Pyrotechnic Smoke Compositions Containing Boron Carbide

Anthony P. Shaw,* Jay C. Poret, Robert A. Gilbert,
Jared D. Moretti, Jesse J. Sabatini, Karl D. Oyler, Gary Chen

Pyrotechnics Technology and Prototyping Division,
US Army RDECOM-ARDEC, Bldg 1515, Picatinny Arsenal, New Jersey 07806 (USA)
***corresponding author; e-mail: anthony.p.shaw@us.army.mil**

ABSTRACT

Smokes are used on the battlefield for signaling, for marking targets, and for screening troop movements. Many high-performance compositions are toxic or hazardous, while non-toxic alternatives offer sub-par performance. The environmentally benign compositions described herein use boron carbide as a pyrotechnic fuel to produce thick clouds of white smoke. Experimentation and thermodynamic modeling were used in conjunction to develop the compositions which were then evaluated both visually and by transmittance-based measurements. Small scale smoke chamber tests indicate that some of these new systems can approach the performance of the AN-M8 HC composition (Al/ZnO/C_2Cl_6).

Introduction

Smokes have been used on the battlefield for over 300 years. The first documented use involved the intentional burning of damp straw to screen Swedish troops crossing the Western Dvina in 1701.[1] Since that time, smoke technology has undergone significant development and smokes continue to serve an important role in the theater of war. Smokes are used for signaling, for marking targets, and for screening troop movements. Many high-performance obscurant smoke compositions and the smoke they produce are toxic or hazardous. These qualities increase the likelihood of collateral damage and increase the risk to the warfighter when such smokes are used for screening.

While smokes may be dispersed by several different mechanisms, the use of pyrotechnic compositions is arguably the most adaptable method, since they may used in many different smoke devices including grenades, smoke pots, mortar and artillery projectiles. However, screening smoke compositions are among the most difficult pyrotechnic compositions to design. This difficulty arises from a large number of quantitative and qualitative requirements which often conflict. These requirements may be separated into three distinct categories which are outlined below.

Performance:

- The composition should produce a maximum amount of finely dispersed solid or liquid products, with a minimum amount of flame and light, and should leave little residue.
- The products of the pyrotechnic reaction should be hygroscopic to maximize the mass of the resulting smoke cloud by absorption of atmospheric moisture.
- The rate of burning should be controllable to suit different applications.
- The smoke should have the appropriate qualitative performance characteristics for the desired application (thickness, volume, dispersion, tendency to rise or fall).

Environmental:

- The components of the composition should be non-hazardous to the environment and to production personnel.
- Remaining residue should not be an environmental hazard.

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14. ABSTRACT

Smokes are used on the battlefield for signaling, for marking targets, and for screening troop movements. Many high-performance compositions are toxic or hazardous, while non-toxic alternatives offer sub-par performance. The environmentally benign compositions described herein use boron carbide as a pyrotechnic fuel to produce thick clouds of white smoke. Experimentation and thermodynamic modeling were used in conjunction to develop the compositions which were then evaluated both visually and by transmittance-based measurements. Small scale smoke chamber tests indicate that some of these new systems can approach the performance of the AN-M8 HC composition (Al/ZnO/C2Cl6).

15. SUBJECT TERMS

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Standard Form 298 (Rev. 8-98)
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- The smoke cloud should be safe to breathe.

Safety:

- The composition should be insensitive to stimuli other than the intended ignition source.
- The composition should not degrade upon long-term storage.

The interplay and conflicts between these ideal requirements are well-illustrated by consideration of the common pyrotechnic military smoke formulations RP, HC, and TA. Red phosphorus (RP) compositions are typically fuel-rich mixtures of red phosphorus, a pyrotechnic oxidizer, and an organic binder. Sometimes additional metallic fuels are added to increase the energy of the mixtures. These compositions produce a very thick smoke and are extremely efficient. Excess phosphorus burns in the air forming phosphorus oxides which are extremely hygroscopic. Unfortunately, the compositions are notorious for their high sensitivity,[2, 3] and for the release of toxic and flammable phosphine gas over time.[4, 5] The compositions are often incendiary,[3, 6] and the smoke they produce is acidic.

HC-type pyrotechnic smoke compositions generally contain hexachloroethane (HC), a source of zinc (either zinc metal or zinc oxide) and other chemicals. The AN-M8 smoke grenade contains 44.5% hexachloroethane, 46.5% zinc oxide, and 9% aluminum by weight. The smoke is highly effective, since the primary component is zinc chloride which is vigorously hygroscopic. HC smoke compositions are no longer manufactured for use by the US Army because of the high toxicity of the hexachloroethane,[7] and the high toxicity of the resulting smoke. The inhalation of zinc fumes is known to cause "metal fume fever" and the smoke also contains various chlorinated organic compounds which are suspected to be carcinogens.[8] It was identified as the worst smoke in a combined health/environmental ranking.[9]

To address the health and environmental problems of HC smoke, the US Army developed TA (terephthalic acid) smoke compositions. These compositions use sugar/potassium chlorate as a low temperature fuel/oxidizer pair. The heat from this reaction volatilizes terephthalic acid which re-condenses in the air to give a white smoke. A toxicological study confirmed the relative safety of TA smoke, but also anecdotally mentioned its poor performance: "[The M83] grenade [containing a TA composition] would be used for training purposes only since its burn time is approximately 1/3 to 1/5 the burn time of the HC smoke."[10] In addition to burn time issues, TA smoke compositions are relatively inefficient. The large amount of ash and residue created upon burning necessitates the use of "core-burning" designs. The smoke is not particularly hygroscopic and therefore does not benefit from atmospheric moisture the way RP and HC smokes do. The warfighter must throw two or three TA smoke grenades to obtain the volume and thickness of smoke comparable to that from one HC smoke grenade.

