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Effect of Adding 5-Aminotetrazole to a Modified U.S. Army Terephthalic Acid White Smoke Composition

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Abstract: Military visible obscuration compositions (obscurants, smokes) play an important role on today's battlefield. For many years, the known toxicity or ageing problems of established formulations were commonly accepted since there was a lack of alternatives. Since the U.S. Army stopped producing the AN-M8 hexachloroethane (HC) smoke grenade, the M83 terephthalic acid (TA) smoke grenade has been used in its place. This cool-burning, less toxic, but also low efficiency white smoke formulation cannot compete with HC-based formulations in terms of obscuration performance. In this context, we have explored the use of 5-aminotetrazole (5-AT) as an additive and fuel in the known TA system. Remarkably, it has been found that sugar is not necessarily required in the formulations, which has implications for the future improvement of sublimation-condensation smoke compositions, including coloured smoke compositions. In small-scale tests, it was found that replacing sucrose with 5-AT in the formulations resulted in significantly improved smoke persistence.

1 Introduction

Military smoke or obscurant formulations are used on the battlefield for signaling, marking targets and screening troop movements [1]. The earliest reported application in Europe dates from 1701, but the development of modern smoke technology was launched later, with the introduction of the Berger mixture during WWI [2]. The American (type C) HC (hexachloroethane) smoke (as used in the AN-M8 smoke grenade), traces its origins to the Berger mixture, and was used by the U.S. Army until it was largely replaced by terephthalic acid-based (TA) compositions in the 1990s and 2000s. Combustion of formulations containing hexachloroethane, zinc oxide and aluminum produce volatilized metal chlorides which undergo further reactions with moisture from the atmosphere to give the desired aerosol [3]. In addition to the desired hygroscopic combustion products, in reality the smoke emitted by HC compositions contained as much as 10% of highly toxic chlorinated compounds such as CCl_4, C_2Cl_4, C_6Cl_6 and polychlorinated dibenzodioxins [4]. Since hexachloroethane is itself toxic, and several injuries and deaths were correlated to HC smoke exposure, there was a need for less toxic alternatives [5]. The requirements for potential new compositions are not only limited to performance issues, they also include toxicity issues, ageing, sensitivities and burning properties [1, 6]. It is obvious that such an ideal composition is not yet available and that smoke compositions are generally characterized by a safety/performance trade-off.

Compositions based on for example white and red phosphorus, rely on atmospheric burning to generate phosphorus pentoxide, which is further hydrolyzed to give the aerosol cloud [7]. Such formulations have been used since WWI and WWII respectively and are superior to any other smoke material in terms of yield factor (Y) [7a]. Y is the quotient of the total amount of aerosol produced and the pyrotechnical payload. Yield may be expressed as a ratio or as a percentage (wt.%), although the term "yield factor" almost always refers to a ratio. It is therefore important to distinguish between hygroscopic and non-hygroscopic aerosols. Lane *et al.* and Sordoni *et al.* [8] reported the influence of various relative humidities (RH) on the performance of red phosphorus and HC containing formulations. Y increased from 3.73 (20% RH) to 5.77 (80% RH) for red phosphorus and from 1.25 (20% RH) to 2.77 (80% RH) for HC compositions [8]. All experimental measurements should therefore be accompanied by RH values, as even minor hygroscopic combustion products could influence the observed obscuring properties.

Whereas white phosphorus is toxic and incendiary, most compositions containing red phosphorus have serious ageing and sensitivity issues [1, 9]. Red phosphorus suffers from hydrolytic degradation, which leads to the formation of highly toxic and flammable phosphine gas, as well as phosphoric acid [10]. This problem has been known for decades and drives the search for alternatives. In 2016 Shaw *et al.* [11] predicted boron phosphide, BP, to be a suitable candidate after theoretically studying a system based on BP/KNO_3. BP is resistant to hydrolysis, which might solve the degradation problems correlated with red phosphorus containing formulations [11]. However, the compound BP is not yet commercially available and this currently hinders further experimental investigations [12]. In a recent publication by Koch *et al.* [9], phosphorus(V) nitride, P_3N_5, was suggested as a replacement candidate for red phosphorus. P_3N_5 is stable towards moisture and is reportedly safe to handle in combination with a range of oxidants, including nitrates, chlorates and perchlorates. Koch and coworkers did not detect any phosphine release from the compositions, while at the same time demonstrating smoke performance competitive with red phosphorus-based compositions [9a]. Unfortunately, the alpha form of P_3N_5 (crystalline density = 2.77 $g \cdot cm^{-3}$, phosphorus density = 1.58 $g \cdot cm^{-3}$), which is the phase stable at atmospheric pressure, has a low phosphorus density compared to white phosphorus (1.82 $g \cdot cm^{-3}$), red phosphorus (2.0-2.4 $g \cdot cm^{-3}$), and BP (crystalline density = 2.97 $g \cdot cm^{-3}$, phosphorus density = 2.20 $g \cdot cm^{-3}$) [9a, 12, 13].

