Advanced Boron Carbide-Based Visual Obscurants for Military Smoke Grenades

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Synopsis: Pyrotechnic boron carbide-based smoke compositions are candidates for use in new nonhazardous smoke grenades.

ABSTRACT

Military visible obscuration compositions (obscurants, smokes) are characterized by a hazard/ performance trade-off. New compositions with improved performance, but containing only benign materials, are needed for the next generation of U.S. Army smoke munitions. Advanced boron carbide-based smoke compositions have been developed to address this need. These experimental compositions contain B_4C/KNO_3 as a pyrotechnic fuel/oxidizer pair, KCl as a diluent, and calcium stearate as a burning rate modifier. Both the B_4C particle size and the amount of calcium stearate may be used to control grenade burning times over a wide range (24-100 s demonstrated in the end-burning configuration). The dustiness of these dry compositions may be reduced by granulating them with a variety of polymeric binders. Granulation with polyvinyl acetate reduced dust and did not adversely affect composition burning rate or visible obscuration performance. In field and smoke chamber tests, prototype smoke grenades outperformed the U.S. Army M83 TA grenade by a wide margin. The best prototypes are functionally equivalent to nearly two M83 TA smoke grenades and are candidates for the eventual improvement/replacement of this grenade.

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INTRODUCTION

Visible obscuration compositions (obscurants, smokes) are used on the battlefield for signaling, marking targets, and screening troop movements. These 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. Others are unstable upon storage or require complex equipment to deploy. Some U.S. Army compositions are listed and described in Table 1. In the tradition of U.S. Army two-letter smoke acronyms, the experimental boron carbide system has been designated "BC".

The best performing (and the most hazardous) composition is arguably white phosphorus. Typically dispersed by a bursting device, this pyrophoric material is incendiary, toxic, and can cause environmental damage to wetland areas.[1] Red phosphorus compositions, less incendiary and less toxic than white phosphorus, present serious sensitivity and aging issues.[2-4] Pyrotechnic hexachloroethane compositions (HC), which produce a thick hygroscopic zinc chloride aerosol laced with soot and chlorinated organics, have been responsible for several injuries and deaths.[5] Hexachloroethane itself is also toxic.[6] Hygroscopic liquids such as titanium tetrachloride or

Table 1. Characteristics of some U.S. Army visible obscurants.

Designators or Names	Component(s)	Device Configuration	Mechanism	Atmospheric Reactivity	Notes [a)]
WP	P_4 (white/yellow)	bursting, neat or felt wedges	atmospheric burning	hygroscopic oxides	toxic, incendiary
RP	P_x (red) [b)]	bursting or can	atmospheric burning	hygroscopic oxides	aging and sensitivity issues
HC	$Al/ZnO/C_2Cl_6$ [c)]	core- or end-burning can	combustion products	hygroscopic $ZnCl_2$	toxic
BC	$B_4C/KNO_3/KCl$/additive	core- or end-burning can	combustion products		high efficiency, versatile
FM, FS	$TiCl_4$, HSO_3Cl/SO_3	bursting or spraying	dispersal	hygroscopic liquids	corrosive [d)]
SGF2, diesel, PEG	hydrocarbons, polyethylene glycols	smoke generator [e)]	vaporization/re-condensation		effective but inconvenient
titania	TiO_2	bursting	dispersal		low efficiency, short duration
CA, TA	*trans*-cinnamic acid, terephthalic acid [f)]	core-burning can	sublimation/re-condensation		low efficiency

a) Efficiency refers to the amount of material aerosolized in comparison to the mass of initial composition.
b) Additional components are often nitrates or other oxidizers, metal additives, and organic binders.
c) This particular mixture is Type C but there are many metal/oxide/chlorocarbon variants.
d) The acidity of these clouds can be reduced by co-aerosolizing basic materials such as dolomite.
e) Smoke pots and grenades that aerosolize these liquids are not currently used by the U.S. Army.
f) Typically mixed with sucrose/$KClO_3$ and various carbonates.

chlorosulfonic acid/oleum create decent clouds upon dispersal, but the resulting acidic fogs are corrosive.[7] Volatilized oils (hydrocarbons, glycols) create a very effective and relatively nontoxic smoke screen, but this usually requires the use of a smoke generator.[8,9] Fine titania powder is a good nontoxic visible obscurant although it is difficult to disperse efficiently and the resulting screen has a short duration.[10,11] Pyrotechnic smokes based on the sublimation/recondensation of *trans*-cinnamic acid or terephthalic acid (CA, TA) are also not particularly hazardous but their obscuration performance is inadequate for tactical use.

In the 1970s, Douda invented CA smoke compositions for fire simulation and training use.[12] In the 1990s, the U.S. Army began using TA compositions (derivatives of Douda's invention) in the M83 grenade. These M83 TA grenades were intended for training use only and in this capacity their low obscuration performance was not problematic. However, with high performance AN-M8 HC grenades no longer produced due to toxicity concerns, soldiers must now use the M83 TA smoke grenade in combat. 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. Soldiers risk not being able to create an adequate smoke screen unless enough M83 TA grenades are available. As the load carried by each soldier is limited, this has created a problematic situation. Meanwhile, munitions designers tasked with developing less hazardous mortar and artillery smoke rounds face the prospect of greatly reduced performance unless alternative advanced compositions become available. Matching or exceeding the performance of HC is no longer a firm requirement for a new visible obscuration composition. Instead, in recognition of the hazard/performance trade-off, there is now a need for compositions with acceptable hazard profiles that also significantly outperform TA in the field.

Much research has been directed towards the development of improved visual obscurants but just a few examples will be described here for the sake of brevity. Dillehay patented multi-compartment smoke devices containing both red phosphorus compositions and those based on organic acid sublimation/recondensation.[13] Acid scavengers aerosolized from one or both of the compartments neutralize phosphorus acids within the mixed smoke cloud. The benefits of this scheme come at the cost of increased device complexity. Also, any munition containing red phosphorus may produce toxic and flammable phosphine gas in storage.[14] Koch proposed a particularly clever solution to the red phosphorus aging problem by suggesting the use of *black* phosphorus instead.[15] Unfortunately, this more stable allotrope is not readily available from commercial sources. Several compositions containing common materials have recently been designed to aerosolize a variety of organic[16] and inorganic compounds. For the latter, highly energetic fuel/oxidizer pairs are diluted with inert additives to control exothermicity and burning rate. The smoke produced by Webb's $Mg/NaClO_3/CaCO_3$/cellulose compositions is intended to mimic aerosolized sea salt.[17] Blau and Seidner have experimented with B/KNO_3/alkali chloride compositions although the high cost of elemental boron limits their practicality.[18] These types of inorganic fuel/oxidizer/diluent systems are related to earlier experimental U.S. Navy smoke compositions[19] and the training smokes proposed by Krone.[20,21] The BC smoke compositions described in this report fall into the same category.

Boron carbide has been known as a pyrotechnic fuel since the 1950s, if not earlier. Several smoke compositions containing B_4C, $KMnO_4$, and other oxidizers were briefly described in a 1961 patent.[22] Some binary B_4C/oxidizer mixtures were evaluated as smoke compositions by Lane and co-workers in the 1960s.[23,24] There has also been interest in using boron carbide as a component of solid fuels for ramjet engines.[25] 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 demonstrated boron carbide-based time delays and green light-emitting compositions.[26,27] 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.[28,29] These BC compositions produce an effective smoke screen and do not contain hazardous materials. Because of this, they are candidates for use in future U.S. Army smoke grenades. Herein, we describe recent grenade prototype tests relevant to the continuing development and evaluation of the system.

EXPERIMENTAL SECTION

Material Properties. Boron carbide powders (carbon rich, 19.0-21.7 wt% C) were obtained from Atlantic Equipment Engineers (AEE) and Alfa Aesar. A Microtrac S3500 laser diffraction particle size analyzer was used to determine volume-based diameter distributions of aqueous boron carbide suspensions. Potassium nitrate (MIL-P-156B, 15 μm) and potassium chloride (−50 mesh) were obtained from Hummel Croton and contained 0.2 wt% fumed silica, Cabot CAB-O-SIL M-5, as an anticaking agent. Calcium stearate (monohydrate, 10 μm) was also obtained from Hummel Croton. Polyacrylate elastomer (Zeon Chemicals HyTemp 4451CG) and nitrocellulose (Scholle Chemicals) were dissolved in acetone before use. Polyvinyl alcohol was obtained from Celanese as a 9 wt% aqueous solution. Polyvinyl acetate aqueous emulsion, Elmer's Glue-All, was found to contain 34.5 wt% solids. Epoxy resin (EPON 828) and polyamide curing agent (EPIKURE 3140) were obtained from Momentive.

