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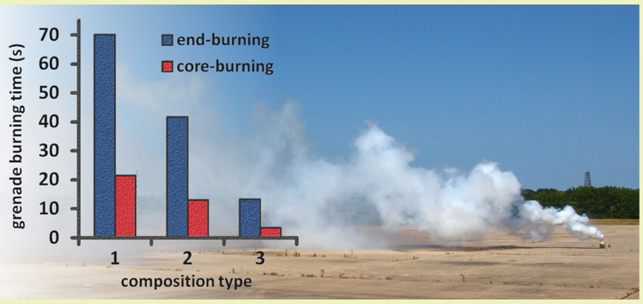
Versatile Boron Carbide-Based Visual Obscurant Compositions for Smoke Munitions

Anthony P. Shaw,*[†] Giancarlo Diviacchi,[‡] Ernest L. Black,[‡] Jared D. Moretti,[†] Rajendra K. Sadangi,[†] Henry A. Grau, Jr.,[†] and Robert A. Gilbert, Jr.[†]

[†]Armament Research, Development and Engineering Center, U.S. Army RDECOM-ARDEC, Picatinny Arsenal, New Jersey 07806, United States

[‡]Edgewood Chemical Biological Center, U.S. Army RDECOM-ECBC, Aberdeen Proving Ground, Maryland 21010, United States

Supporting Information



ABSTRACT: New pyrotechnic smoke compositions, containing only environmentally benign materials, have been demonstrated to produce thick white smoke clouds upon combustion. These compositions use powdered boron carbide (B_4C) as a pyrotechnic fuel, KNO_3 as a pyrotechnic oxidizer, and KCl as a combustion temperature moderator. Small amounts of calcium stearate and polymeric binders may be added to moderate burning rate and for composition granulation. Prototype tests involving three preferred compositions were conducted in end- and core-burning grenade and canister configurations. Smoke release times ranged from 3.5 to 70 s for the grenades and from 8 to 100 s for the canisters. Notably, any desired smoke release time within these ranges may be obtained by fine adjustment to the calcium stearate content of the compositions and/or small changes to the device containers. Aerosolization efficiency and quantitative performance, as determined by smoke chamber measurements, remain consistent regardless of smoke release time. Impact, friction, and electrostatic discharge tests show that the compositions are insensitive to accidental ignition and are safe to handle.

KEYWORDS: *Smoke, Obscurants, Pyrotechnics, Boron carbide, Sustainable chemistry*

■ INTRODUCTION

Visible obscuration compositions (obscurants, smokes) are used on the battlefield and in military training exercises for signaling, marking targets, and screening troop movements. Such compositions are characterized by a hazard/performance trade-off. The most effective ones tend to be toxic or incendiary, while the performance of convenient and safe alternatives is often lacking. For example, phosphorus-based compositions arguably offer the greatest obscuration performance, but their use is complicated by the toxic and incendiary nature of white phosphorus and the poor aging characteristics of red phosphorus.[1−4] Similarly, pyrotechnic compositions based on hexachloroethane, a known toxin and suspected carcinogen,[5] produce a thick hygroscopic zinc chloride aerosol laced with soot and chlorinated organic compounds. Smoke grenades containing these "HC" compositions have been responsible for several smoke inhalation-related injuries and deaths.[6]

Other pyrotechnic smokes based on the sublimation of *trans*-cinnamic acid or terephthalic acid (CA, TA) are not particularly hazardous, but their obscuration performance is inadequate for tactical use. In fact, these types of compositions were originally developed for fire simulation and training purposes.[7] In the 1990s, the U.S. Army began producing smoke grenades containing TA compositions for training use. Shortly thereafter, production of tactical HC smoke grenades was discontinued due to the aforementioned toxicity concerns. Absent an alternative high-performance replacement, soldiers must now use the TA smoke grenades in combat, with unsatisfactory results. As many as *three* M83 TA grenades must be thrown to give a smoke screen comparable to that produced by just one AN-M8 HC grenade. Meanwhile, munitions designers tasked with developing less hazardous mortar and artillery smoke projectiles face the prospect of greatly reduced performance unless alternative advanced compositions become available. Matching or exceeding the performance of HC compositions is no longer a firm requirement for a new visible obscurant. Instead, in recognition of the hazard/performance trade-off, there is now a need for smokes with acceptable hazard profiles that also significantly outperform TA compositions in the field.