It is apparent that a gap exists between the performance of pyrotechnic smoke compositions and the environmental and safety factors which are also desired. To address this gap, a project was initiated under the Environmental Quality Technology (EQT) Program. In the first phase of the project, boron carbide was identified as a suitable pyrotechnic fuel for smoke compositions. Mixtures of boron carbide with potassium nitrate, inorganic salts, and organic additives produce thick clouds of white smoke upon ignition. This report describes the rationale behind boron carbide-based pyrotechnic smokes and the initial experimentation which indicates that they may be suitable for use in military smoke devices.

Experimental

Materials characterization data for the components of the boron carbide-based smoke mixes are presented in Table 1. A Malvern Morphologi G3S optical microscopy particle size analyzer was used to determine number-based CE diameter distributions. Potassium chloride and ammonium chloride were granular and were ball-milled so that they passed through a 50 mesh screen. Melamine ($C_3H_6N_6$, Sigma Aldrich), 5-aminotetrazole (CH_3N_5, Sigma Aldrich), and imidazole ($C_3H_4N_2$, Alfa Aesar) were powders and were used as received.

Table 1. Materials characterization.

Material Name	Material Formula	Source	Mesh Size	Particle Size Mean	Standard Deviation
			#	μm	μm
boron carbide	B_4C	Alfa Aesar		3.48	4.05
potassium nitrate	KNO_3	Hummel Croton		7.31	6.04
potassium chloride	KCl	Alfa Aesar	< 50		
lithium phosphate	Li_3PO_4	Sigma Aldrich		7.31	4.91
ammonium chloride	NH_4Cl	Alfa Aesar	< 50		
calcium stearate	$C_{36}H_{70}O_4Ca$	Alfa Aesar		5.83	4.60
stearic acid	$C_{18}H_{36}O_2$	Hummel Croton		11.50	14.25
poly(vinyl alcohol)	$(C_2H_4O)_x$	J.T. Baker		5.66	8.61

No wet binders were used in this study. The dry boron carbide-based smoke mixes were prepared by a combination of tumbling (15-30 min) and screening (20 or 30 mesh). Three different configurations were studied. Hand-held signal (HHS) tubes were made of kraft fiberboard and had an inner diameter of 3.12 cm. Stainless steel cans, cylindrical and closed on one end, had a 1.75 cm inner diameter, 4.0 cm height, and a 1.0 mm wall. Bare pellets had a 0.95 cm diameter. All compositions were consolidated at 10 kpsi (69 MPa) with a 10 second dwell time. HHS tubes were pressed in three increments of 20 grams each, while the cans (14-15 grams composition) and the bare pellets (1 gram) were pressed in one increment. The HHS tubes were then cut down to fit the height of the consolidated mixes. An igniter slurry composed of 33 wt% potassium nitrate, 24.5 wt% silicon, 20.8 wt% black iron oxide, 12.3 wt% aluminum, 3.8 wt% charcoal, and 5.6 wt% nitrocellulose in acetone was applied to the compositions in HHS tubes and cans. These items were dried overnight in a 65 °C oven. No igniter slurry was used on the bare pellets. Electric matches were used to ignite the slurried items. Bare pellets were ignited with electrically heated nickel-chromium wire (hot wire).

Small HC smoke pellets were used as a baseline for smoke chamber studies. Aluminum (type 2, grade E, class 6 per MIL-DTL-512C) was obtained from AEE. Its particle size mean and standard deviation were 12.6 and 13.3 μm, respectively. Zinc oxide was obtained from Fisher Scientific. Its particle size mean and standard deviation were 4.2 and 3.8 μm, respectively. Hexachloroethane (from Skylighter) was granular and screening gave the following weight distribution: 13.8% > 20 mesh, 50.6% 20-50 mesh, 18.5% 50-100 mesh, 17.1% < 100 mesh. A mixture of 9.0 wt% aluminum, 46.5 wt% zinc oxide, and 44.5 wt% hexachloroethane was prepared by the mixing method described above. Bare pellets (1 gram) were prepared as described above. These pellets would not ignite using a hot wire, so igniter slurry was applied to the top face. The pellets were air-dried for several hours (hexachloroethane is too volatile for oven drying). The dried weight of igniter composition on each pellet was roughly 40 mg. The slurried side was ignited with hot wire.

