be noted, however, that this effect is not significant in small rocket motors, where the metal is not in the combustion chamber long enough to be consumed, and is mostly expelled in the exhaust gasses in the molten form. The addition of aluminum to a propellant will also serve to dampen acoustic oscillations, thus minimizing the possibility of grain fracture at ignition, and also making ignition easier, especially in small motors. The net effect of aluminum on burn rate is usually not large and may be positive or negative.

When considering metallic fuels other than aluminum, those with low molecular weight are desirable. Those which might be of benefit to propellant application may be determined by considering the density and the heat of formation of the metal oxide. Beryllium heads the list and has been reportedly used, but has the problem of producing toxic combustion products. Boron, lithium and silicon all have higher heat content per gram than aluminum, and are potential additives. Magnesium has also been used, but imposes a hardship on the binder due to its lower heat content and lower density.

Burn Rate Modifiers

Numerous compounds are utilized to modify the burn rate of propellant systems. Most exert a positive catalytic effect, while some such as oxamide decrease the burn rate by insulating the heat wave and slowing the progression of combustion. Addition of inert compounds (chalk) or substituting less active oxidizers (am-

monium chloride, sulfate) for a portion of the AP in a propellant will also slow the rate of burn.

By far, the majority of modifiers are catalysts which in some manner enhance the rate of burning. The effects that these compounds have on the dynamics of combustion are an exceedingly complex area of research.

At this point, it will suffice to say that catalysts exert their effects in relationship to combustion pressure and concentration. An effective range may be determined, above which the increase of catalyst percentage has diminishing returns without significant increase in burn rate.

The following is a partial listing of some frequently utilized burn rate catalysts with brief comments about each one:

Promoters

❖ Manganese Dioxide (MnO_2) — Positively catalyzes solid phase reactions. MnO_2 is a strong positive catalyst for the decomposition, but is a negative catalyst for the deflagration of AP.

❖ Iron(III) Oxide (Fe_2O_3) — An excellent and readily available catalyst. It will increase burn rate more than MnO_2 will at same level. Fe_2O_3 promotes the complete decomposition of AP at 270–280 °C.

❖ Chromium(III) Oxide (Cr_2O_3) — Primarily enhances the low temperature decomposition of AP, allowing that reaction to go to completion. Chromium oxide exerts a much greater effect on burn rate than manganese dioxide, and at the 2% level is superior to iron oxide in low pressures, up to about 600 psia.

❖ Copper Chromite ($\text{Cu}_2\text{Cr}_2\text{O}_7$ or $\text{CuO} \cdot \text{CuCr}_2\text{O}_3$) — has a significant, but varied effect on burn rate. Analysis has shown that copper chromite catalysts differ from company to company and may not even be the same from batch to batch. Propellants containing copper chromite become brittle and do not age well.

❖ Cupric and Cuprous Oxide (CuO and Cu_2O) — Both catalyze the low and high temperature decomposition of AP, and promote ignition. Cupric oxide (CuO) is superior to copper chromite and even chromium oxide as a burning rate promoter.

❖ Ferrocene (Dicyclopentadienyliron, $\text{C}_{10}\text{H}_{10}\text{Fe}$) and its derivatives Catocene and N-Butylferrocene — These liquid burn rate promoters are based on two five-membered cyclopentadienyl groups with a ferrous ion (Fe^{2+}) sandwiched between. These compounds interact with aluminum during combustion. Decreasing the particle size and thus increasing the surface area of aluminum to react will increase the burn rate of propellants containing these compounds.

Burn Rate Inhibitors

The burn rate of a propellant may be decreased by the substitution of up to 20% of the oxidizer with ammonium chloride or ammonium sulfate. The addition of zinc powder to a propellant will also slow the rate of burn, while also generating a dense, black exhaust. A fuel rich propellant or one to which an inert component such as calcium carbonate has been added, will also burn slower. The use of an inhibiting compound which will contribute to the combustion reaction, however, seems to be the more sensible approach.