Preparation of Compositions. Dry mixtures were prepared by combining the components in a cylindrical polyethylene container and rolling for 15 min. The compositions were passed through a 20 mesh screen to remove any clumps and then rolled again for 10 min. Compositions containing dust-reducing binders were prepared in a planetary bowl mixer equipped with a flat beater paddle. For the polyacrylate elastomer and nitrocellulose compositions, the dry components were combined and mixed with acetone solutions of the binders in the mixing bowl. Additional acetone was added during mixing to achieve a paste consistency. Mixing was continued until a substantial amount of acetone had evaporated and a granular consistency was obtained. For the polyvinyl alcohol and polyvinyl acetate compositions, the dry components were premixed before addition to the aqueous binder solution or emulsion. No additional water was added and the compositions were mixed until they were homogeneous and granulated. For the epoxy composition, epoxy resin and polyamide curing agent were combined in a 4:1 ratio in the bowl and mixed. Premixed dry components were combined with the epoxy and mixed. The epoxy composition was loaded into grenade cans immediately after mixing. These grenade cans were oven-cured overnight at 65 °C. The other wet mix compositions were oven-dried in trays overnight at 65 °C before loading.

Test and Analysis Protocols. Full-size experimental grenades were prepared for field and chamber testing (Figure 1). All the experimental grenades contained 350 g of smoke composition loaded at 7000 kg force (25.2 MPa). M83 and AN-M8 grenades manufactured at Pine Bluff Arsenal were tested for comparison. The M83 contained 350 g of TA smoke composition and the AN-M8 contained 480 g of HC smoke composition (Type C). All the experimental grenades and the AN-M8 were of the "end-burning" configuration which consisted of a solid pyrotechnic pellet that burned from one end to the other, emitting smoke through vent holes on one end of the grenade can. The M83 was of the "core-burning" configuration, burning from the top down and outward from a central core, emitting smoke from a vent hole aligned with the core.

Figure 1. Preparation of prototype BC smoke grenades.

Field tests were used to assess qualitative smoke characteristics and to determine burning times. Two or three experimental grenades of each type were tested for these purposes; the variability between grenades of the same type was generally low. Average linear burning rates (cm/s) were calculated by dividing the composition pellet lengths by the burning times. Mass-based burning rates (g/s) were also calculated.

Obscuration measurements were performed in the Edgewood Chemical Biological Center's 190 m^3 smoke chamber. Two or three experimental grenades of each type were tested. Temperature, relative humidity, and other relevant test data are appended. After each grenade was functioned 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 that was weighted to the photopic response of the human eye was used calculate photopic α_m and FM_m values.[30]

RESULTS AND DISCUSSION

Prior Research and Rationale for Continued Development. In principle, the B_4C/KNO_3 system should be a good starting point for the development of a pyrotechnic smoke composition. At appropriate fuel/oxidizer ratios, the reaction products are volatile at the temperature of combustion and a substantial portion of these products are solids at ambient temperature. However, binary B_4C/KNO_3 mixtures with B_4C in the 10-20 wt% range produce too much light and flame to be used for smoke applications. Combustion temperature and associated light emission are readily reduced by the addition of nonenergetic diluents. Diluents that are volatile at the reduced combustion temperature can also contribute to the smoke cloud. Potassium chloride was found to be particularly effective in this role. The combustion of certain ternary $B_4C/KNO_3/KCl$ mixtures (such as 13/62/25) aerosolizes reaction products and KCl with high efficiency and reduced light emission. When pressed into pellets, these ternary mixtures burn too quickly for practical use in smoke grenades where long burning times (over 45 s) are usually desired. Small amounts of waxy materials, particularly calcium stearate, were found to reduce pellet burning rates into an acceptable range.[28] As a dry lubricant, calcium stearate also reduces the abrasiveness of the compositions and improves the mechanical strength of consolidated pellets.

A quaternary composition containing a 13/60/25/2 ratio of $B_4C/KNO_3/KCl$/calcium stearate was selected for initial grenade prototyping. These prototypes outperformed the M83 TA grenade in preliminary field and smoke chamber tests.[29] However, the reproducibility and practicality of the new system were still in question. The burning rates of boron carbide-based pyrotechnics are highly sensitive to B_4C particle size. Additionally, in the subject smoke compositions, small changes to calcium stearate content can cause large burning rate variations. It is therefore crucial to understand how these variables affect the burning times of prototype smoke grenades. While the BC system in its most elegant form is a four-component dry mixture, dust could be problematic when working with the compositions on a large scale. Solvent-based or liquid binders can mitigate dustiness but the effect of these additional components on grenade burning time must be accounted for. Also, how these factors affect smoke cloud thickness and perceived visible obscuration performance must be understood.

Controlling Grenade Burning Time. As boron carbide remains in the solid state during combustion, the particle surface area (and therefore particle size) strongly influences the burning rates of pyrotechnic compositions containing this fuel. In the related $B_4C/NaIO_4$/PTFE system, a gassy pyrotechnic delay, burning rates were well correlated with the size and amount of boron carbide fines. Just a 6 µm change in the tenth percentile of the particle size distribution caused a six-fold change in burning rate.[26] Four boron carbide samples spanning a similar range were acquired for smoke grenade tests (Table 2).

For each type of boron carbide, compositions were prepared with three different amounts of calcium stearate. The resulting grenade burning times are shown in Figure 2. Corresponding plots showing the linear and mass-based burning rates are appended. The burning times and linear burning rates were well correlated (pellet lengths were similar). Despite the apparent similarity of the Alfa Aesar and AEE 1500 grit samples, the subtle difference in particle size between the two causes a small but distinct change in burning times and rates. Significantly longer burning times were obtained with AEE 1200 grit and very coarse AEE 800 grit material. Burning times for grenades containing finer boron carbide are more sensitive to changes in calcium stearate content. In Figure 2, burning times vary by over 150% for grenades containing the finest type but by less than 20% for those containing the coarsest.

At first, the burning time variability shown in Figure 2 may appear problematic. Coinci-

Table 2. Particle size data for B_4C samples (µm).

B_4C Type	D[4,3] [a)]	D[v, 0.1] [b)]	D[v, 0.5] [b)]	D[v, 0.9] [b)]
Alfa Aesar	3.99	0.84	2.81	8.67
AEE 1500 grit	4.37	1.04	3.23	9.28
AEE 1200 grit	6.36	2.59	5.88	10.71
AEE 800 grit	10.94	6.72	10.51	15.71

a) Volume-based mean diameter. b) D[v, x] is the diameter that $(100 \cdot x)$% of the volume distribution is below.

dentally (and fortunately), boron carbide is used industrially as an abrasive. Many different particle sizes are commercially available on a

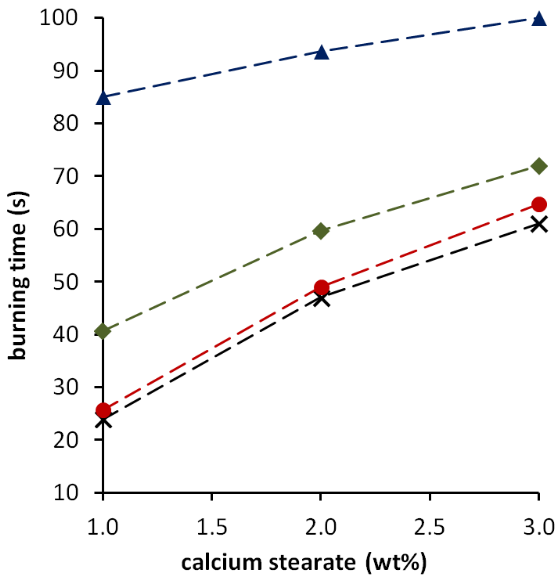

Figure 2. Burning times (s) for grenades containing 13/(62−*x*)/25/*x* mixtures of $B_4C/KNO_3/KCl$/calcium stearate. Alfa Aesar B_4C (black x); AEE 1500 grit B_4C (red circles); AEE 1200 grit B_4C (green diamonds); AEE 800 grit B_4C (blue triangles).

large scale at reasonable prices. And, as long as the boron carbide is not too coarse, the effect of small size differences can be countered simply by changing calcium stearate content by 1 wt% or less. For example, grenades containing AEE 1200 grit B_4C and 2 wt% calcium stearate burned for 60 s, while those containing Alfa Aesar B_4C and 3 wt% calcium stearate burned for nearly the same time, 61 s.