The smoke chamber was a 0.61 x 0.61 x 1.83 m (0.68 m^3) poly(methyl methacrylate) (Plexiglas) enclosure with two opposing borosilicate glass windows (Corning 7056). The distance between the windows (the path length) was 0.61 m. Broadband light was supplied by a 75 W xenon lamp with an F/2.5 elliptical reflector (Optical Building Blocks). To reduce the divergence of the beam exiting the Xe lamp housing, a 75 mm diameter aspheric condenser lens with a 50 mm focal length (Melles Griot) was placed approximately 5 cm in front of the focal point of the lamp. This lens shaped the beam exiting the elliptical reflector into a column which traversed the path length. The light exiting the chamber passed through an ND2 reflective filter and into a solarization-resistant 115 µm core diameter optical fiber with a 0.22 numerical aperture. Spectra were measured with a 2048 element silicon CCD spectrometer with a 25 µm slit and a high gain lens (Ocean Optics HR2000). Without any smoke in the chamber, the integration time of the spectrometer was chosen so that the wavelength with the highest signal was just below the saturation level of the system. This spectrum served as the baseline (I_0). The test container consisted of an insulating ceramic fiber disk placed inside a steel cup (1.27 cm tall, 2.22 cm diameter). Each pellet was placed on the insulating disk in this cup, which was then put inside the smoke chamber. Five spectra were recorded every second for 350 seconds, starting at the time of ignition. Transmittance (T), as a function of wavelength and time, was calculated by dividing these spectra by the baseline. The smoke did not have any distinct spectral features in the visible spectrum (380-780 nm) except for a slight concave curve. The smoke was well-equilibrated in the 125-325 second time range. Therefore, transmittance was averaged over these wavelength and time ranges for each test. These average T were then used to calculate figures of merit for each pellet. Finally, these FOM were averaged.

Impact sensitivity tests were performed with a BAM drop hammer. Friction sensitivity tests were performed with a BAM friction tester. Electrostatic discharge (ESD) sensitivity tests were performed with an Albany Ballistic Laboratories instrument. DSC/TGA measurements were done with a TA Instruments SDT Q600. Alumina pans were used, and the experiments were run at 10 °C/min under a 100 mL/min flow of nitrogen.

Results and Discussion

Encouraged by other work with boron carbide in our laboratories,[11] we considered the use of this fuel in smoke compositions. Upon further investigation, it was found that Lane and co-workers reported in 1968 that "A 30/70 mix of boron carbide and lithium perchlorate generated a good cloud of smoke."[12] This appears to be the first documented use of boron carbide as a fuel in a pyrotechnic composition. Calculations using the NASA CEA Code[13] suggest that B_4C is a very energetic fuel, as indicated by the predicted adiabatic flame temperatures of B_4C/KNO_3 mixtures (Figure 1). The main combustion products of a 15/85 B_4C/KNO_3 mixture are predicted to be 68.1% KBO_2, 11.7% N_2, 5.1% BO_2, 4.9% CO, 4.5% B_2O_3, and 4.2% CO_2 (all chemical percentages in this report are weight percentages). The permanent gas products N_2, CO, and CO_2 should help disperse the smoke. The main predicted product, KBO_2, should be mildly hygroscopic, a factor that benefits smoke performance. Despite these indications, binary B_4C/oxidizer mixtures are not expected to be ideal smoke compositions due to high temperatures which cause the emission of flame and light (note the predicted 5.1% BO_2, a green light emitter, in the above example).

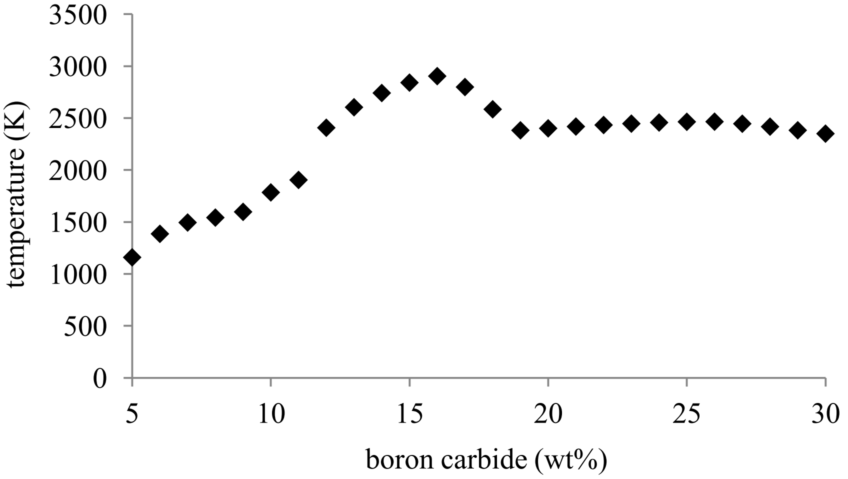

Figure 1. NASA CEA Code adiabatic temperatures for B_4C/KNO_3 mixtures.

To make an effective smoke composition from B_4C/KNO_3, other components are needed to lower the reaction temperature to minimize light output. In this study, we considered three: potassium chloride, lithium phosphate, and ammonium chloride. These chemicals, referred to as "smoke agents" from here on, were chosen for their differing predicted behavior. KCl is significantly volatile at temperatures above 1500 K (Figure 2),[14] and should serve as an inert diluent while also contributing to the smoke cloud. Li_3PO_4 was chosen for its phosphorus content. Phosphates are known to undergo reduction when paired with energetic fuels.[3, 15] Reduction of phosphate gives lower phosphorus oxides or elemental phosphorus, which should increase the performance of the smoke. NH_4Cl undergoes pseudo-sublimation by decomposition to NH_3 and HCl. Subsequent recombination of these gases gives dispersed NH_4Cl which is known to be a good smoke agent in certain compositions (such as the Yershov mixture).[1]