To develop suitable pyrotechnic replacement compositions, one strategy is to consider alternative materials. Boron carbide has been known as a pyrotechnic fuel since the 1950s, if not earlier. Several smoke compositions containing B_4C, $KMnO_4$,

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and other oxidizers were briefly described in a 1961 patent.[8] Some binary B_4C/oxidizer mixtures were evaluated as smoke compositions by Lane and co-workers in the 1960s.[9,10] There has also been interest in using boron carbide as a component of solid fuels for ramjet engines and as a component in advanced pyrotechnic illuminants.[11,12] Even so, boron carbide has largely been overlooked by the pyrotechnics community, and its potential in this context has not been thoroughly investigated. To obtain a better understanding of boron carbide's pyrotechnic properties, our research group has recently investigated boron carbide-based time delays and green light-emitting compositions.[13,14] We have also re-examined boron carbide for its original pyrotechnic application—smoke. In appropriate proportions, B_4C/KNO_3 mixtures containing KCl as a diluent and calcium stearate as a burning rate modifier produce thick white smoke clouds upon combustion.[15−17] A preliminary toxicology assessment by the U.S. Army Public Health Command did not raise any significant environmental or human health concerns.[18] Such compositions therefore appear to be promising candidates for use in future smoke munitions. Herein, we describe the results of our most recent prototype tests involving three preferred compositions in four different configurations, which demonstrate the versatility, robustness, and safety of the system.

■ EXPERIMENTAL SECTION

Material Properties. Boron carbide powder (1200 grit, carbon-rich B_4C, 19.0−21.7 wt % C) was obtained from Atlantic Equipment Engineers (AEE). A Microtrac S3500 laser diffraction particle size analyzer was used to determine a volume-based diameter distribution of an aqueous boron carbide suspension: $D[4,3]$ 6.36 μm; $D[\text{v}, 0.1]$ 2.59 μm; $D[\text{v}, 0.5]$ 5.88 μm; $D[\text{v}, 0.9]$ 10.71 μm. Potassium nitrate and potassium chloride were obtained from Hummel Croton. The potassium nitrate (MIL-P-156B) was hammer milled to approximately 15 μm. The potassium chloride was passed through a 50 mesh (300 μm) screen. Both potassium nitrate and potassium chloride contained 0.2 wt % fumed silica, Cabot CAB-O-SIL M-5, as an anticaking agent. Calcium stearate (monohydrate, approximately 10 μm) was also obtained from Hummel Croton. Polyvinyl acetate aqueous emulsion, Elmer's Glue-All, was found to contain 34.5 wt % solids.

Preparation of Compositions, Grenades, and Canisters. The boron carbide-based smoke compositions were prepared on a 5 or 6 kg scale by combining and mixing the components in a planetary bowl mixer equipped with a flat beater paddle. No additional water was added, and the compositions were mixed until they were homogeneous and granulated (45 min). The compositions were oven-dried in trays overnight at 65 °C before loading.

Experimental smoke grenades were prepared for field and chamber tests. Each contained 350 g of smoke composition and a thin layer of a proprietary titanium-based igniter. A hydraulic press was used to load the grenades in three increments with 7000 kg-force. The grenade lids were fitted with M201A1 fuzes. Each end-burning grenade contained a cylindrical 27.27 cm^2 pyrotechnic pellet that burned from one end to the other, emitting smoke through vent holes in the lid. The pellet within each core-burning grenade had a central core hole approximately 1.15 cm in diameter; the pellet face area was 26.24 cm^2. These burned from one end to the other and outward from the core, emitting smoke from vent holes in the lid and from a can vent hole aligned with the core. The end- and core-burning experimental grenade configurations are illustrated in Figure 1.