Earlier in 2013, new boron carbide (B_4C) smoke formulations were reported by Shaw and coworkers [14]. These formulations used B_4C/KNO_3 as a pyrotechnic fuel/oxidizer pair, KCl as a diluent, and calcium stearate as a burning rate modifier. In field and smoke chamber tests, these prototype smoke grenades outperformed the U.S. Army M83 TA grenade by a wide margin. The best prototypes were functionally equivalent to nearly two M83 TA smoke grenades and have been considered as possible replacement candidates [1]. However, as with HC smoke grenades, the B_4C-based compositions burn at a high temperature, so unintended incendiary effects would not be mitigated.

The original TA white smoke composition consists of potassium chlorate(V), sucrose, terephthalic acid, magnesium carbonate, poly(vinyl alcohol) and stearic acid [15]. Since it was developed in the 1990s, it has replaced the HC composition within the U.S. Army white smoke grenade due to the toxicity concerns mentioned previously [16]. The consequences for soldiers were dramatic, as the effective carry on weight increased. To obtain an obscuring cloud similar to one AN-M8 HC grenade, a soldier nowadays has to use three M83 TA grenades instead [1]. However, a major benefit of the TA system is the low burning temperature, which makes it less likely to be incendiary. In general, the TA system is very similar to coloured smoke formulations, *e.g.* the yellow smoke system published by Moretti *et al.* in 2014 [17]. The organic dye is vaporized through a sublimation/recondensation mechanism. In 2008, Chen *et al.* [18] described the urgent need to replace sulfur as the main fuel in the M18 red and violet coloured smoke grenades. The resulting SO_2 produced upon combustion is toxic and highly irritating to inhale, and is therefore undesirable. Sugar was considered as a less toxic alternative, which resulted in a complete reformulation of the previously mentioned formulations. However, there may be possible replacements for sugar that could improve smoke dispersal, efficiency, and persistence. In our previous work, we reported on the application of 5-aminotetrazole (5-AT) as an additive and additional gas generator in green and blue coloured smoke formulations [19]. Taking this as a starting point, we have developed completely sugar-free white smoke formulations based on TA.

To tackle the above mentioned problems with TA smoke, the authors studied the effect of adding 5-AT to a baseline TA formulation as a gas generator, with the intention of increasing the relatively low aerosolization and dispersal efficiency. Several working formulations were developed with varying burning times. Two formulations using 5-AT *instead* of sucrose were developed and compared to each other. This paper describes the results of the optical measurements performed using a convenient small-scale smoke chamber.

2 Experimental Section

2.1 Materials

Potassium chlorate(V) (≥99%), sucrose (≥99%), sodium bicarbonate, poly(vinyl alcohol) hydrolyzed (99+%), terephthalic acid (98%) and magnesium carbonate hydroxide pentahydrate (BioXtra) were purchased from Sigma-Aldrich. 5-AT (98%) was purchased from abcr chemicals. Stearic acid was purchased from Grüssing GmbH. Sodium carbonate was purchased from Brenntag GmbH. For initial testing, small mixtures (2 g) were carefully mixed manually for 5 min in a mortar by combining the dry compounds. If these tests were successful, larger mixtures (40 g) were then prepared by combining the dry components in a cylindrical rubber barrel and rolling for 120 min. The rotatory rock tumbler (model 67631) was built by "Chicago Electric Power Tools" and operated with steel balls. To remove any clumps, the compositions were passed through a 800 μm screen. 2 g of this thus prepared composition was pressed into a cylindrical steel compartment (diameter 2.0 cm), with the aid of a tooling die and a hydraulic press. Unless stated otherwise a consolidation dead load of 2000 kg was applied for 3 s. For each composition, four pellets were tested and the results were averaged. An electrical resistance wire ("Kanthal A1" (FexCrAl), 0.6 mm diameter, 5.25 $Ohm \cdot m^{-1}$) was used to ignite the pellets.