Incorporation of Dust-Reducing Binders. Dust associated with processing large quantities of fine combustible materials has been responsible for many unintended explosions.[31] In a manufacturing environment, care must be taken to prevent accumulation of combustible dust on surrounding surfaces. Where it is feasible, granulating powdered mixtures with polymeric binders can reduce or eliminate this hazard and inconvenience. Due to its hard waxy nature, calcium stearate serves as a binder in consolidated BC pellets but does nothing to reduce the dustiness of unconsolidated mixtures. Five wet binder systems were therefore evaluated. Polyacrylate elastomer and nitrocellulose (NC) were applied as acetone solutions

Table 3. Burning times for experimental and production grenades.

Entry	Grenade Type [a)]	Calcium Stearate (wt%)	B_4C Type	Dust-Reducing Binder	Average Burning Time (s)
1	BC	1	Alfa Aesar	none	24.0
2	BC	2	AEE 1500 grit	none	49.0
3	BC	3	AEE 1200 grit	none	72.0
4	BC	2	AEE 1500 grit	polyacrylate elastomer	73.5
5	BC	2	AEE 1500 grit	nitrocellulose (NC)	29.5
6	BC	2	AEE 1500 grit	polyvinyl alcohol (PVA)	41.0
7	BC	2	AEE 1500 grit	polyvinyl acetate (PVAc)	51.0
8	BC	2	AEE 1500 grit	epoxy	51.0
9	M83 TA				45-60 [b)]
10	AN-M8 HC				90 [b)]

a) BC grenades with dust-reducing binders contained 13 wt% B_4C, 58 wt% KNO_3, 25 wt% KCl, 2 wt% calcium stearate, and 2 wt% binder solids. Those without contained 13 wt% B_4C, 25 wt% KCl, 1-3 wt% calcium stearate, and 59-61 wt% KNO_3 such that the total was 100 wt%. b) Typical values.

while an aqueous solution of polyvinyl alcohol (PVA) was used. A thick aqueous emulsion of polyvinyl acetate (PVAc), common white glue, was applied without any additional water. Two-part epoxy contained no solvent and was applied neat. At the 2 wt% level (of binder solids), all of these binders significantly reduced the dustiness of the resulting granulated compositions. The acetone- and water-based systems were generally more effective in this role than epoxy, which was viscous and difficult to blend evenly with the powdered components.

Smoke grenade burning times for the BC compositions containing dust-reducing binders are listed in Table 3. Data for selected four-component dry compositions and the M83 TA and AN-M8 HC grenades are listed for comparison. The compositions prepared with wet binder systems (entries 4-8) are derivatives of the dry composition in entry 2, which has an average grenade burning time of 49 s. Polyacrylate elastomer lengthened burning time substantially while NC (which is energetic) had the opposite effect. PVA also shortened burning time, but not dramatically. Surprisingly, PVAc and epoxy did not cause any significant change (entries 7, 8). For manufacturing, this characteristic would be most desirable. In such a situation, where materials and particle sizes can vary from lot to lot, the formulation giving the desired burning time could be rapidly determined by preparing and testing small batches of dry mixtures, *before* large-scale mixing, granulation, and drying of the "reduced dust" variant. Even though the grenade burning times in entries 7 and 8 are the same, the corresponding linear burning rates varied due to significantly different pellet lengths. The epoxy composition, having been pressed wet before curing, was more effectively consolidated (see appended data tables).

The versatility of BC compositions with respect to burning rate is magnified by alternative pellet configurations. While all the prototype grenades described in this report were of the end-burning variety, it is possible to prepare variants with a central core. Earlier tests showed that core-burning BC grenades release smoke three times more rapidly than their end-burning analogues.[29] In a core-burning configuration, the faster-burning BC compositions in Figure 2 and Table 3 would produce thick smoke clouds *very* quickly, but this was not the objective of the current study (see below).

Visible Obscuration Performance. The "performance" of a visible obscurant can mean many different things and depends on the particular requirements of the device it is used in. Devices that release smoke rapidly are useful for immediate and localized screening. In contrast, the obsolete AN-M8 HC grenade and current M83 TA grenade, with burning times ranging from 45-90 s, are intended to produce elongated clouds suitable for screening troop movements across a relatively large area. For any smoke-producing device, the duration of smoke release has a profound influence on the perceived thickness of the resulting cloud. A given quantity of particulates dispersed in a short time produces a thick and short cloud while greater dispersal times result in thinner but longer clouds. At extremely long durations, the emitted smoke is likely to be very thin and ineffective for screening. In practice, prototype BC smoke grenades with burning times from about 40-70 s provided a good compromise between duration and perceived thickness (Figure 3). Qualitatively, the smoke clouds produced by these prototypes were substantially thicker than that produced by the M83 TA grenade.

For smoke grenades with similar burning times, differences in apparent obscuration performance depend on the properties and amount of smoke (aerosol) produced by each grenade. The mass-based extinction coefficient (α_m) is a measure of how well a given mass of aerosol attenuates light. Attenuation is caused by absorption and scattering. Since aerosolization

Figure 3. Field test of a typical end-burning BC prototype grenade. Grenade PH2-3-2 at 25 s (total burning time 61 s).

efficiency varies and some aerosols are hygroscopic, α_m is not always correlated with the effectiveness of smoke *compositions*. An appropriate figure of merit for smoke compositions is obtained by multiplying α_m by the yield factor, Y—the ratio of aerosol mass (m_a) to the mass of initial composition (m_c). The equation below shows how the mass-based composition figure of merit, FM_m, is related to m_c. Here, V is the chamber volume, T is transmittance, and L is the measurement path length. A detailed description of smoke figures of merit and smoke measurement technique is appended.

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

Figures 4 and 5 illustrate the importance of yield factor as a determinant of smoke composition performance. The M83 TA and AN-M8 HC grenades provide the most striking example. The aerosol produced by the M83 TA grenade is effective, as indicated by α_m, but FM_m is lacking because Y is only 0.30. Only a small fraction of the TA composition is aerosolized upon combustion and the resulting aerosol is not hygroscopic. Unlike terephthalic acid, the zinc chloride produced by burning HC compositions

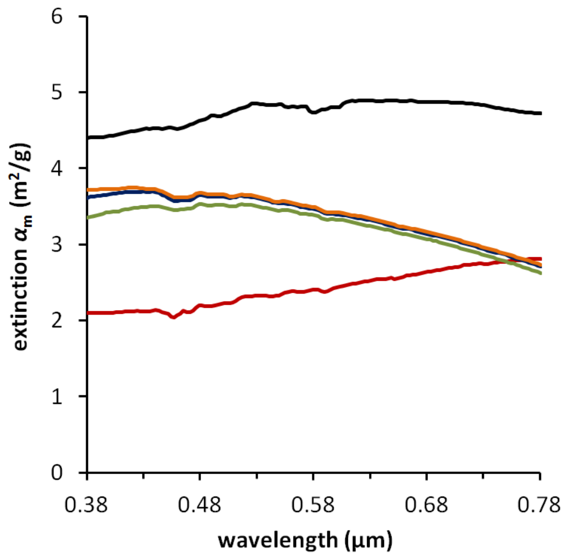

Figure 4. Mass-based extinction coefficient (α_m) versus wavelength. M83 TA (top line, black); AN-M8 HC at 25.0 °C and 32% relative humidity (bottom line, red). BC grenades containing dry compositions with average burning times of 24 s (PH4-1E-3, blue); 49 s (PH4-2E-3, green); 72 s (PH4-3E-2, orange). These traces are for the particular BC grenades with α_m values closest to the average for each type, see appended data tables.