Experimental smoke canisters were prepared for field tests. The canisters were configured to be larger analogues of the experimental grenades, with only minor differences. Each canister contained 2 kg of smoke composition and a thin layer of titanium-based igniter and was loaded in three increments with 29,500 kg-force. End- and core-burning variants had pellet face areas of 113.4 and 111.2 cm^2, respectively. Core-burning prototypes contained a core hole approximately 1.67 cm in diameter. Electric matches were used for ignition instead of fuzes.

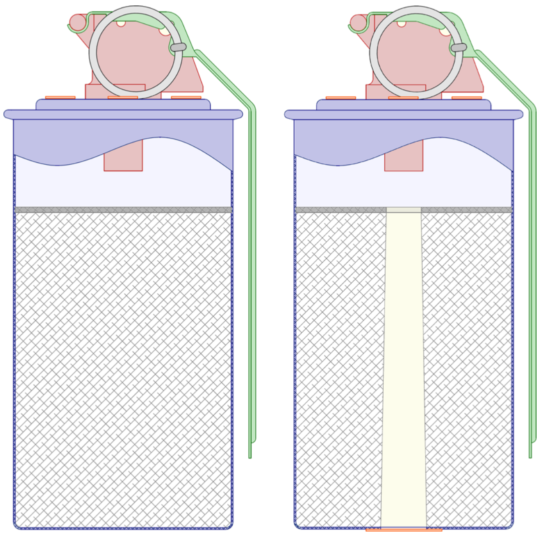

Figure 1. Diagrams of the end-burning (left) and core-burning (right) experimental grenade configurations. Partial cross sections show the solid end-burning pellet and the core-burning pellet with an axial core hole. The grenade lids and/or can (blue) contain vent holes covered by tape (orange). Other parts, common to both configurations, include the fuze (red), pull ring and pin (gray), and lever (green).

Test and Analysis Protocols. Experimental pellet densities as a percentage of the theoretical maxima (%TMD) were calculated using 2.52, 2.11, 1.98, 1.05, and 1.19 g/cm^3 for the crystalline/maximum densities of B_4C, KNO_3, KCl, calcium stearate monohydrate, and polyvinyl acetate, respectively. Field tests were used to assess qualitative smoke characteristics and to determine burning times. Three experimental grenades and one canister of each type were tested for these purposes; the burning time variability between grenades of the same type was negligible. For end-burning prototypes, average linear burning rates (cm/s) were calculated by dividing the composition pellet lengths by the burning times. Mass consumption rates (g/s) were calculated for all prototypes.

AN-M8 and M83 smoke grenades manufactured at Pine Bluff Arsenal were obtained and tested for comparison.[17] The end-burning AN-M8 contains approximately 480 g of HC smoke composition (type C). The M83 is core-burning and is fitted with a sealed lid, so that smoke exits only through a single can vent hole aligned with the core. The M83 contains approximately 350 g of TA smoke composition.

Obscuration measurements were performed in the Edgewood Chemical Biological Center's 190 m^3 smoke chamber. Three experimental grenades of each type were tested at 23−25 °C and 40−68% relative humidity. The M83 was tested at 22 °C and 61% relative humidity. The AN-M8 was tested at 25 °C and 32% relative humidity. The aerosols produced by the experimental grenades and the M83 are not particularly hygroscopic and therefore are not affected by moderate variations in relative humidity. The aerosol produced by the AN-M8 is vigorously hygroscopic, and reported data (especially yield factor, Y) correspond only to the test conditions given above.