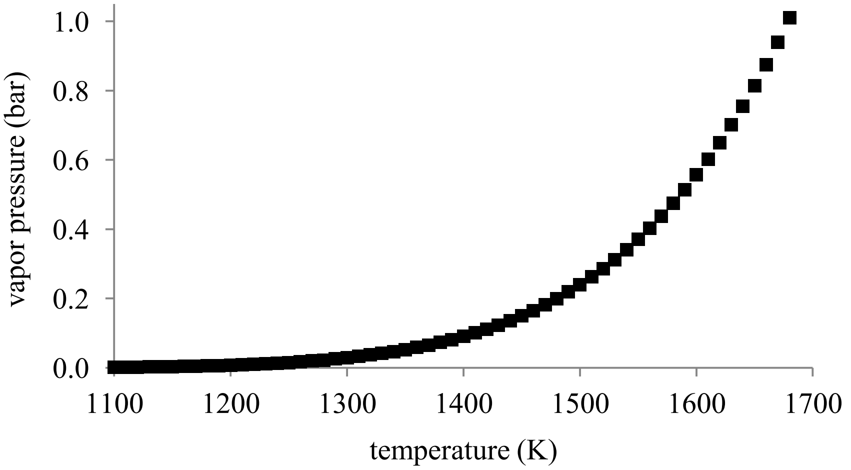

Figure 2. Vapor pressure of KCl as a function of temperature.

Hand-held signal (HHS) tubes, made of kraft fiberboard, were loaded with 70/15/15 mixtures of KNO_3/B_4C/smoke agent. Even with the 15% "smoke agent" in these mixes, there was still a substantial amount of flame, light, and spark output (Table 2). The mixes burned quickly, with inverse rates ranging from 2.4 to 4.9 s/cm. However, the compositions did produce a substantial amount of white smoke, as intended.

Table 2. HHS tubes containing 70% KNO_3 / 15% B_4C / 15% smoke agent.

Smoke Agent	Inverse Burn Rate (s/cm)	Smoke	Flame	Sparks
KCl	2.6	high	medium	high
Li_3PO_4	4.9	medium	medium	high
NH_4Cl	2.4	high	medium	medium

The above results indicated that an additional component was needed to suppress flame and spark output. Six organic additives were tested for this purpose (Table 3). Generally, the qualitative aspects (smoke, flame, sparks) of the Li_3PO_4 compositions were insensitive to the presence of additives. The NH_4Cl and KCl compositions were more responsive. Calcium stearate had a profound effect on the KCl and NH_4Cl compositions, reducing flame and spark output substantially. The composition containing KCl and calcium stearate gave high smoke output with minimal flame and no sparking, and qualitatively was the best composition in this set of experiments. Four of the additives, poly(vinyl alcohol), melamine, 5-aminotetrazole, and imidazole, had little influence on the burn rates. In contrast, calcium stearate and stearic acid reduced the burn rates dramatically. Stearic acid gave the slowest rates, but these compositions exhibit more flaming than their calcium stearate analogs.

Table 3. HHS tubes containing 65% KNO_3 / 15% B_4C / 15% smoke agent / 5% additive.

Smoke Agent	Additive	Inverse Burn Rate (s/cm)	Smoke	Flame	Sparks
KCl	poly(vinyl alcohol)	2.5	medium	medium	high
KCl	calcium stearate	13.4	high	low	none
KCl	melamine	2.8	medium	medium	high
KCl	5-aminotetrazole	2.6	high	high	low
KCl	imidazole	2.6	medium	low	low
KCl	stearic acid	20.9	high	medium	low
Li_3PO_4	poly(vinyl alcohol)	5.2	medium	medium	high
Li_3PO_4	calcium stearate	12.0	medium	medium	high
Li_3PO_4	melamine	4.4	medium	medium	high
Li_3PO_4	5-aminotetrazole	3.5	medium	high	high
Li_3PO_4	imidazole	3.4	medium	low	high
Li_3PO_4	stearic acid	13.3	high	medium	high
NH_4Cl	poly(vinyl alcohol)	2.6	medium	high	high
NH_4Cl	calcium stearate	17.7	medium	low	low
NH_4Cl	melamine	2.9	medium	medium	medium
NH_4Cl	5-aminotetrazole	2.4	high	high	high
NH_4Cl	imidazole	2.0	high	medium	low
NH_4Cl	stearic acid	21.3	medium	medium	low

The calcium stearate content may be used to control burn rate. HHS tubes containing an 85/15 ratio of KNO_3/B_4C, a fixed 20% level of KCl, and varying amounts of calcium stearate were tested in HHS tubes (Table 4). Changing from zero to 1% calcium stearate gave a large decrease in the burn rate, while further increases resulted in smaller decreases.

Table 4. HHS tubes containing an 85/15 ratio of KNO_3/B_4C, 20% KCl, and various amounts of calcium stearate.

Ca Stearate (wt%)	Inverse Burn Rate (s/cm)	Smoke	Flame	Sparks	Slag
0	2.5	high	medium	none	low
1	10.2	high	low	none	low
2	11.4	high	low	none	low
3	12.8	high	low	none	medium
4	14.1	medium	medium	none	medium
5	15.3	medium	medium	none	high

A plot of inverse burn rate versus calcium stearate level is linear in the 1-5% range (Figure 3). Therefore, small changes in the calcium stearate content may be used to fine-tune the burn rate in a predictable way. Levels above 5% are not practical, as the amount of slag upon burning increased noticeably when calcium stearate was changed from 3 to 5%. The 2% level was identified as the sweet spot, where slag formation was still low and also where sub-percent changes in the additive level did not have a large effect on burn rate. (This last point is applicable to reliable and reproducible *manufacturing*.) Figure 4 shows the 2% calcium stearate composition being tested.