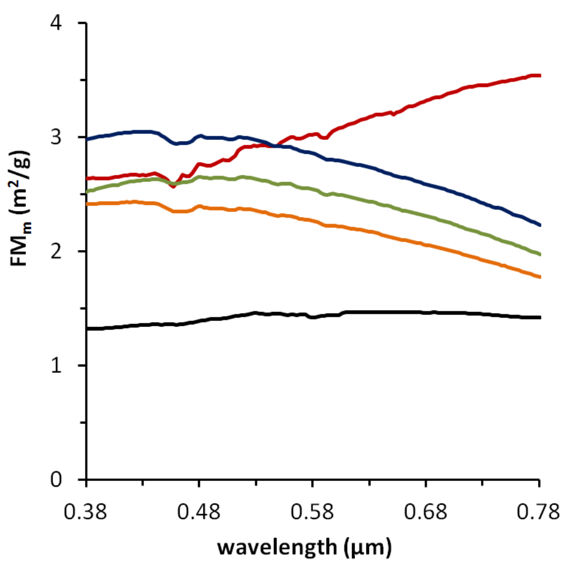

Figure 5. Mass-based composition figure of merit (FM_m) versus wavelength for the grenades in Figure 4. M83 TA (Y = 0.30, bottom line, black); AN-M8 HC at 25.0 °C and 32% relative humidity (Y = 1.26, top line, red). BC 24 s (PH4-1E-3, Y = 0.82, blue); BC 49 s (PH4-2E-3, Y = 0.75, green); BC 72 s (PH4-3E-2, Y = 0.65, orange).

is vigorously hygroscopic. Measured yield factors for HC compositions often 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.

BC grenades containing dry compositions with burning times of 24, 49, and 72 s (described in Table 3) gave almost overlapping α_m lines (Figure 4). This was expected, as the formulations differ by no more than a few percent. However, faster burning times were associated with greater yield factors, which ranged from 0.64 to 0.82, and this caused the calculated figures of merit to vary (Figure 5). The aerosol produced by BC smoke compositions is not particularly hygroscopic. Throughout this study, prototype grenades were tested between 35 and 48% relative humidity but measured yield factors never approached or exceeded unity. Much greater humidity would likely cause an increase in Y, but this has not been studied yet. Even relatively nonhygroscopic substances will absorb water from very humid air.[32]

Generally, very little residue remains after the combustion of BC smoke compositions. In many instances, particularly with faster burning grenades, the post-test cans are almost empty with just a small layer of residue remaining on the inner walls and around the vent holes. In the BC system, the amount of combustion residue (unaerosolized material) varies as KCl content changes—this material is a diluent and controls exothermicity.[29] However, all of the compositions described here contain the same amount of KCl and otherwise differ only slightly. Small changes in boron carbide particle size and calcium stearate content do not cause a discernible change in the amount of residue left by small unconfined pellets (see appended description). Yet, the yield factors (and FM_m) for the prototype grenades in Figures 4 and 5 are distinctly different. Differences in aerosolization efficiency appear to be responsible for this phenomenon. Faster burning compositions develop greater pressure within the grenade can causing material to be ejected and aerosolized more effectively. Although, additional experiments involving variations in the size and

Table 4. Visible obscuration data for experimental and production grenades. [a)]

Entry [b)]	Grenade Type [c)]	Dust-Reducing Binder	Y	α_m (m^2/g) [d)]	FM_m (m^2/g) [d)]
1	BC (24.0 s)	none	0.82	3.50	2.85
2	BC (49.0 s)	none	0.76	3.42	2.58
3	BC (72.0 s)	none	0.64	3.55	2.28
4	BC (73.5 s)	polyacrylate elastomer	0.53	3.88	2.07
5	BC (29.5 s)	nitrocellulose (NC)	0.74	3.54	2.62
6	BC (41.0 s)	polyvinyl alcohol (PVA)	0.63	3.57	2.24
7	BC (51.0 s)	polyvinyl acetate (PVAc)	0.75	3.50	2.64
8	BC (51.0 s)	epoxy	0.69	3.55	2.44
9	M83 TA		0.30	4.80	1.44
10	AN-M8 HC		1.26 [e)]	2.36	2.97

a) Average values. b) Entries correspond to those in Table 3. c) Average burning times for experimental grenades listed in parentheses. d) Photopic values. e) Determined at 25.0 °C, 32% relative humidity.

number of vent holes would be needed to verify this hypothesis conclusively.

In field tests of the prototype grenades, the visual characteristics of the smoke clouds were primarily influenced by burning time (as described above) and variations in the total amount and thickness of the smoke were difficult to distinguish with confidence. Nonetheless, it is important to know whether the wet binder systems affect α_m, Y, and FM_m. Tabular visible obscuration data for the grenades in Table 3 and Figures 4 and 5 are given in Table 4. The entries in Table 4 correspond to those in Table 3. (The compositions containing dust-reducing binders, entries 4-8, are derivatives of the dry composition in entry 2.) At the 2 wt% level, it would not be likely for any binder to cause substantial changes in the nature of the aerosol. This is indeed the case, as α_m varied by only 13%. Yield factors varied by over 40% with polyacrylate elastomer giving a low value (0.53) and NC and PVAc giving values comparable to the parent dry composition (0.74, 0.75, 0.76, respectively). Intermediate values were determined for the others. The best performing prototypes, according to FM_m, were therefore the ones with the greatest yield factors. Of these, the PVAc variant had the greatest measured FM_m value (compared to entry 2). Since this dust-reducing binder also did not affect grenade burning time, it is most appropriate for use in future prototyping.

Although FM_m is a mass- and composition-based metric, it may be used for grenade-to-grenade comparison provided the amount of smoke composition in each grenade is the same. (The influence of burning time must also be considered, as previously discussed.) The BC prototypes and the M83 TA grenade all contain 350 g of smoke composition. Therefore, prototypes with comparable burning times, such as entries 2 and 7 in Tables 3 and 4, provide almost twice the obscuration performance of one M83 TA grenade. These prototypes would also be comparable to a smoke grenade containing 350 g of HC composition on a dry day. Before production ended, AN-M8 grenades were loaded with a greater mass of HC composition due to the high density of the main components, hexachloroethane and zinc oxide. This makes one AN-M8 HC grenade functionally equivalent to about three M83 TA grenades, and the performance of the former further improves with increasing humidity. Nevertheless, the weight savings provided by lighter smoke grenades, containing no more than 350 g of smoke composition, is beneficial. In comparison to the M83 TA smoke grenade, BC prototypes deliver *substantially* improved obscuration performance without any increase in grenade weight or size.

CONCLUSIONS

In conclusion, a multitude of favorable characteristics make BC smoke compositions promising candidates for use in future U.S. Army smoke grenades and other smoke munitions. In field and smoke chamber tests, the best prototype BC smoke grenades greatly outperformed the U.S. Army M83 TA smoke grenade. BC compositions do not contain hazardous materials and may be tuned to give a wide range of burning rates. Granulating the compositions with 2 wt% PVAc reduces dust and does not adversely affect grenade burning time or visible obscuration performance. Unlike some other binder systems that require organic solvents, PVAc may be applied as an aqueous emulsion. The BC system is the subject of continuing research and development. Future work will include studies to determine the effect of varying PVAc content, chemical characterization of the aerosol, and an inhalation toxicity assessment.

NOTE

This document has been approved by the U.S. Government for public release; distribution is unlimited.

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ABBREVIATIONS

ARDEC, Armament Research Development and Engineering Center

BC, boron carbide-based smoke composition

ECBC, Edgewood Chemical Biological Center

HC, hexachloroethane-based smoke composition

NC, nitrocellulose

PTFE, polytetrafluoroethylene

PVA, polyvinyl alcohol

PVAc, polyvinyl acetate

RDECOM, Research, Development and Engineering Command

TA, terephthalic acid-based smoke composition

wt%, weight percentage

REFERENCES

(1) Rivera, Y. B.; Olin, T.; Bricka, R. M. *Summary and Evaluation for White Phosphorus Remediation: A Literature Review*; Accession Number CPIAC-1996-5148; Defense Technical Information Center (DTIC): Fort Belvoir, VA, 1996; pp 1-72.

(2) Collins, P. J. D.; Smit, K. J.; Hubble, B. R. *The Use of Red Phosphorus in Pyrotechnics – Results of an International Investigation*; Accession Number CPIAC-2004-0319AR; Defense Technical Information Center (DTIC): Fort Belvoir, VA, 2004; pp 1-6.

(3) Koch, E.-C. Special Materials in Pyrotechnics: IV. The Chemistry of Phosphorus and its Compounds. *J. Pyrotech.* **2005**, *21*, 39-50.

(4) Koch, E.-C. Special Materials in Pyrotechnics: V. Military Applications of Phosphorus and its Compounds. *Propellants, Explos., Pyrotech.* **2008**, *33*, 165-176.