After each grenade was functioned in the smoke chamber and the smoke was equilibrated with a mixing fan, the aerosol concentration was determined gravimetrically by passing a known volume through a filter disk. The calculated total aerosol mass was divided by the initial mass of smoke composition to give the yield factor (Y). An Ocean Optics DH2000 deuterium tungsten halogen light source and HR2000 UV−vis spectrometer were used to determine transmittance as a function of wavelength in the visible spectrum across a 6 m path length. Smoke was vented from the chamber until the transmittance (T) was about 0.2, at which point it was recorded and the aerosol concentration was determined again. These data were used to calculate the mass-based extinction coefficient (α_m) as a function of wavelength in the visible spectrum. Mass-based composition figures of merit (FM_m) were calculated by multiplying α_m by Y. A simple average of T over the visible spectrum (380−780 nm) was used to calculate averaged visible α_m and FM_m. Likewise, T was weighted to the photopic response of the human eye to calculate photopic α_m and FM_m values.[17,19]

Impact sensitivity tests were performed with a BAM drop hammer.[20] A Chilworth BAM friction apparatus was used for friction sensitivity testing.[21] A Safety Management Services ABL apparatus was used to test for electrostatic discharge (ESD) sensitivity.[22] Each composition was subjected to 10 impact and friction tests and 20 electrostatic discharge tests. No ignition was observed. Thermal onset temperatures were determined with a PerkinElmer Diamond TGA/DSC. Alumina pans were used, and the samples were heated at 5 °C/min under a 40 mL/min flow of nitrogen. The results of duplicate runs were averaged.

RESULTS AND DISCUSSION

Boron Carbide-Based Smoke Compositions. The subject smoke compositions rely on the heat produced by the combustion of B_4C/KNO_3 to volatilize and disperse reaction products and inert diluents. Unlike the refractory oxides of common pyrotechnic fuels such as magnesium and aluminum, boron oxides are volatile at considerably lower temperatures. Potassium metaborate (KBO_2), the expected boron-containing product of B_4C/KNO_3 combustion, boils at just 1402 °C.[12,23] While certain binary B_4C/KNO_3 mixtures effectively produce smoke upon combustion, the addition of diluents is needed to lower the reaction temperature to reduce undesirable flaming and light emission. Potassium chloride was found to be particularly effective in this role, in part because it is volatile in an appropriate temperature range (vapor pressure of 0.20 bar at 1207 °C; T_b = 1406 °C).[15,24] Consolidated pellets of ternary $B_4C/KNO_3/KCl$ mixtures, especially those containing a 13/62/25 weight ratio of these components, produce copious amounts of white smoke upon combustion with reduced flaming but generally burn very quickly.

Recent investigations in our laboratory have shown that the burning rates of boron carbide-based pyrotechnics are greatly influenced by the fuel particle size, particularly the amount and size of the fines. The burning rate of the related $B_4C/NaIO_4/PTFE$ delay composition varied by over 6-fold with only a 6 μm change in the tenth percentile of the boron carbide particle size distribution.[13] The burning rates of the subject smoke compositions display a similar, but less extreme, dependency.[17] The addition of waxy materials such as stearic acid or stearate soaps is another way to control burning rate. Just 1−3 wt % of added calcium stearate can be used to slow the burning rate of the smoke compositions by about 70−85%.[15,16] Thus, slow to moderate burning rates in the 0.1−0.35 cm/s range can be achieved with rather fine (sub-10 μm) boron carbide, which promotes high combustion efficiency. Adjusting calcium stearate content appears to be the more practical way of moderating and controlling burning rate because the boron carbide particle size will inevitably vary across different lots in a production environment.

While calcium stearate or other waxy additives serve as dry binders in consolidated smoke pellets, they do nothing to reduce the dustiness of unconsolidated mixtures. Dust associated with processing large quantities of fine combustible materials has been responsible for many unintended explosions.[25] Where it is feasible, granulating powdered mixtures with polymeric binders can reduce or eliminate nuisance dust. In a previous study, quaternary $B_4C/KNO_3/KCl$/calcium stearate mixtures were granulated with several different "wet" binder systems.[17] An aqueous emulsion of polyvinyl acetate (PVAc, common white glue) was found to be acceptable. At the 2 wt % level (of polymer solids), this binder reduced dust during processing and also did not harm smoke performance or significantly affect burning rate.