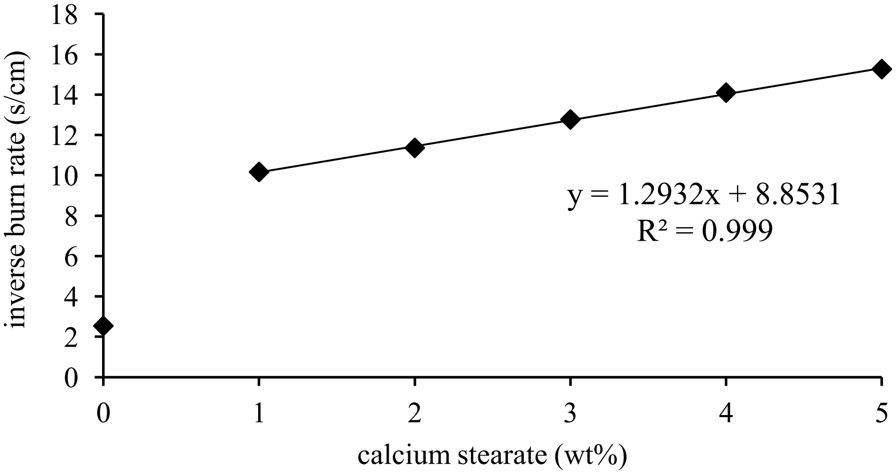

Figure 3. Inverse burn rates from Table 4 as a function of calcium stearate content.

Figure 4. Test of an HHS tube containing the 2% calcium stearate composition from Table 4.

With calcium stearate identified as in ideal additive for KNO_3/B_4C-based smoke mixes, a series of experiments was devised to test the effect of changing the smoke agent content. The calcium stearate and B_4C levels were fixed at 2% and 13%, respectively. Smoke agents were varied from 15-40% as KNO_3 content changed from 70-45%. These compositions were pressed into small stainless steel cans, a convenient configuration for small scale testing (Table 5). The smoke agent level had little influence on the burn rates. Some compositions did not sustain propagation. One of the KCl compositions and many of the NH_4Cl compositions did not continue burning after being initiated by the igniter slurry. Surprisingly, the 15% KCl composition did not sustain propagation, even though this should be the most energetic mixture in this series (since KCl serves as a diluent). It is conceivable that, in this case, not enough slag is generated by the reaction to transmit sufficient heat to the next layer. Other 15% KCl compositions burned well in HHS tubes, which are considerably larger, so the item diameter may also be a contributing factor. Many of the NH_4Cl compositions did not propagate. NH_4Cl undergoes pseudo-sublimation at a relatively low temperature (200-250 °C) and this process is highly endothermic. Meanwhile, B_4C/KNO_3 does not ignite until it is heated above 450 °C (Figure 5). Indeed, the DSC/TGA plots of the 15% NH_4Cl composition (which did sustain propagation) show the complete loss of NH_4Cl before any exothermic processes occur (Figure 6). This mismatch between the smoke agent sublimation point and the ignition/combustion temperature of B_4C/KNO_3 is responsible for the failure of compositions containing over 20% NH_4Cl. In general, endothermic processes which occur at low temperatures (below the temperature required for fuel/oxidizer reaction) can inhibit reaction propagation in pressed pyrotechnic compositions. A wet newspaper provides a suitable analogy – the paper will not ignite until the water has evaporated.

Table 5. Stainless steel cans containing 13% B_4C, 2% calcium stearate, and various amounts of KNO_3 and smoke agent.

KNO_3 (wt%)	Smoke Agent	Smoke Agent (wt%)	Propagation	Inverse Burn Rate (s/cm)	Smoke	Flame	Sparks	Slag
70	KCl	15	no					
65	KCl	20	yes	14.4	high	low	none	low
60	KCl	25	yes	13.0	high	low	none	low
55	KCl	30	yes	13.3	high	low	none	low
50	KCl	35	yes	13.5	medium	low	low	medium
45	KCl	40	yes	13.6	medium	low	low	high
70	Li_3PO_4	15	yes	11.9	high	medium	medium	medium
65	Li_3PO_4	20	yes	12.6	high	medium	medium	medium
60	Li_3PO_4	25	yes	11.8	medium	medium	low	medium
55	Li_3PO_4	30	yes	11.1	medium	medium	medium	high
50	Li_3PO_4	35	yes	11.0	medium	low	medium	high
45	Li_3PO_4	40	yes	11.7	low	low	low	high
70	NH_4Cl	15	yes	15.2	medium	low	low	medium
65	NH_4Cl	20	yes	20.7	low	low	low	medium
60	NH_4Cl	25	no					
55	NH_4Cl	30	no					
50	NH_4Cl	35	no					
45	NH_4Cl	40	no					