(5) Eaton, J. C.; Lopinto, R. J.; Palmer, W. G. *Health Effects of Hexachloroethane (HC) Smoke*; Accession Number ADA277838; Defense Technical Information Center (DTIC): Fort Belvoir, VA, 1994; pp 1-60.

(6) Agency for Toxic Substances and Disease Registry. *Toxicological Profile for Hexachloroethane*; Accession Number CBRNIAC-CB-069808; Defense Technical Information Center (DTIC): Fort Belvoir, VA, 1997; pp 1-190.

(7) Carbonates have been used in bursting-type FM grenades to reduce aerosol acidity: Wulvik, E. A.; Halsnes, O.; Jakobsen, L. S. Smoke Hand Grenade. European Patent 0791164, April 26, 2000.

(8) Cramer, A. *M56/M58 Smoke Systems – Visual and Infrared Obscuration*; Accession Number CBRNIAC-CB-102916; Defense Technical Information Center (DTIC): Fort Belvoir, VA, 1997; pp 1-4.

(9) Smoke pots and grenades have been designed to aerosolize fog oil but these munitions are inherently complex and are no longer used by the U.S. Army: DeAngelis, T. P. *Analysis of SGF2 Smoke Pot Oil and Recommendation for Reuse*; Accession Number ADA401779; Defense Technical Information Center (DTIC): Fort Belvoir, VA, 2002; pp 1-21.

(10) Embury, J. F.; Walker, D.; Zimmermann, C. J. *Screening Smoke Performance of Commercially Available Powders. II. Visible Screening by Titanium Dioxide*; Accession Number ADA284072; Defense Technical Information Center (DTIC): Fort Belvoir, VA, 1994; pp 1-30.

(11) DeLacy, B.; Redding, D.; Matthews, J. Mass Extinction Coefficients of Surface Modified Titanium Dioxide. *2011 Obscurants Symposium*; Baltimore, MD, U.S.A., May 10-12, 2011.

(12) Douda, B. E.; Tanner Jr., J. E. Cinnamic Acid Containing Pyrotechnic Smoke Composition. U.S. Patent 4,032,374, June 28, 1977.

(13) Dillehay, D. R. Low-Toxicity Obscuring Smoke Formulation. U.S. Patent 5,522,320, June 4, 1996.

(14) Red phosphorus aging is such a serious problem that phosphine getter materials have been developed for use in ammunition containers: Manton, G.; Endsor, R. M.; Hammond, M. An Effective Mitigation for Phosphine Present in Ammunition Container Assemblies and in Munitions Containing Red Phosphorus. *Propellants, Explos., Pyrotech.* **2013**, in press, DOI: 10.1002/prep.201300021.

(15) Koch, E.-C. Pyrotechnic Smoke Composition. U.S. Patent Application 11/128,860, Publication US20050252590, November 17, 2005.

(16) Lombardi, J. L. Nontoxic Obscurant Compositions and Method of Using Same. U.S. Patent Application 13/159,324, Publication US20120267016, October 25, 2012.

(17) Webb, R.; Ramlal, D. R.; Langenberg, J. P.; Alblas, M. J. *Technical Feasibility Study of an Effective Low-Toxicity Obscurant Material*; Strategic Environmental Research and Development Program (SERDP) Project WP-2148 Final Report, August 2012.

(18) Blau, R.; Seidner, N. *Hexachloroethane Obscurant Replacement*; Strategic Environmental Research and Development Program (SERDP) Project WP-2149 Final Report, April 2012.

(19) Hanley, J. T.; Mack, E. J. *A Laboratory Investigation of Aerosol and Extinction Characteristics for Salty Dog, NWC 29 and NWC 78 Pyrotechnics*; Accession Number ADA093098; Defense Technical Information Center (DTIC): Fort Belvoir, VA, 1980; pp 1-44.

(20) Krone, U. Pyrotechnical Mixture for Producing a Smoke Screen. U.S. Patent 4,968,365, November 6, 1990.

(21) Krone, U. A Non-Toxic Pyrotechnic Screening Smoke for Training Purposes. *Proceedings of the 15th International Pyrotechnics Seminar*; Boulder, CO, U.S.A., July 9-13, 1990; pp 581-586.

(22) De Ment, J. Composition for Smoke Production. U.S. Patent 2,995,526, August 8, 1961.

(23) Lane, G. A.; Jankowiak, E. M.; Smith, W. A. *Techniques in Smoke Application*; Accession Number CBRNIAC-CB-136829; Defense Technical Information Center (DTIC): Fort Belvoir, VA, 1968; pp 1-64.

(24) Lane, G. A.; Smith, W. A.; Jankowiak, E. M. Novel Pyrotechnic Compositions for Screening Smokes. *Proceedings of the 1st International Pyrotechnics Seminar*; Estes Park, CO, U.S.A., August 12-16, 1968; pp 263-291.

(25) Natan, B.; Netzer, D. W. Boron Carbide Combustion in Solid-Fuel Ramjets Using Bypass Air. Part I: Experimental Investigation. *Propellants, Explos., Pyrotech.* **1996**, *21*, 289-294.

(26) Poret, J. C.; Shaw, A. P.; Csernica, C. M.; Oyler, K. D.; Vanatta, J. A.; Chen, G. Versatile Boron Carbide-Based Energetic Time Delay Compositions. *ACS Sustainable Chem. Eng.* **2013**, *1*, 1333-1338.

(27) Sabatini, J. J.; Poret, J. C.; Broad, R. N. Boron Carbide as a Barium-Free Green Light Emitter and Burn-Rate Modifier in Pyrotechnics. *Angew. Chem., Int. Ed.* **2011**, *50*, 4624-4626.

(28) Shaw, A. P.; Poret, J. C.; Gilbert, R. A.; Moretti, J. D.; Sabatini, J. J.; Oyler, K. D.; Chen, G. Pyrotechnic Smoke Compositions Containing Boron Carbide. *Proceedings of the 38th International Pyrotechnics Seminar*; Denver, CO, U.S.A., June 10-15, 2012; pp 569-582.

(29) Shaw, A. P.; Poret, J. C.; Gilbert, R. A.; Domanico, J. A.; Black, E. L. Development and Performance of Boron Carbide-Based Smoke Compositions. *Propellants, Explos., Pyrotech.* **2013**, *38*, 622-628.

(30) *Commission Internationale de l'Éclairage (CIE) Proceedings, 1931*; Cambridge University Press: Cambridge, U.K., 1932.

(31) Amyotte, P. R.; Eckhoff, R. K. Dust Explosion Causation, Prevention and Mitigation: An Overview. *J. Chem. Health and Safety* **2010**, *17*, 15-28.

(32) The relative humidity at which a material begins to absorb water from the air (the critical relative humidity) depends on temperature. For a salt, it may be determined by measuring the equilibrium relative humidity above a saturated aqueous solution. Such solutions are often used for humidity control: Greenspan, L. Humidity Fixed Points of Binary Saturated Aqueous Solutions. *J. Res. Natl. Bur. Stand., Sect. A* **1977**, *81A*, 89-96.

APPENDIX

Burning Rate Plots

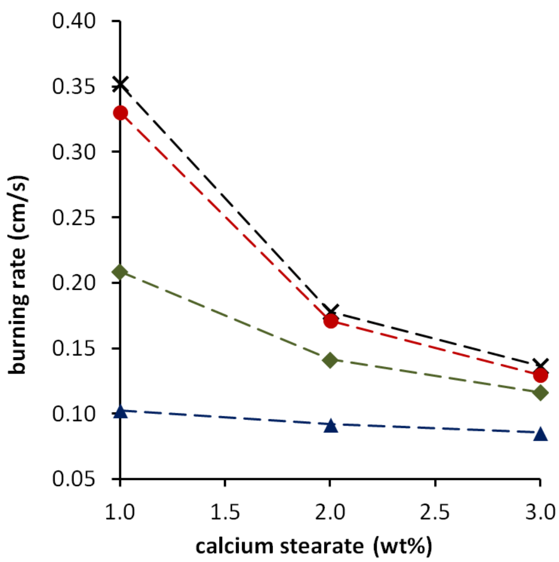

Figure A1. Burning rates (cm/s) for the grenades in Figure 2. Alfa Aesar B_4C (black x); AEE 1500 grit B_4C (red circles); AEE 1200 grit B_4C (green diamonds); AEE 800 grit B_4C (blue triangles).