All of these developments have now led to the three preferred variants shown in Table 1: a slow-burning composition (type 1), an intermediate burning rate (type 2), and a very fast-burning composition (type 3). As described above, the amount of calcium stearate required to achieve slow and intermediate burning rates depends on the boron carbide particle size but is generally about 1−3 wt %, provided fine micron-sized boron carbide is used. Following the tradition of other U.S. Army two-letter smoke acronyms, the boron carbide-based compositions have been designated "BC".

Table 1. Boron Carbide-Based Smoke Compositions

composition	B_4C (wt %)[a]	KNO_3 (wt %)[b]	KCl (wt %)	Ca stearate (wt %)[b]	PVAc (wt %)[c]
type 1	13	58	25	2	2
type 2	13	59	25	1	2
type 3	13	60	25		2

[a] Sub-10 μm mean particle size, see Experimental Section. [b] Particular amounts used in this study. [c] Polyvinyl acetate aqueous emulsion; amount refers to solids.

Smoke Release Time and Qualitative Field Characteristics. Smoke munitions that release smoke rapidly are useful for immediate, localized screening. In contrast, those that release smoke over a longer period of time produce elongated clouds intended for screening troop movements across a larger area. For example, an explosive bursting charge rapidly disperses powdered titania from the M106 fast obscurant grenade (FOG), providing immediate cover during vehicle dismount or for operations in an urban environment.[26] Pyrotechnic smoke grenades such as the current M83 and obsolete AN-M8 release smoke over 45−90 s as the compositions within them burn and are suitable for obscuring open areas. Achieving these differing objectives has required the use of different materials systems and substantially different hardware.

Generally, pyrotechnic smoke grenades may be prepared by loading smoke compositions into cylindrical steel cans in end-burning or core-burning configurations. In the former, a solid pellet of smoke composition burns from one end to the other, emitting smoke through vent holes in the cap that also holds the initiating fuze. In the latter, the pellet contains a core hole and burns from the top down and outward from the center. Smoke may be emitted from a hole in the can aligned with the core hole and optionally from additional vent holes in the fuzed cap on the opposite end. Either configuration may be prepared with only minor alterations to the cans and lids.

Figure 2 shows smoke release times (burning times) for end- and core-burning grenades containing the three BC smoke compositions: types 1, 2, and 3. This figure illustrates the versatility of the system, as there is a *20-fold* variation in smoke release time between the longest-burning grenade (70 s) and the shortest (3.5 s), with only minor changes to composition and configuration. For any particular composition, the core-burning grenades burn and emit smoke three to four times as quickly as the end-burning ones. Finer adjustments to the

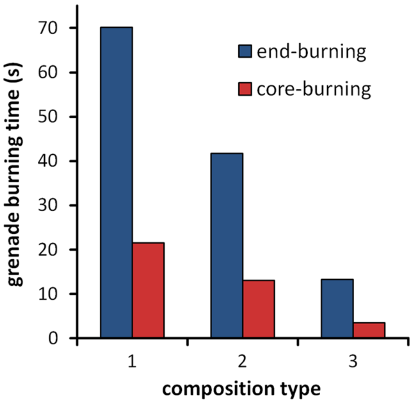

Figure 2. Burning times (smoke release times) for BC smoke grenades. Times for the three compositions in Table 1 are plotted for end-burning (blue) and core-burning (red) grenades.

calcium stearate content of the compositions may be used to obtain any intermediate smoke release time.

Additional details pertaining to the BC smoke grenades are shown in Table 2. Consolidated densities and %TMD generally increase with increasing calcium stearate content, a manifestation of the lubricating properties of this material. It is also evident from the data in Table 2 that a very slow linear burning rate is required to achieve a long smoke release time in an end-burning grenade (0.13 cm/s for 70 s). Linear burning rates cannot be calculated for the core-burning grenades, but the mass consumption rates may be compared instead. The composition within the fast type 3 core-burning grenade was consumed very quickly, at a rate exceeding 100 g/s.