2.2 Optical measurements

Transmittance data were recorded in a smoke chamber fully described in a previous investigation on coloured smoke formulations [19]. The starting time ($t = 0$ s) for recording the transmittance values at 555 nm over a period of time was determined by the time needed to fully equilibrate the smoke. A fully equilibrated smoke cloud was indicated by a constant transmittance value. If the transmittance value remained constant for a period of 5 s, data recording was started. In our experiments, we experienced a total time period of 13-18 s to be suitable for equilibration. At this point the cloud was evenly dispersed within the smoke chamber. As the compositions are intended for visual obscuration, we chose the peak photopic response of the human eye at 555 nm for recording all of the transmittance values. The recorded spectra were normalized with a recorded spectrum of the empty chamber before each measurement.

2.3 Thermal and energetic properties

The impact and friction sensitivities were determined using a BAM drophammer and a BAM friction tester. The sensitivities of the compositions are indicated according to the UN Recommendations on the Transport of Dangerous Goods (+): impact: insensitive >40 J, less sensitive >35 J, sensitive >4 J, very sensitive <4 J; friction: insensitive >360 N, less sensitive = 360 N, sensitive 360>N>80 N, very sensitive <80 N, extremely sensitive <10 N. Thermal stability measurements: the onset temperatures were measured with a OZM Research DTA 552-Ex Differential Thermal Analyzer at a heating rate of 5 °C/min.

3 Results and Discussion

The baseline TA white smoke composition in Table 1 was the starting point for our studies [15]. TA (terephthalic acid) was applied as the white pigment. The molecular structure, especially the electron-withdrawing carboxy groups, makes it highly deactivated and therefore more resistant to oxidation. By contrast, dyes containing for example azo- or amino-groups are more likely to be oxidized to the azoxy or N-oxide species, respectively [20]. Based on this formulation, we examined varying coolants, including magnesium carbonate hydroxide pentahydrate (MCHP), sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3), to give formulations **A**, **B** and **C** respectively (Table 1). Unfortunately all three formulations burned with an open flame after ignition and no further white smoke production was observed. This behaviour indicated that excessively high temperatures were produced and might be explained by the difference in configuration compared to a full scale smoke grenade. The thermal environment within a conductive steel grenade canister is quite different to a bare pellet. Another reason might be the chemicals themselves. Fish and Chen [21] reported a study performed on six samples of magnesium carbonate received from different suppliers. One of the samples was identified as magnesite, while the other five were identified as hydromagnesite. Within those five similar samples, three were morphologically different. Fish and Chen proposed that these differences can affect pyrotechnic performance. For these reasons, in the work presented here, we were only able to compare the performance of the developed formulations with each other.

Table 1. Baseline TA formulation with varying coolants[a]

	$KClO_3$ [wt.%]	Sucrose [wt.%]	TA [wt.%]	$MgCO_3$ [wt.%]	MCHP [wt.%]	$NaHCO_3$ [wt.%]	Na_2CO_3 [wt.%]	Stearic acid [wt.%]
base-line mix	23	14	57	3	-	-	-	3
A	23	14	57	-	3	-	-	3
B	23	14	57	-	-	3	-	3
C	23	14	57	-	-	-	3	3

[a] In these formulations, 1 wt.% PVA was added in excess to all formulations, making the total to 101 wt.%.

All four reference formulations (Table 1) only differ in the coolant applied. $KClO_3$/sucrose is the oxidizer/fuel pair and generates the necessary heat to vaporize the TA. The coolant is applied to keep the burning temperature in the desired range and prevents thermal degradation of TA. Stearic acid is used as a processing aid, burning rate modifier and dry binder. PVA serves as a binder that can optionally be used to granulate the compositions if it is applied as a concentrated aqueous solution. However, in these studies, all the components were prepared and mixed in a dry state.

Table 2. Developed TA formulations containing 5-AT[a]

	$KClO_3$ [wt.%]	Sucrose [wt.%]	TA [wt.%]	MCHP [wt.%]	$NaHCO_3$ [wt.%]	Stearic acid [wt.%]	5-AT [wt.%]
1	22.8	13.8	41.6	3.0	-	3.0	14.8
2	22.8	4.9	56.4	3.0	-	3.0	8.9
3	22.8	-	56.4	-	3.0	3.0	13.8
4	22.1	-	51.9	-	5.8	2.9	16.3

[a] In these formulations, 1 wt.% PVA was added in excess to all formulations, making the total to 100 wt.%.