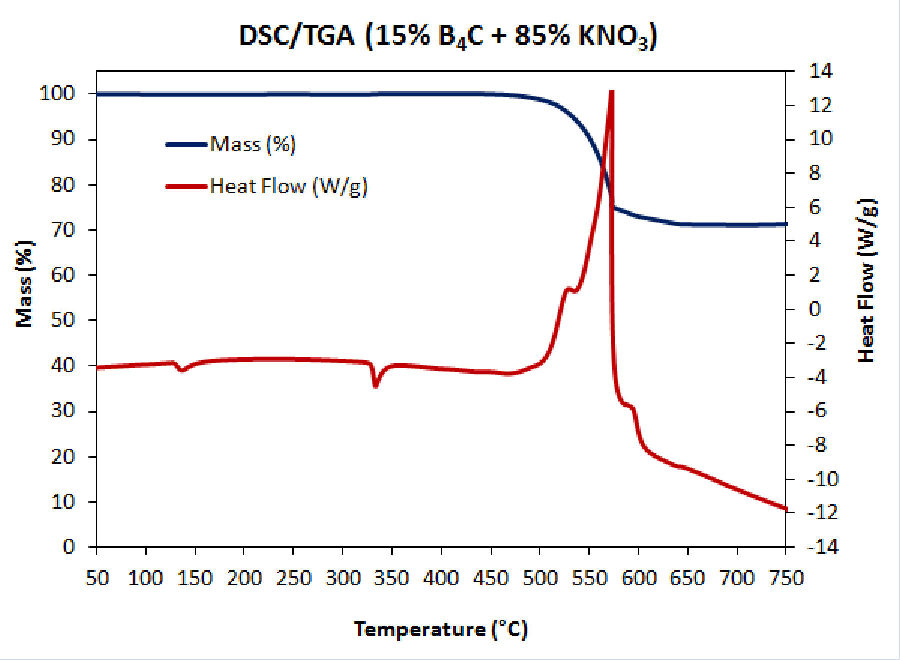

Figure 5. DSC/TGA of a 15/85 B_4C/KNO_3 mixture.

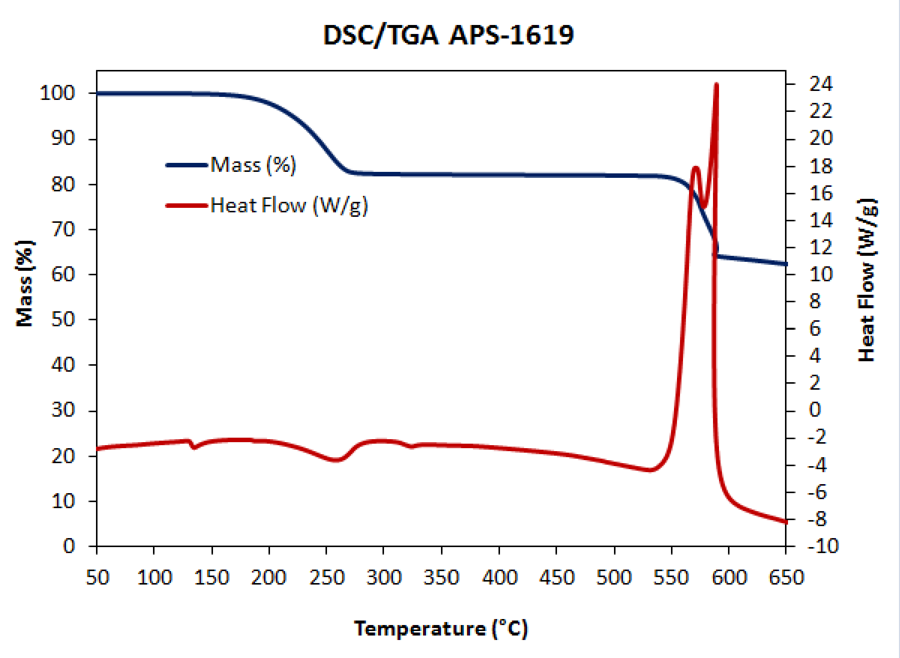

Figure 6. DSC/TGA of the 15% NH_4Cl composition (APS-1619) from Table 5. Note the large endothermic peak at about 250 °C due to pseudo-sublimation of NH_4Cl.

Unlike NH_4Cl, the other smoke agents KCl and Li_3PO_4 do not undergo any endothermic processes at low temperatures. DSC/TGA plots of the 25% KCl composition and the 15% Li_3PO_4 composition show only endotherms associated with the KNO_3 phase transition (135 °C) and melting (332 °C) prior to thermal onset (Figures 7 and 8).