For any smoke-producing device, the smoke release time has a profound influence on the perceived thickness of the resulting cloud. The clouds emitted from end-burning BC smoke grenades (Figure 3) illustrate this concept well. Smoke released over a longer period is more likely to thin as it is drawn away by a light wind. Faster release times generally give thicker, more compact clouds. The qualitative behavior of the clouds is also affected by ambient weather conditions, which cannot be controlled. In the absence of any wind (which is rare), emitted smoke accumulates and provides a thick screen locally regardless of smoke release time. In contrast, a strong wind will elongate, thin, and remove the aerosol emitted from even the fastest-emitting device.

Figure 3. Smoke screens produced by end-burning BC smoke grenades, midburn: type 1 (top), type 2 (middle), and type 3 (bottom).

The core-burning BC grenades were configured to emit smoke from both ends. This is advisible for very fast-burning smoke grenades to prevent them from being propelled by the thrust of a single rapid jet of aerosol. Figure 4 shows a sequence of photographs from a test of the fastest-burning grenade (3.5 s). In this case, the grenade contents were aerosolized well before the resulting cloud spread out to give an effective screen at 8 s.

The BC smoke compositions in Table 1 were also loaded into larger end- and core-burning canisters, analogous to the grenade configurations described above. These canisters each contained 2 kg of smoke composition, more than five times as much as that within a grenade. Data for canister field tests is shown in Table 3. A 12-fold variation in smoke release time was observed, with the slowest canister burning for nearly 100 s and the fastest for just 8 s. The linear burning rates for the end-burning canisters were very similar to the analogous grenades, although burning times were extended because the canisters contained a greater length of consolidated composition. The fastest core-burning canister achieved a mass consumption rate of 256 g/s, effectively aerosolizing a grenade's worth of smoke composition every 1.4 s over the course of 8 s! Given their larger size, the canisters produced correspondingly thicker and

Table 2. Burning Characteristics of BC Smoke Grenades[a]

composition	configuration[b]	ρ_c (g/cm^3)[c]	%TMD[d]	burning time (s)	mass consumption rate (g/s)	linear burning rate (cm/s)
type 1	end-burning	1.51	73.6	70.2	5.1	0.13
type 2	end-burning	1.49	72.0	41.7	8.6	0.21
type 3	end-burning	1.43	68.5	13.3	27.1	0.70
type 1	core-burning	1.52	74.4	21.5	16.8	
type 2	core-burning	1.51	72.9	13.1	27.6	
type 3	core-burning	1.44	68.9	3.5	103.9	

[a] Each grenade contained 350 g of smoke composition. [b] End- and core-burning grenades were consolidated at 25.3 and 26.3 MPa, respectively. [c] Consolidated density. [d] Consolidated density as a percentage of the theoretical maximum.

Figure 4. Time sequence for a core-burning BC smoke grenade containing the type 3 composition. Images show smoke screen formation at 0.4 s (top), 2.8 s (middle), and 8.0 s (bottom). Total grenade burning time was 3.5 s.

larger clouds than the grenades but with similar qualitative behavior (Supporting Information).

Quantitative Smoke Chamber Metrics. The aggregate opacity of a smoke cloud, independent of smoke release time, may be determined in a suitably sized smoke chamber. The mass-based extinction coefficient (α_m) is a measure of how well a given mass of aerosol attenuates light. Because aerosolization efficiency may vary and some aerosols are hygroscopic, α_m is not always correlated with the effectiveness of smoke *compositions* or *devices*. A figure of merit for smoke compositions is obtained by multiplying α_m by the yield factor, Y, which is the ratio of aerosol mass (m_a) to the mass of initial composition (m_c). The mass-based composition figure of merit, FM_m, is related to m_c (eq 1). Here, V is the chamber volume, T is transmittance, and L is the measurement path length.

$$FM_m = \alpha_m Y = \left(\frac{-V \cdot \ln(T)}{m_a L}\right)\left(\frac{m_a}{m_c}\right) = \frac{-V \cdot \ln(T)}{m_c L} \qquad (1)$$