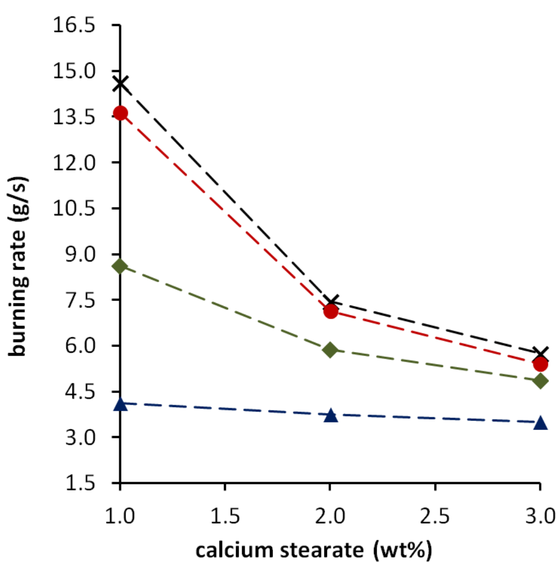

Figure A2. Burning rates (g/s) for the grenades in Figures 2 and A1.

Residue Determination Experiments

Two dry compositions were prepared for small pellet residue tests. The first, a fast-burning composition, contained a 13/61/25/1 ratio of B_4C/KNO_3/KCl/calcium stearate (with Alfa Aesar B_4C). The second, a slow-burning composition, contained a 13/59/25/3 ratio of these components (with AEE 1200 grit B_4C). Full-size grenades containing these compositions burned for 24 and 72 seconds, respectively, see Tables A2 and A3. Small cylindrical pellets (1.8 g, 1.27 cm diameter) were prepared by pressing compositions at 445 kg force (34.5 MPa). 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 and then ignited with an electrically heated nichrome wire. The combustion residue as a percentage of original pellet mass was determined by weighing the cups before and after combustion. For each composition, ten pellets were tested and the results were averaged. The fast- and slow-burning pellets burned for 5-6 and 12-15 s, respectively. The fast-burning pellets left 13.1 (2.7) percent residue and the slow-burning pellets left 13.5 (4.3) percent residue (standard deviations in parentheses).

APPENDIX

Description of Smoke Figures of Merit and Measurement Technique

Table A1. Smoke measurement variables, definitions, and units.

Variable	Definition	Units
T	transmittance, I/I_0	
L	path length	m
V	cloud or chamber volume	m^3
c	concentration	g/m^3
α_m	mass-based extinction coefficient	m^2/g
FM_m	mass-based composition figure of merit	m^2/g
FM_v	volume-based composition figure of merit	m^2/cm^3
FM_{md}	mass-based device figure of merit	m^2/g
FM_{vd}	volume-based device figure of merit	m^2/cm^3
m_a	mass of aerosol	g
m_c	mass of composition	g
m_d	mass of device	g
v_c	volume of composition	cm^3
v_d	volume of device	cm^3
ρ_c	density of composition, m_c/v_c	g/cm^3
Y	composition yield factor, m_a/m_c	
F_m	mass fill fraction, m_c/m_d	
F_v	volume fill fraction, v_c/v_d	

Visual screening smokes may be quantitatively assessed in a suitably-sized aerosol chamber. In a typical experiment, the total attenuation of visible light from both scattering and absorption is measured by determining transmittance (T), the ratio of transmitted light intensity (I) to that of the incident beam (I_0). The Beer-Lambert law (equation 1) relates T to the aerosol concentration (c), the path length the light travels through (L), and the extinction coefficient (α).

$$T = {}^{I}/_{I_0} = e^{-cL\alpha} \qquad \text{(eq 1)}$$

The extinction coefficient, which is independent of concentration and path length, determines the effectiveness of an aerosol as an obscurant [A1]. The units of α are such that the term $cL\alpha$ (the optical depth) is dimensionless. Therefore, when L is measured in meters and c is defined as the mass of aerosol particles divided by the volume of the chamber (g/m^3), the units of α are m^2/g. This is a mass-based extinction coefficient (α_m). Rearranging the terms and substituting m_a/V for c, where m_a is the aerosol mass and V is the chamber volume, gives equation 2.

$$\alpha_m = \frac{-\ln(T)}{cL} = \frac{-V \cdot \ln(T)}{m_a L} \qquad \text{(eq 2)}$$

Since α_m is only a characteristic of the aerosol, it does not account for the properties of the initial smoke-producing material. Two practical factors, unaccounted for by α_m, are the composition/device efficiency and whether or not the volatilized materials absorb atmospheric constituents. Various *figures of merit* have been used to account for these factors with the goal of quantifying actual smoke composition performance. In 1968, Lane and co-workers described “total obscuring power” (TOP) which was intended to represent the area in square feet that could be obscured by a pound of smoke composition. This figure of merit incorporated a factor to account for the “discrimination capability of the human eye” [A2]. A figure of merit more closely related to the Beer-Lambert law may be obtained by multiplying α_m by the yield factor (Y). Here, Y is the ratio of aerosol mass (m_a) to the mass of initial composition (m_c). Equation 3 shows how the resulting mass-based figure of merit, FM_m, is related to the initial smoke composition mass. Like α_m, the units of FM_m are m^2/g.

APPENDIX

$$\mathrm{FM_m} = \alpha_\mathrm{m} Y = \left(\frac{-V \cdot \ln(T)}{m_\mathrm{a} L}\right)\left(\frac{m_\mathrm{a}}{m_\mathrm{c}}\right) = \frac{-V \cdot \ln(T)}{m_\mathrm{c} L} \qquad \text{(eq 3)}$$

If all the smoke from the composition is kept in the chamber, the technique is greatly simplified as only T must be measured to determine $\mathrm{FM_m}$ (V, L, and m_c are known). In practice, the cloud generated by just one smoke grenade is too thick even for large smoke chambers and smoke must be partially vented to obtain a reasonable measurement of T (usually in the 0.1-0.5 range). In this case, aerosol sampling to determine m_a must be performed before and after the venting step. The first determination is used to calculate Y. The second is used to calculate α_m at the time of optical measurement. These two values are then multiplied to give $\mathrm{FM_m}$ (as shown in equation 3). It is assumed that the aerosol does not change during the process. Even if it is possible to determine $\mathrm{FM_m}$ without chamber venting and aerosol sampling, α_m and Y are still quite informative. A yield factor greater than unity indicates with certainty that the smoke has absorbed mass from the air (usually water).

In actual devices, the amount of smoke composition is often limited by the device *volume*. Thus, for different compositions with comparable $\mathrm{FM_m}$ values, the one with greater density is preferable provided a heavier device is acceptable. A volume-based figure of merit that accounts for this is obtained by multiplying $\mathrm{FM_m}$ by the composition density (ρ_c, g/cm^3). The units of $\mathrm{FM_v}$ are m^2/cm^3 (equation 4). This figure of merit, which is related to the initial volume of smoke composition (v_c), has been used since the 1980s if not earlier [A3,A4].

$$\mathrm{FM_v} = \mathrm{FM_m}\rho_\mathrm{c} = \alpha_\mathrm{m} Y \rho_\mathrm{c} = \frac{-V \cdot \ln(T)}{v_\mathrm{c} L} \qquad \text{(eq 4)}$$

Figures of merit suitable for direct device-to-device comparison are obtained by incorporating fill fractions, F_m or F_v, the ratio of composition mass or volume to that of the device [A5]. Multiplying $\mathrm{FM_m}$ or $\mathrm{FM_v}$ by F_m or F_v, respectively, gives device-based figures of merit that are related to the total device mass or volume (equations 5 and 6).

$$\mathrm{FM_{md}} = \mathrm{FM_m} F_\mathrm{m} = \alpha_\mathrm{m} Y F_\mathrm{m} = \frac{-V \cdot \ln(T)}{m_\mathrm{d} L} \qquad \text{(eq 5)}$$

$$\mathrm{FM_{vd}} = \mathrm{FM_v} F_\mathrm{v} = \alpha_\mathrm{m} Y \rho_\mathrm{c} F_\mathrm{v} = \frac{-V \cdot \ln(T)}{v_\mathrm{d} L} \qquad \text{(eq 6)}$$

A broadband light source (tungsten-halogen bulb or xenon arc lamp) combined with a spectrometer as the detector is the most flexible experimental setup. Measurements of T may be obtained at specific wavelengths, averaged across the visible spectrum, or weighted to the photopic response of the human eye [A6]. Any reported α or FM value should therefore be accompanied by the wavelength, wavelength range, or weighting operation that was used to calculate it.