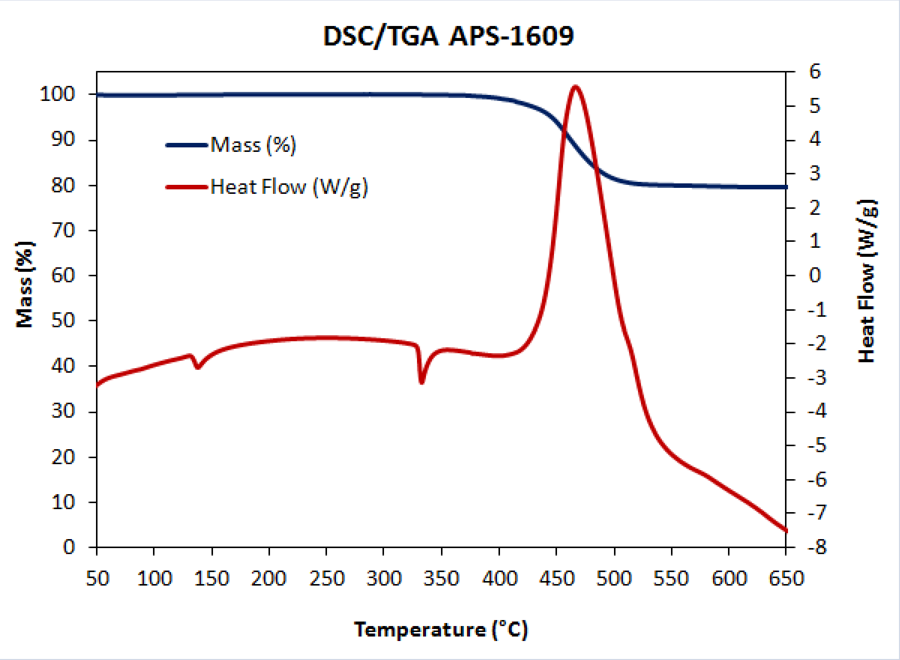

Figure 7. DSC/TGA of the 25% KCl composition (APS-1609) from Table 5.

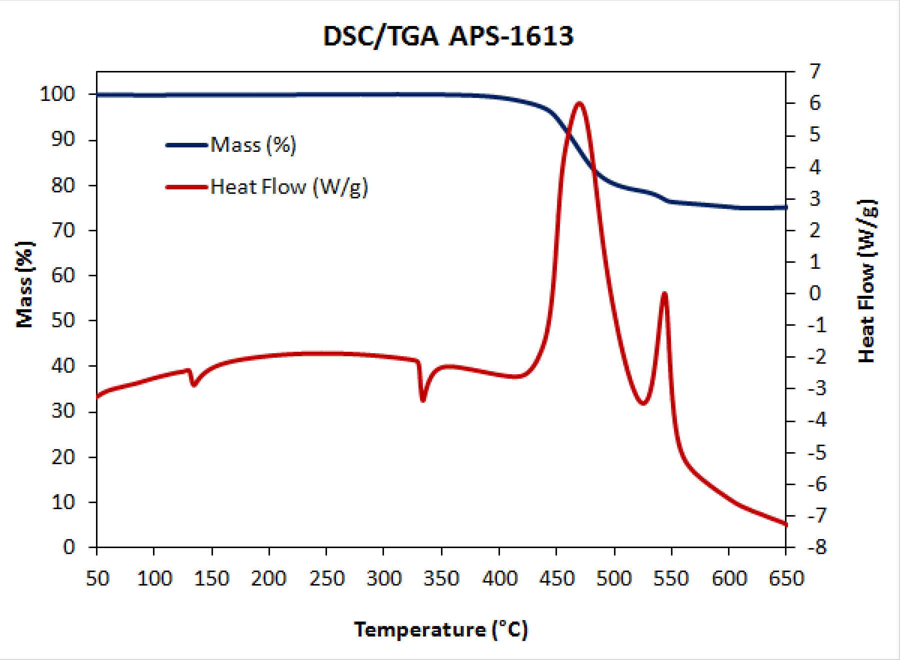

Figure 8. DSC/TGA of the 15% Li_3PO_4 composition (APS-1613) from Table 5.

Transmittance-based measurements may be used to quantify the effectiveness of screening smokes. The Beer-Lambert law is used to define the figures of merit FOM_{mc} (mass composition figure of merit) and FOM_{vc} (volume composition figure of merit). In the first, transmittance is related to the starting *mass* of the composition. In the second, transmittance is related to the starting *volume* of the composition. The two figures of merit are related by the density of the composition. In these equations, V is the volume of the smoke chamber (m^3), T is the transmittance, L is the path length (m), m_c is the composition mass (g), v_c is the composition volume (cm^3), and ρ_c is the composition density (g/cm^3). The units of FOM_{mc} and FOM_{vc} are m^2/g and m^2/cm^3, respectively.

$$\mathrm{FOM_{mc}} = \frac{-V \cdot \ln(T)}{m_c L}$$

$$\mathrm{FOM_{vc}} = \frac{-V \cdot \ln(T)}{v_c L}$$

$$\rho_c = \frac{\mathrm{FOM_{vc}}}{\mathrm{FOM_{mc}}}$$

For each smoke agent in Table 5, the best composition was qualitatively selected. These compositions (Table 6) were pressed into 1-gram bare pellets and used for quantitative smoke chamber tests. AN-M8 HC pellets were tested for comparison. Five to seven pellets were tested per composition and the results were averaged. The results are presented in Table 7.

Table 6. Components (wt%) of experimental compositions selected for smoke chamber testing.

Composition	B_4C	KNO_3	KCl	Li_3PO_4	NH_4Cl	Ca Stearate
APS-1609	13	60	25			2
APS-1613	13	70		15		2
APS-1619	13	70			15	2

Table 7. Results of smoke chamber tests. (Standard deviations in parentheses.)