Conclusion

It is hoped that the preceding discussion provides the reader with a basic understanding of the many variables involved in the design and fabrication of composite propellant systems, and of their great potential. This is a dynamic area of technology and development, with contributions continuing to be made by amateurs and professionals alike.

A solid theoretical background is important, but in the end, any new motor or propellant design is always qualified by an extensive static testing program. For those interested, an increasing amount of information including motor and propellant development programs for PC's, and instructional manuals are becoming available. An invaluable reference source for anyone working with liquid or composite propellants, as well as for those with a more theoretical orientation is *Rocket Propulsion Elements, An Introduction to the Engineering of Rockets*, Sixth Edition, by George P. Sutton. It is available from John Wiley & Sons, Inc. Professional, Reference and Trade Group, 605 Third Avenue, New York, NY 10158-0012 USA. Many Rock-

etry enthusiasts have become members of the Tripoli Rocketry Association, Inc. PO Box 339, Kenner, LA 70063-0339 USA. This organization encompasses all aspects of non-professional

rocketry, and is currently forming a research branch for members interested in more development.

Errata — Issue No. 2

“Errata for Issue Number 1” One of the corrections for Issue Number 1 contained further errors.

Page 14 **“An Introduction to PROPEP, A Propellant Evaluation Program for Personal Computers”** Page 15 Right column, middle of the page, one line of text was not properly superscripted, it should read:

$$p_c = c \cdot K_n^{(1/1-n)}$$

Issue No. 2:

“Introductory Chemistry for Pyrotechnists, Part 2: The Effects of Electrons”

Page 19 Left column, 2nd paragraph, lactose was incorrect. It should be:

Some elements find themselves in valence states with an excess of electrons. Lactose ($C_{12}H_{22}O_{11}$), for instance contains carbon with a valence state of zero [$12(0) + 22(+1) + 11(-2) = 0$].

Page 21 Table 4, Commonly Used Color Agents.

Copper(II) Carbonate should be Basic Copper Carbonate, with the empirical formula of

(I) $CuCO_3 \cdot Cu(OH)_2$,

(II) $2CuCO_3 \cdot Cu(OH)_2$ [Shimizu, p. 112]. Commercially available material is usually a mixture of (I) and (II).

Sodium Disilicate should be synthetic Ultramarine, with the empirical formula $Na_2S_2 \cdot 3NaAlSiO_4$ [Shimizu, p. 148].

[Shimizu, T. *Fireworks: The Art, Science and Technique*, Reprinted by Pyrotechnica Publications, 1986.]

Events Calendar

Pyrotechnics

27th International Conference of the Institute of Chemical Technology

June 25 – 28, 1996, Karlsruhe, Germany

Contact: Fraunhofer - Inst. für Chem. Tech.

P.O. Box 1240

D-76318 Pfinztal (Berghausen)

Germany

Phone: +49-721-4640-121

FAX: +49-721-4640-111

22nd International Pyrotechnics Society Seminar

July 15 – 19, 1996, Ft. Collins, Colorado, USA

Contact: IIT Research Institute

10 W. 35th Street

Chicago, IL 60616 USA

Phone: 312-567-4280 or 312-567-4293

FAX: 312-567-4543 or 708-790-9526

e-mail: TULIS@EAGLE.HQ.IITRI.COM

John Conkling — 1996 – One-Week Seminars

Chem. of Pyrotechnics & Explosives, Jul. 21–26

Application of Pyrotechnic Principles to Solve

Performance and Safety Problems, Jul. 28–Aug. 2

Contact: Dr. John Conkling

Summer Pyrotechnic Seminars, P.O. Box 213

Chestertown, MD 21620 USA

Phone: 410-778-6825

FAX: 410-778-5013

26th International Symp. on Combustion

July 28 – August 6, Naples, Italy

Contact: The Combustion Institute

5001 Baum Boulevard, Suite 635

Pittsburgh, PA 15213-1851 USA

Phone: 412-687-1366

FAX: 412-687-0340

email: combust@telerama.lm.com

International Autumn Seminar on Propellants, Explosives and Pyrotechnics

October 7 – 10 1996, Beijing, China

Contact: Prof. Changgen Feng

Mechanics and Engineering Dept.