APPENDIX

The behavior of many pyrotechnic smoke compositions depends on device configuration, although some are less configuration-sensitive than others. Information about the test containers and sample sizes should be noted. Additionally, performance (as determined by a figure of merit) can depend on humidity. Compositions that aerosolize hygroscopic compounds perform better as humidity and yield factor increase. In such cases, the extinction coefficient also varies, but not nearly as much as the yield factor does [A7,A8]. Yield factors for nonhygroscopic smokes are governed by aerosolization efficiency.

[A1] Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; Wiley-VCH: Weinheim, Germany, 2004; Section 3.4, pp 69-81.

[A2] Lane, G. A.; Smith, W. A.; Jankowiak, E. M. Novel Pyrotechnic Compositions for Screening Smokes. *Proceedings of the 1st International Pyrotechnics Seminar*; Estes Park, CO, U.S.A., August 12-16, 1968; pp 263-291.

[A3] Turetsky, A. L.; Young, G. P. Advances in Pyrotechnically Based Visual Smoke Systems. *Proceedings of the 13th International Pyrotechnics Seminar*; Grand Junction, CO, U.S.A., July 11-15, 1988; pp 805-810.

[A4] Embury, J. F.; Walker, D.; Zimmermann, C. J. *Screening Smoke Performance of Commercially Available Powders. II. Visible Screening by Titanium Dioxide*; Accession Number ADA284072; Defense Technical Information Center (DTIC): Fort Belvoir, VA, 1994; pp 1-30.

[A5] DeLacy, B.; Redding, D.; Matthews, J. Mass Extinction Coefficients of Surface Modified Titanium Dioxide. *2011 Obscurants Symposium*; Baltimore, MD, U.S.A., May 10-12, 2011.

[A6] The 1931 CIE standard luminosity function is often used. Many slight modifications have since been suggested: Sharpe, L. T.; Stockman, A.; Jagla, W.; Jägle, H. A Luminous Efficiency Function, $V^*(\lambda)$, For Daylight Adaptation. *Journal of Vision* **2005**, *5*, 948-968.

[A7] Milham, M. E.; Anderson, D. H. *Obscuration Sciences Smoke Data Compendium – Standard Smokes*; Accession Number CBRNIAC-CB-153496; Defense Technical Information Center (DTIC): Fort Belvoir, VA, 1983; pp 1-56.

[A8] Sordoni, N.; Heard, W.; Rouse, W. *Pyrotechnic Smoke Analysis Volume I*; Accession Number CBRNIAC-CB-027023; Defense Technical Information Center (DTIC): Fort Belvoir, VA, 1993; pp 1-49.

APPENDIX

Table A2. Density, burning times, and burning rate data for dry compositions.

Grenade [a)]	B_4C Type	Calcium Stearate (wt%)	Pellet Density (g/cm^3)	Pellet %TMD [b)]	Burning Time (s)	Burning Rate (cm/s)	Burning Rate (g/s)
PH2-1-1	Alfa Aesar	1	1.520	72.42	23	0.367	15.217
PH2-1-2	Alfa Aesar	1	1.524	72.60	25	0.337	14.000
PH2-1-3	Alfa Aesar	1	1.521	72.47	24	0.352	14.583
PH2-1 Average			**1.523**	**72.50**	**24.0**	**0.352**	**14.600**
PH2-2-1	Alfa Aesar	2	1.536	73.91	47	0.178	7.447
PH2-2-2	Alfa Aesar	2	1.531	73.69	47	0.178	7.447
PH2-2-3	Alfa Aesar	2	1.531	73.67	47	0.178	7.447
PH2-2 Average			**1.533**	**73.76**	**47.0**	**0.178**	**7.447**
PH2-3-1	Alfa Aesar	3	1.540	74.87	61	0.137	5.738
PH2-3-2	Alfa Aesar	3	1.543	75.01	61	0.136	5.738
PH2-3-3	Alfa Aesar	3	1.548	75.24	61	0.136	5.738
PH2-3 Average			**1.544**	**75.04**	**61.0**	**0.136**	**5.738**
PH2-4-1	AEE 1500 grit	1	1.510	71.95	26	0.327	13.462
PH2-4-2	AEE 1500 grit	1	1.520	72.42	25	0.338	14.000
PH2-4-3	AEE 1500 grit	1	1.511	71.99	26	0.327	13.462
PH2-4 Average			**1.514**	**72.12**	**25.7**	**0.330**	**13.641**
PH2-5-1	AEE 1500 grit	2	1.531	73.69	49	0.171	7.143
PH2-5-2	AEE 1500 grit	2	1.534	73.82	49	0.171	7.143
PH2-5-3	AEE 1500 grit	2	1.529	73.58	49	0.171	7.143
PH2-5 Average			**1.531**	**73.70**	**49.0**	**0.171**	**7.143**
PH2-6-1	AEE 1500 grit	3	1.537	74.71	64	0.130	5.469
PH2-6-2	AEE 1500 grit	3	1.531	74.42	65	0.129	5.385
PH2-6-3	AEE 1500 grit	3	1.531	74.42	65	0.129	5.385
PH2-6 Average			**1.533**	**74.52**	**64.7**	**0.129**	**5.413**

a) Grenades contained 13 wt% B_4C, 25 wt% KCl, 1-3 wt% calcium stearate, and 59-61 wt% KNO_3 such that the total was 100 wt%. b) Density as a percentage of theoretical maximum.

APPENDIX

Table A3. Density, burning times, and burning rate data for dry compositions.

Grenade [a)]	B_4C Type	Calcium Stearate (wt%)	Pellet Density (g/cm^3)	Pellet %TMD [b)]	Burning Time (s)	Burning Rate (cm/s)	Burning Rate (g/s)
PH2-7-1	AEE 1200 grit	1	1.513	72.08	40	0.212	8.750
PH2-7-2	AEE 1200 grit	1	1.517	72.25	41	0.206	8.537
PH2-7-3	AEE 1200 grit	1	1.512	72.06	41	0.207	8.537
PH2-7 Average			**1.514**	**72.13**	**40.7**	**0.208**	**8.608**
PH2-8-1	AEE 1200 grit	2	1.522	73.27	60	0.141	5.833
PH2-8-2	AEE 1200 grit	2	1.515	72.92	60	0.141	5.833
PH2-8-3	AEE 1200 grit	2	1.523	73.31	59	0.143	5.932
PH2-8 Average			**1.520**	**73.16**	**59.7**	**0.141**	**5.866**
PH2-9-1	AEE 1200 grit	3	1.536	74.67	71	0.118	4.930
PH2-9-2	AEE 1200 grit	3	1.533	74.51	73	0.115	4.795
PH2-9-3	AEE 1200 grit	3	1.528	74.26	72	0.117	4.861
PH2-9 Average			**1.532**	**74.48**	**72.0**	**0.116**	**4.862**
PH2-10-1	AEE 800 grit	1	1.474	70.21	85	0.102	4.118
PH2-10-2	AEE 800 grit	1	1.471	70.06	85	0.103	4.118
PH2-10-3	AEE 800 grit	1	1.469	69.96	85	0.103	4.118
PH2-10 Average			**1.471**	**70.08**	**85.0**	**0.103**	**4.118**
PH2-11-1	AEE 800 grit	2	1.496	71.99	94	0.091	3.723
PH2-11-2	AEE 800 grit	2	1.485	71.46	93	0.093	3.763
PH2-11-3	AEE 800 grit	2	1.499	72.14	94	0.091	3.723
PH2-11 Average			**1.493**	**71.86**	**93.7**	**0.092**	**3.737**
PH2-12-1	AEE 800 grit	3	1.495	72.68	102	0.084	3.431
PH2-12-2	AEE 800 grit	3	1.507	73.26	102	0.083	3.431
PH2-12-3	AEE 800 grit	3	1.507	73.24	96	0.089	3.646
PH2-12 Average			**1.503**	**73.06**	**100.0**	**0.085**	**3.503**

a) Grenades contained 13 wt% B_4C, 25 wt% KCl, 1-3 wt% calcium stearate, and 59-61 wt% KNO_3 such that the total was 100 wt%. b) Density as a percentage of theoretical maximum.