The design of many smoke munitions is limited more by internal dimensions than by smoke composition mass. It is therefore worthwhile to calculate a volume-based composition figure of merit, FM_v, by multiplying FM_m by the consolidated smoke composition density (eq 2). A detailed description of smoke figures of merit and smoke measurement technique has been published previously.[17]

$$FM_v = FM_m \rho_c = \frac{-V \cdot \ln(T)}{v_c L} \qquad (2)$$

The results for TA and HC smoke compositions in Table 4 illustrate the importance of yield factor as a determinant of performance. The aerosol produced by TA compositions is effective, as indicated by α_m, but FM_m is lacking because Y is quite low. Only a small fraction of the TA composition is aerosolized and dispersed upon combustion, and the resulting aerosol is not hygroscopic. Unlike terephthalic acid, the zinc chloride dispersed by burning HC compositions is vigorously hygroscopic. Measured yield factors for HC compositions routinely exceed 1.2 even though only 40−60% of the composition mass is volatilized upon combustion. These high yield factors, which depend on atmospheric humidity, result in correspondingly high FM_m values even though α_m is unimpressive.

Both end- and core-burning grenades containing the three compositions in Table 1 were subjected to smoke chamber tests (Table 4). No distinct trends in the data were apparent, regardless of configuration or smoke release time. A very subtle correlation between yield factor and smoke release time had been observed previously with end-burning grenades containing dry, four-component BC smoke compositions.[17] Yield factors for the grenades in this study were all similar, averaging 0.75. The aerosol, consisting of potassium chloride and borates (Supporting Information), is not particularly hygroscopic. The relatively high yield factors are therefore the result of remarkable aerosolization efficiency—generally, very little residue remains after combustion.[15−17]

An average yield factor of 0.75 combined with α_m averaging 4.0 m^2/g gives an FM_m of about 3.0 m^2/g, indicating that the BC compositions are comparable to HC on a mass basis (Table 4). Densities at 72% of the theoretical maxima, typical of pressed pyrotechnic pellets, were used to calculate FM_v values. These show that HC is more effective volumetrically. Due to the high density of the HC composition, more may be pressed into a grenade can and these grenades produce correspondingly thicker smoke clouds of long duration. However, the BC compositions clearly outperform TA by a wide margin as

Table 3. Burning Characteristics of BC Smoke Canisters[a]

composition	configuration[b]	ρ_c (g/cm^3)[c]	%TMD[d]	burning time (s)	mass consumption rate (g/s)	linear burning rate (cm/s)
type 1	end-burning	1.53	74.6	99.6	20.6	0.12
type 2	end-burning	1.52	73.7	59.3	34.5	0.20
type 3	end-burning	1.45	69.6	18.9	108.4	0.66
type 1	core-burning	1.51	73.8	44.2	46.3	
type 2	core-burning	1.50	72.8	24.1	84.9	
type 3	core-burning	1.44	69.0	8.0	256.1	

[a] Each canister contained 2 kg of smoke composition. [b] End- and core-burning canisters were consolidated at 25.5 and 26.0 MPa, respectively. [c] Consolidated density. [d] Consolidated density as a percentage of the theoretical maximum.

Table 4. Photopic Smoke Chamber Performance

composition	Y[a]	α_m (m^2/g)[b]	FM$_m$ (m^2/g)[c]	ρ_c (g/cm^3)[d]	FM$_v$ (m^2/cm^3)[e]
BC (average)[f]	0.75 (0.03)	4.01 (0.43)	3.03 (0.42)	1.48 (0.04)	4.48 (0.62)
TA	0.30[g]	4.80[g]	1.44[g]	1.2	1.73
HC	1.26[h]	2.36[h]	2.97[h]	2.2	6.53

[a] Yield factor. [b] Mass-based extinction coefficient. [c] Mass-based composition figure of merit. [d] Density at 72% of the theoretical maximum. [e] Volume-based composition figure of merit. [f] Averages for all BC grenades tested with standard deviations in parentheses. [g] Data for a typical M83 TA grenade. [h] Data for an AN-M8 grenade at 25 °C and 32% relative humidity.

measured by both FM$_m$ and FM$_v$. These results are in agreement with qualitative observations from the field tests. The compositions may therefore be ranked by efficacy in the following order: TA ≪ BC < HC.

