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Combining Higher Efficiency with Lower Costs: an Alternative Hexamine-Based White Smoke Signal

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Abstract: The effect of applying hexamine as main fuel in terephthalic acid-based white smoke formulations is discussed. For this reason, a simple four ingredients mixture only consisting of terephthalic acid, hexamine, potassium chlorate and a magnesium carbonate derivative was introduced. We started from a minimum amount of dye and constantly increased the dye percentage in 5.0 wt-% steps to investigate the influence on emerging smoke properties. This procedure ensures that the amount of dye present in the aerosol can be optimized to obtain the most persistent, thick white smoke cloud. Previous research on white smokes in our group indicated an overall higher smoke performance in terms of efficiency and advanced persistence by using 5-amino-1*H*-tetrazole as main fuel instead of sugar. From a costs point of view, hexamine would be favored, since it offers a low-cost alternative to 5-amino-1*H*-tetrazole.

Keywords: Pyrotechnic · Smoke · Obscurants · Hexamine

1 Introduction

Smoke-generating pyrotechnics are commonly applied in the military sector. In this context, white smoke is used predominantly as obscurants for self-protection, while colored smoke is applied for both ground and ground-to-air signaling as well as marking [1,2]. Rarely, smoke signals find application in the civil sector as daylight firework, however, such events become more popular nowadays [3]. Today, the main consumer of white smoke still remains the military [4]. Historically, the AN-M8 hexachloroethane (HC) smoke grenade was used due to its high efficiency. In this case, the underlying smoke-generating mechanism is very different to colored smoke formulations: a typical HC mixture contains aluminum, zinc oxide and HC. During the combustion reaction, highly hygroscopic zinc(II) chloride is formed rapidly absorbing moisture from the air to generate a dense white smoke cloud [1,5–7]. As a result, smoke yields above 100% can be reached under optimal conditions mainly depending on the humidity. However, Shinn indicated this kind of smoke as the worst for health and environment [8]. During the combustion, highly toxic polychlorinated organic compounds can arise, which are believed to be carcinogenic [5,9]. Therefore, due to toxicity issues the HC-based obscurants are no longer produced [7]. Up to now, the AN-M83 smoke grenade based on terephthalic acid (TA) served as an environmentally benign alternative. This mixture is very similar to the colored ones and follows the same sublimation-recondensation mechanism. However, the TA-based smoke cannot compete with the historically used HC grenade in terms of thickness, smoke volume or optical properties making further research mandatory [1,5,7].

In general, these kind of smoke signals can be referred to as cool-burning pyrotechnics reaching only temperatures in the range of the sublimation point of the applied dyes [1,5]. In contrast to this, HC-based smoke mixtures decompose at very high temperatures up to over 800 °C under luminous flame presence [10]. A cool-burning smoke mixture has the ability to gradually and slowly rise from the ground serving an effective screening and obscuration tool for military use [1,5]. If the resulting combustion temperature is in the optimal range, the dye is sublimate, leaves the compartment and recondensate in the surroundings. Additionally, the resulting dye particles are dispersed through the gaseous products of the proceeding redox reaction, creating a large dense smoke cloud [1,5,11,12]. The specific characterization of white and colored smoke signals include the color impression, quality and thickness of the emerging smoke cloud, the duration of smoke generation and the time it takes for the aerosol to sedimentate [5,13]. The produced aerosol not only consists of dye, but also other solid combustion products can arise [14]. The performance and in particular the yield of hygroscopic smoke mixtures is strongly dependent on the relative humidity, since at a higher humidity higher yields can be reached [14]. There-

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/prep.201800245 fore, it is mandatory to determine all smoke properties at the same ambient conditions to ensure reproducibility, however, minor changes in the humidity may have an influence on the results [14,15]. Further, the most important characteristic for white smoke is the optical performance with respect to their application as obscurant [10,16,17]. The mass-based figure of merit FM_m is a promising value in this context to compare the efficiency of various obscurants to each other [14,18].