APPENDIX

Table A4. Density, burning times, and burning rate data for compositions containing dust-reducing binders.

Grenade [a)]	Binder System	B_4C Type	Pellet Density (g/cm^3)	Pellet %TMD [b)]	Burning Time (s)	Burning Rate (cm/s)	Burning Rate (g/s)
PH3-1-1	polyacrylate elastomer	AEE 1500 grit	1.571	76.98	74	0.110	4.730
PH3-1-2	polyacrylate elastomer	AEE 1500 grit	1.581	77.44	73	0.111	4.795
PH3-1 Average			**1.576**	**77.21**	**73.5**	**0.111**	**4.762**
PH3-2-1	nitrocellulose (NC)	AEE 1500 grit	1.566	76.52	29	0.283	12.069
PH3-2-2	nitrocellulose (NC)	AEE 1500 grit	1.564	76.43	30	0.273	11.667
PH3-2 Average			**1.565**	**76.47**	**29.5**	**0.278**	**11.868**
PH3-3-1	polyvinyl alcohol (PVA)	AEE 1500 grit	1.450	70.83	41	0.216	8.537
PH3-3-2	polyvinyl alcohol (PVA)	AEE 1500 grit	1.447	70.69	41	0.216	8.537
PH3-3 Average			**1.449**	**70.76**	**41.0**	**0.216**	**8.537**
PH3-4-1	polyvinyl acetate (PVAc)	AEE 1500 grit	1.412	68.97	51	0.178	6.863
PH3-4-2	polyvinyl acetate (PVAc)	AEE 1500 grit	1.421	69.42	51	0.177	6.863
PH3-4 Average			**1.417**	**69.20**	**51.0**	**0.178**	**6.863**
PH3-5-1	epoxy	AEE 1500 grit	1.661	81.32	51	0.152	6.863
PH3-5-2	epoxy	AEE 1500 grit	1.659	81.24	51	0.152	6.863
PH3-5 Average			**1.660**	**81.28**	**51.0**	**0.152**	**6.863**

a) Grenades contained 13 wt% B_4C (AEE 1500 grit), 58 wt% KNO_3, 25 wt% KCl, 2 wt% calcium stearate, and 2 wt% binder solids.
b) Density as a percentage of theoretical maximum.

Notes for Tables A5b and A6b:

A simple average of T over the visible spectrum was used to calculate α_m and FM_m designated *380-780 nm*.

T at 555 nm was used to calculate α_m and FM_m designated *555 nm*.

T that was weighted to the photopic response of the human eye was used calculate α_m and FM_m designated *photopic*.

APPENDIX

Table A5a. Details and burning times for dry composition grenades used for smoke chamber testing.

Grenade Type [a)]	B_4C Type	Calcium Stearate (wt%)	Average Burning Time (s) [b)]
PH4-1E / PH2-1	Alfa Aesar	1	24.0
PH4-2E / PH2-5	AEE 1500 grit	2	49.0
PH4-3E / PH2-9	AEE 1200 grit	3	72.0

a) Grenades contained 13 wt% B_4C, 25 wt% KCl, 1-3 wt% calcium stearate, and 59-61 wt% KNO_3 such that the total was 100 wt%. b) From Tables A2 and A3.

Table A5b. Smoke chamber data for reference/control grenades and experimental grenades containing dry compositions.

Grenade [a)]	T (°C)	RH (%) [b)]	*Y*	α_m (m^2/g) 380-780 nm	α_m (m^2/g) 555 nm	α_m (m^2/g) photopic	FM_m (m^2/g) 380-780 nm	FM_m (m^2/g) 555 nm	FM_m (m^2/g) photopic
AN-M8 HC [c)]	25.0	32	1.26	2.42	2.36	2.36	3.04	2.97	2.97
M83 TA [c)]	21.7	61	0.30	4.74	4.85	4.80	1.42	1.46	1.44
PH4-1E-1	23.7	38	0.793	3.25	3.41	3.38	2.57	2.71	2.68
PH4-1E-2	23.1	45	0.829	3.44	3.64	3.61	2.85	3.02	2.99
PH4-1E-3	23.1	45	0.824	3.35	3.54	3.50	2.76	2.91	2.89
PH4-1E Average	**23.3**	**42.7**	**0.815**	**3.35**	**3.53**	**3.50**	**2.73**	**2.88**	**2.85**
PH4-2E-1	23.9	38	0.767	3.30	3.49	3.46	2.53	2.68	2.65
PH4-2E-2	23.9	38	0.749	3.23	3.42	3.38	2.42	2.56	2.53
PH4-2E-3	23.9	38	0.751	3.23	3.45	3.41	2.43	2.59	2.56
PH4-2E Average	**23.9**	**38.0**	**0.756**	**3.25**	**3.45**	**3.42**	**2.46**	**2.61**	**2.58**
PH4-3E-1	24.1	41	0.627	3.36	3.55	3.51	2.11	2.22	2.20
PH4-3E-2	23.5	48	0.649	3.37	3.57	3.53	2.19	2.31	2.29
PH4-3E-3	23.9	41	0.654	3.43	3.63	3.60	2.24	2.38	2.35
PH4-3E Average	**23.8**	**43.3**	**0.643**	**3.39**	**3.58**	**3.55**	**2.18**	**2.30**	**2.28**

a) See Table A5a for experimental grenade descriptions and burning times. b) Relative humidity. c) Manufactured at Pine Bluff Arsenal.

APPENDIX

Table A6a. Grenades containing compositions with dust-reducing binders.

Grenade Type [a)]	Binder System	Solvent	Average Burning Time (s) [b)]
PH3-1	polyacrylate elastomer	acetone	73.5
PH3-2	nitrocellulose (NC)	acetone	29.5
PH3-3	polyvinyl alcohol (PVA)	water [c)]	41.0
PH3-4	polyvinyl acetate (PVAc)	water [d)]	51.0
PH3-5	epoxy	none	51.0

a) Grenades contained 13 wt% B_4C (AEE 1500 grit), 58 wt% KNO_3, 25 wt% KCl, 2 wt% calcium stearate, and 2 wt% binder solids. b) From Table A4. c) 9 wt% solution. d) 34.5 wt% emulsion.

Table A6b. Smoke chamber data for compositions with dust-reducing binders.

Grenade [a)]	T (°C)	RH (%) [b)]	*Y*	α_m (m^2/g) 380-780 nm	α_m (m^2/g) 555 nm	α_m (m^2/g) photopic	FM_m (m^2/g) 380-780 nm	FM_m (m^2/g) 555 nm	FM_m (m^2/g) photopic
PH3-1-3	23.1	36	0.512	3.51	3.74	3.70	1.80	1.92	1.89
PH3-1-4	23.9	41	0.554	3.78	4.10	4.05	2.09	2.27	2.24
PH3-1 Average	**23.5**	**38.5**	**0.533**	**3.65**	**3.92**	**3.88**	**1.95**	**2.10**	**2.07**
PH3-2-3	23.9	41	0.749	3.41	3.61	3.57	2.56	2.71	2.68
PH3-2-4	23.1	36	0.730	3.34	3.55	3.51	2.44	2.59	2.56
PH3-2 Average	**23.5**	**38.5**	**0.740**	**3.38**	**3.58**	**3.54**	**2.50**	**2.65**	**2.62**
PH3-3-3	22.9	39	0.621	3.34	3.55	3.51	2.07	2.20	2.18
PH3-3-4	22.9	39	0.635	3.44	3.67	3.63	2.19	2.33	2.30
PH3-3 Average	**22.9**	**39.0**	**0.628**	**3.39**	**3.61**	**3.57**	**2.13**	**2.27**	**2.24**
PH3-4-3	22.4	35	0.746	3.37	3.60	3.56	2.51	2.69	2.66
PH3-4-4	22.9	39	0.761	3.28	3.47	3.44	2.50	2.64	2.62
PH3-4 Average	**22.7**	**37.0**	**0.754**	**3.33**	**3.54**	**3.50**	**2.51**	**2.67**	**2.64**
PH3-5-3	22.4	35	0.704	3.40	3.64	3.59	2.39	2.56	2.53
PH3-5-4	22.4	35	0.668	3.32	3.55	3.51	2.22	2.50	2.35
PH3-5 Average	**22.4**	**35.0**	**0.686**	**3.36**	**3.60**	**3.55**	**2.31**	**2.53**	**2.44**

a) See Table A6a for grenade descriptions and burning times. b) Relative humidity.