5-AT was applied as an additional fuel and gas generator with the intention of improving smoke dispersion and efficiency. This strategy was successfully applied in previous work dealing with coloured smoke formulations [19]. Both the mentioned coloured smoke formulations and the TA smoke composition rely on the same sublimation/recondensation mechanism. Formulations **1-4** used 5-AT in different amounts, in the range of 9-16 wt.% (Table 2). Additionally formulations **3** and **4** contained 5-AT as the main fuel, in place of sucrose. Two different coolants, MCHP and $NaHCO_3$, were applied.

For smoke devices with similar burning times, differences in the visual obscuration performance depend on the properties and the amount of smoke (aerosol) produced [1]. White pigments with high refractive indices would provide the best obscuring properties, however it is very difficult to effectively disperse TiO_2, for example, to achieve a long-duration aerosol cloud [22].

Table 3. Energetic properties of the developed TA smoke compositions

	FS [N]	IS [J]	ESD [J]	T_{onset} [°C]
A	360	40	1.5	178
B	360	35	1.0	174
C	360	35	0.9	175
1	360	35	1.0	164
2	360	40	1.0	158
3	360	35	1.0	172
4	360	40	0.9	175

Legend: FS = friction sensitivity, IS = impact sensitivity, ESD = electrostatic discharge sensitivity, T_{onset} = thermal decomposition given as the onset point.

All of the tested formulations were insensitive towards friction and only slightly sensitive towards impact (Table 3). Regarding the ESD sensitivity, all formulations were in the range of 0.9-1.5 J, with formulation **C** having 0.9 J. The onset temperature of all of the formulations was in the range of 158-178 °C (see supporting information for DTA evaluation of the formulations, as well as single components). The observed burning times of formulations **1-4** were in the range of 26-33 s (Table 4). With the exception of formulation **2** (33 s), all of the other formulations had similar burning times.

Table 4. Visual obscuration data for 2 g pellets

	BT [s][a]	Average transmittance (555 nm) over time[b]	SD (555 nm)[c]	RH [%][d]
1	28	0.585	0.026	26.6
2	33	0.531	0.041	25.0
3	28	0.216	0.023	23.1
4	26	0.228	0.011	23.0

[a] burning time; [b] average of collected transmittance values at 555 nm over time for all pellets; [c] standard deviation; [d] relative humidity.

For the reasons described earlier, it was only possible to compare the formulations with each other and not to the intended reference formulations.

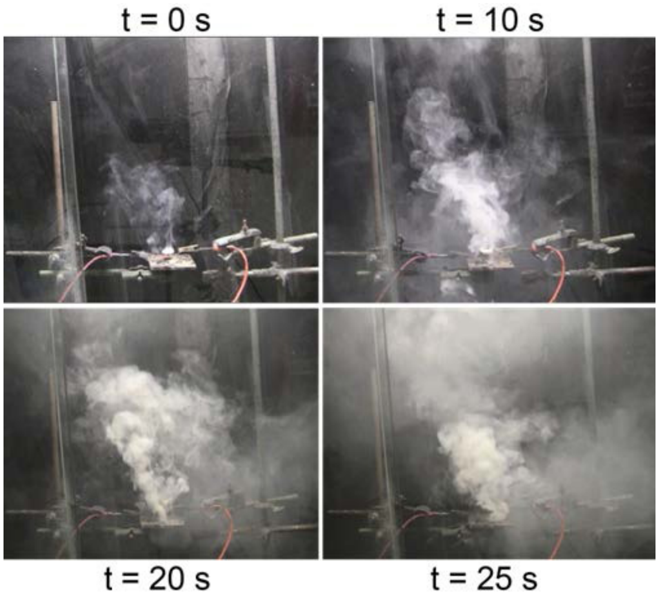

Figure 1. Burning of a 2 g pellet of formulation **4**

In formulations **1** and **2**, both 5-AT and sucrose were applied as fuels, with **1** having the higher 5-AT content but less TA. Alternatively, 5-AT was applied as the main fuel in place of sucrose in formulations **3** and **4**. These formulations differ in the 5-AT/coolant/TA content ratio, but showed nearly the same burning time.