Beijing Institute of Technology

P.O. Box 327, Beijing 100081, China

Phone: +841-6688 ext. 2941 or 2764

FAX: +841-2889

American Defence Preparedness Association (ADPA) Pyrotechnics Section — in conjunction with Munitions Technology Symposium IV and Statistical Process Control Meeting

February 10–12, 1997, Reno, Nevada, USA.

Contact:

Jason Burkett

Olin Ordinance

10101 9th St. N.

St. Petersburg, FL 33716

Phone: 813-578-8280

FAX: 813-578-8146

e-mail: Bullet Dr@aol.com [Yes, it is a space.]

23rd International Pyrotechnics Seminar

September 30–October 4, 1997, Tsukuba, Japan

Contact: Prof. Tadao Yoshida

College of Engineering of Hosei University

3 – 7 – 2 Kajino-cho, Koganei-shi

Tokyo 184 Japan

Phone: +81-423-87-6132

FAX: +81-423-87-6381

Fireworks

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

Dates and Competitors:

June 15 Marutamaya Ogatsu, Japan

June 20 Sunny International, China

June 23 Pirotecnica Soldi, Italy

(Continued on next page)

June 27 Kimbolton Fireworks, England
June 30 Weco Pyrotechnique Fab., Germany
July 4 Pirotechia Igual, Spain
July 7 Foti's International, Australia
July 11 Performance Pyro. Assoc., USA
July 14 Ampleman, Canada
July 18 Closing by Panzera of Spain

Contact: AMARC

Île Notre-Dame

Montreal, Quebec H3C 1A9 Canada

Phone: 514-872-6241

FAX: 514-872-8711

Symphony of Fire – Fireworks Displays

Toronto, Canada 1996 Schedule:

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

Vancouver, Canada 1996 Schedule:

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

Contact: Frank Furtado

3054 Lacombe

Montreal, Quebec H3T 1L4 Canada

Phone: 514-866-3335

FAX: 514-398-9287

Summer Fireworks Festival

July 15 – 19, 1996, Auburn, New York USA

Contact: Charles Hill

4533 Foster Valley Road

Endicott, NY 13760

Phone: 607-748-0667

FAX: 607-748-0899

Pyrotechnics Guild International Conv.

August 11–16, 1996, Muskegon, Michigan USA

Contact: Ed Vanasek, Secretary-Treasurer

18021 Baseline Avenue

Jordan, MN 55352 USA

Phone: 612-492-2061

3rd International Symposium on Fireworks

September 16 – 20, 1996, Walt Disney World,
Lake Buena Vista, Florida, USA

Contact: Ettore Contestabile, Canadian Explosives
Research Laboratory, CANMET

555 Booth Street

Ottawa, Ontario K1A 0G1 Canada

Phone: 613-995-1363

FAX: 613-995-1230

e-mail: pyrotechnics@nrca.gc.ca

Florida Fall Fireworks Festival

November 1 – 3, 1996 site undetermined, but will
be in Florida, USA

Contact: John Driver, Treasurer FPAG

2382 NW 30th Road

Boca Raton, FL 33431 USA

Phone: 407-483-7737

FAX: 407-483-4198

e-mail: 70233.1654@Compuserve.com

Western Winter Blast

February 14–16, 1997, Lake Havasu, Ariz. USA

Contact: Western Pyrotechnic Association

2230 Aralia Street

Newport Beach, CA 92660 USA

Phone/FAX: none listed

High Power Rocketry

LDRS

July 4–7, 1996; Orangeburg, So. Carolina USA

Contact: Jim Conn

Phone: 803-831-0979

Model Rocketry

NARAM – 38

August 2 – 10, 1996, Evansville, Indiana USA

Contact: Chad Ring, Contest Director

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