Sensitivity to Ignition Stimuli. It is important to understand the sensitivity of energetic materials to various ignition stimuli. Ideally, energetic compositions and munitions should be designed to minimize the risk of accidental ignition, deflagration, or explosion. Smoke compositions have not always had favorable safety profiles. Red phosphorus compositions are notoriously sensitive to friction and impact.[2−4] White phosphorus spontaneously combusts in warm air.[1] White phosphorus munitions are preferably stored near a source of water, so that they may be submerged if damaged.[27] Earlier HC-type compositions, containing zinc metal powder, were known to spontaneously ignite in the presence of moisture.[28]

Having identified the BC smoke compositions as promising alternatives, we sought to quantify their safety characteristics by subjecting them to impact, friction, and electrostatic discharge tests (Table 5). Thermal onset temperatures were determined by TGA/DSC. No ignition was observed in any of the sensitivity tests. Surprisingly, even the type 3 composition (which is abrasive due to the absence of calcium stearate) is insensitive to impact and friction. The compositions are only initiated by high temperatures, well above the melting point of KNO$_3$, as the oxide layer surrounding the B$_4$C particles is etched and exothermic reactions begin.

Table 5. Sensitivity and Thermal Onset Data for BC Smoke Compositions

composition	impact (J)	friction (N)	electrostatic discharge (mJ)	thermal onset (°C)
type 1	>31.9	>360	>250	425
type 2	>31.9	>360	>250	460
type 3	>31.9	>360	>250	495

CONCLUSIONS

Prototype tests of three BC smoke compositions in end- and core-burning grenade and canister configurations have demonstrated the viability of this materials system for use in a variety of smoke munitions. An exceptional degree of control over smoke release time is achieved through minor changes to the compositions and configurations, with a 20-fold variation (3.5−70 s) realized for grenades and a 12-fold variation obtained for larger smoke canisters (8−100 s). Aerosolization efficiency, as determined by measured yield factor, remains high and consistent regardless of burning time. The very fast-burning BC grenades are potential pyrotechnic alternatives to explosive fast obscurant grenades (FOGs) such as the M106. Longer-burning BC grenades could be used in place of the current M83 TA and obsolete AN-M8 HC smoke grenades. Likewise, fast-burning BC canisters could be used in artillery or mortar projectiles, in place of traditional white or red phosphorus-based payloads. Smoke projectiles containing HC canisters could be replaced with ones containing the slow-burning BC compositions. Importantly, the new compositions appear to pose a minimal environmental and human health risk.[18] They are markedly insensitive to accidental ignition and therefore are safe to manufacture, handle, transport, and store. Additionally, they are composed of inexpensive components and do not require specialized equipment to manufacture.

ASSOCIATED CONTENT

Supporting Information

Mass-based smoke chamber data (Table S1); large format version of Figure 1 (Figure S1); XRD/XRF experiments and XRD pattern (Figure S2); large format versions of Figures 3 and 4 (Figures S3 and S4); photographs of canister field tests (Figures S5−S10). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* E-mail: anthony.p.shaw.civ@mail.mil.

Notes

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The authors declare no competing financial interest.

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DEDICATION

Dedicated to Professor Jack R. Norton on the occasion of his 70th birthday.

ABBREVIATIONS

ABL, Allegany Ballistics Laboratory; AEE, Atlantic Equipment Engineers; ARDEC, Armament Research, Development and Engineering Center; BAM, Bundesanstalt für Materialforschung und -prüfung; BC, boron carbide-based smoke composition; CA, *trans*-cinnamic acid-based smoke composition; DSC, differential scanning calorimetry; ECBC, Edgewood Chemical Biological Center; ESD, electrostatic discharge; FOG, fast obscurant grenade; HC, hexachloroethane-based smoke composition; PVAc, polyvinyl acetate; RDECOM, Research, Development, and Engineering Command; TA, terephthalic acid-based smoke composition; TGA, thermogravimetric analysis; %TMD, consolidated density as a percentage of theoretical maximum density

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