The transmittance (555 nm) over time of formulations **1** and **2** changed dramatically (Figure 2). We observed a steady increase of transmittance from 18% to 87% (**1**) and 23% to 75% (**2**) over 6 min of measurement. By contrast, the transmittance over time for formulations **3** and **4** remained quite constant (15-23% and 19-25%, respectively). In general, the average transmittance over time of **3** and **4** was the lowest observed in all of our tests (Table 4).

These results have important implications regarding the effective dispersal and persistence of pyrotechnically generated smoke. Surprisingly, relatively minor changes to the compositions can markedly influence the measured opacity of the resulting smoke clouds over time. This is despite the fact that the initial equilibrated transmittance values are quite similar in several cases. Steadily increasing transmittance values indicate sedimentation of smoke particles. This may be due to larger particles having been formed initially, or to agglomeration of the particles over time. Notably, the compositions containing 5-AT as the main fuel, and no sucrose, displayed the lowest transmittance values over time, and remained stable over the entire measurement period. This suggests that certain formulations containing 5-AT are able to produce a thick, yet well-dispersed aerosol that is quite persistent and resistant to sedimentation.

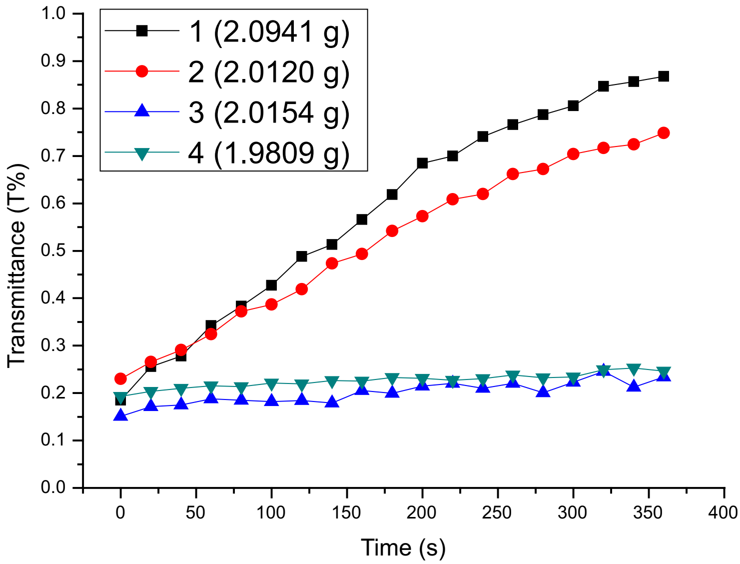

Figure 2. Transmittance (555 nm) over time for a representative pellet of each composition

Interestingly, measurements of the yield factor (Y) indicate that formulations **3** and **4** do not produce a larger amount of aerosol (see additional aerosol quantification in the supporting information section). This implies that the improved performance, in this case, is the result of other aerosol properties, the investigation of which is beyond the scope of this particular report. It is also apparent that the performance of the compositions is not directly related to, or controlled by, the TA content (as a comparison of formulations **2** and **4** demonstrates). However, it is clear that sucrose is not required in the compositions and 5-AT can be used instead, in similar amounts. Finally, the behaviour of formulations **3** and **4** suggests that in future work, 5-AT should be investigated as the main fuel in a variety of sublimation/condensation-type smoke systems.

4 Conclusions

The development of four new white smoke formulations based on TA was reported. All formulations were characterized by means of IS/FS/ESD/T_{onset} as well as their obscuration properties (transmittance). The low sensitivity towards physical stimuli is a promising fact for safe handling and manufacturing. In two out of the four formulations, a fuel mixture of 5-AT and sucrose was applied. Applying 5-AT as the main fuel resulted in the two best performing formulations, **3** and **4**, in terms of transmittance values and this provides a reason to explore 5-AT as the main fuel in other smoke formulations. Furthermore the behaviour of these two formulations suggests that a higher amount of 5-AT can compensate for a reduced amount of TA, resulting in the same transmittance values. Firm answers regarding the performance in actual devices can only be obtained once the compositions are tested on a larger scale in representative configurations. This includes a comparison to the M83 TA white smoke grenade in a full-scale test. In future work, the characterization of the aerosols produced by selected compositions, as well as determination of the aerosol particle size distribution should be performed. A scanning mobility particle size spectrometer (SMPS) may be appropriate for these investigations.

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