Composition	Burn Efficiency (%)	Residue (%)	FOM_{mc} (m^2/g)	FOM_{vc} (m^2/cm^3)	°C	% RH
HC (AN-M8)		49.0 (0.8)	1.99 (0.14)	4.82 (0.35)	22.6 (1.3)	32.7 (2.4)
APS-1609	95.0 (3.8)	10.2 (2.3)	1.80 (0.05)	3.16 (0.09)	28.8 (0.4)	38.4 (1.5)
APS-1613		45.7 (2.7)	1.29 (0.05)	2.27 (0.09)	29.7 (0.2)	36.4 (0.5)
APS-1619		38.0 (3.9)	1.04 (0.12)	1.77 (0.20)	29.8 (0.1)	37.3 (1.7)

The KCl composition, APS-1609, burned with high efficiency as indicated by the low amount of residue (slag) remaining after burning. These pellets also exhibited the unusual tendency to leave small crescent-shaped rinds of *unburnt* material, which were easily distinguished from combustion residue. These rinds could be separated from the residue, which allowed a calculation of burn efficiency (the mass percentage of pellet that burned). The other compositions left much more slag and no unburnt material could be detected. The most effective smoke was generated by the HC pellets, which had an FOM_{mc} of 1.99 ± 0.14 m^2/g. APS-1609, with a value of 1.80 ± 0.05 m^2/g, was remarkably competitive. The Li_3PO_4 (APS-1613) and NH_4Cl (APS-1619) compositions were not as effective and left a considerable amount of slag.

The FOM_{mc} values were not directly correlated with the percentage of remaining slag. Clearly, it is beneficial for a smoke composition to leave minimal slag, since more material will be volatilized and become smoke. However, the nature of the volatilized material is also quite important. $ZnCl_2$ is highly hygroscopic, even at low relative humidity. This makes HC smoke incredibly effective even though half the mass of the composition is not volatilized. APS-1609, containing KCl, derives its performance mainly from its high efficiency (only 10% slag). The components of this smoke are not vigorously hygroscopic. APS-1619, containing NH_4Cl, is also not expected to produce any vigorously hygroscopic products. It leaves a large amount of slag, and its performance suffers as a result. APS-1613, containing Li_3PO_4, performed fairly well given the large amount of slag it left. It was hypothesized that burning Li_3PO_4 compositions would result in reduction of phosphate. This hypothesis was confirmed in an unexpected and alarming way, when the strong fishy-garlic odor of phosphorus and phosphines emanated from the residues. Clearly, the reduction was extensive! It is likely that phosphorus oxides were formed in the smoke cloud. These are extremely hygroscopic and help to improve the effectiveness of the smoke.

While APS-1609 is comparable to HC on a *mass* basis, its FOM_{vc} value is significantly lower. This is due to the high density of the HC pellets (2.43 g/cm^3). The experimental pellets of APS-1609, APS-1613, and APS-1619 had densities of 1.75, 1.76, and 1.70 g/cm^3, respectively. Density is important for smoke compositions since many smoke items are limited by volume. Of course, the density of pressed compositions depends on consolidation pressure. The densities listed above are for 1-gram pellets consolidated at 69 MPa.

The smoke chamber tests described above show that small scale testing is *feasible* for the characterization of experimental smoke compositions. However, it is important to remember that many pyrotechnic compositions are sensitive to configuration, and it cannot be assumed that small scale tests will yield the same results as larger ones. Some smoke compositions simply fail to burn reliably on a small scale, making quantification by small scale tests difficult or impossible. In our experience, TA compositions are particularly troublesome. Many variations were attempted, but the pellets either burned with a strong flame (and little smoke) or did not sustain propagation. This is not surprising, since the thermal balance in an organic sublimation smoke, such as TA, is quite delicate. Drastic changes in configuration (from a grenade can down to a small bare pellet) disrupt this balance. Inorganic smokes, such as HC and the experimental boron carbide-based compositions, appear to be more robust and less sensitive to configuration changes. From large fiberboard tubes, to stainless steel cans, to small bare pellets, the B_4C-based smokes described in this study display clear trends which hold across these different configurations. This robustness may be due to the fact that the compositions burn at a relatively high temperature, thus minimizing the role of heat transfer to the surroundings.

Sensitivity testing was also performed on the same three experimental compositions selected for smoke chamber testing. The compositions are remarkably insensitive to impact, friction, and electrostatic discharge (ESD). No ignition was observed, even at the highest settings available (31.9 J for impact, 360 N for friction, and 9.4 J for ESD). The 9.4 J sparks violently scattered the powdered compositions, but no ignition occurred. Further tests are required to determine whether this spark insensitivity holds for thin wafers of *consolidated* material. Nonetheless, these initial results are beneficial for the future development of these compositions.

Conclusion

We have developed environmentally benign white smoke compositions that use boron carbide as a pyrotechnic fuel. The compositions were developed by a combination of first principles reasoning and empirical experimentation. Calcium stearate was found to have a large effect on the burn rates, slowing them considerably. This additive was also particularly good at reducing flame and sparks in some formulations. Small scale smoke chamber studies indicate that one formulation, APS-1609, has performance close to that of HC on a mass basis. The continuing development of boron carbide-based smoke compositions is an active area of research in our laboratories. Recently, it was found that a 13/75/10/2 mixture of $B_4C/KNO_3/H_3BO_3$/calcium stearate (APS-362) also generates thick white smoke.

We are continuing to explore the potential of B_4C-based smokes by examining the use of alternate smoke agents, oxidizers, and organic additives.

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