Recent research on white smokes in our group has found that sugar can be fully exchanged by 5-amino-1*H*-tetrazole (5-AT) in the acquainted TA system resulting in an overall improvement of smoke quality and persistence [16]. Since 5-AT is a comparatively expansive substance, the effect of the much cheaper hexamine was investigated. Sabatini *et al.* stated earlier, that either 5-AT or hexamine could be used to deoxidize the combustion flame in chlorine-free red-burning flares and therefore, is usually applied as main fuel in pyrotechnic formulations [19–23]. The focus lies on novel smoke systems reducing the environmental impact, minimization of production time, production steps and most importantly multi-color signals. In addition, the efficiency of novel pyrotechnic compositions should at least be the same as or higher compared to the old formulations [7,24]. There are several promising approaches in the experimental stage in the literature: Shaw *et al.* discussed the use of boron carbide as pyrotechnic fuel in combination with potassium nitrate as a possible alternative to HC-based smoke [23]. In a further theoretical study, they compared the thermodynamics of this B_4C/KNO_3 composition with a boron phosphide (BP/KNO_3) system [25]. In this case, BP is expected to function as *in situ* phosphorus source, since the commonly applied red phosphorus suffers from the formation of toxic phosphine gas and phosphoric acid during combustion [25,26]. Another theoretical and experimental study is given by Koch *et al.* describing white smoke formulations based on phosphorus(V) nitride with various nitrate, chlorate and perchlorate oxidizers, which also surpass the FM_m of red phosphorus [27].

The effect of hexamine as main fuel on the resulting smoke properties was investigated using a modified US Army white smoke signal. Therefore, TA served as white smoke dye [1,7]. Beneficially, TA is an important ingredient for the plastics industry and is available in high purity at a moderate price [28]. The oxidizer of choice was potassium chlorate, which seems to be the only oxidizing substance to be used in low temperature sublimation smoke due to its exothermic decomposition and relatively low melting point [1,5]. In combination with organic fuels, it generates the ideal temperature range to sublime the dye rather than combust it [29]. Hexamine was applied as the only fuel. The last component of the newly developed smoke mixtures was magnesium carbonate pentahydrate hydroxide (MCPH) as a smooth coolant [30].

2 Experimental Section

Chemicals. 5-Amino-1*H*-tetrazole (98%) was purchased from abcr Chemicals. Hexamethylentetramine (99%) was purchased from Acros Organics. Terephthalic acid (98%), sucrose (99%), sodium bicarbonate (99%) and magnesium carbonate pentahydrate hydroxide (BioXtra) were purchased from Sigma-Aldrich. Potassium chlorate (99%) and stearic acid (95%) were purchased from Grüssing GmbH.

Sample Preparation. All pyrotechnic samples were prepared in 2.0 g scale using the same procedure in order to ensure the reproducibility. Therefore, the different ingredients were weighed into a sample glass according to their respective weight percentages in the formulations. After a rough initial mixing, each sample was transferred into a porcelain mortar and carefully ground to a homogeneous powder. The so-prepared compositions were pressed into a cylindrical shape with the aid of a tooling die using a hydraulic press with a dead load of 3.0 t for approximately 3.0 s. All samples were burned within a smoke chamber (0.6 m × 0.6 m × 1.8 m). Each pellet was ignited using a resistance heating Kanthal® A1 wire (FeCrAl, 0.8 mm diameter, 2.9 $\Omega\,m^{-1}$) [14,16].

Determination of Smoke Properties. The experimental setups for optical measurements, collecting the aerosol as well as the determination of burn rate and burn time were described previously (see ESI) [14,16]. The transmittance mainly characterizes the ability of a smoke composition for visual obscuration, for this reason the peak photopic response of the human eye at 555 nm was chosen as fixed wavelengths for the evaluation of transmittance values.

Sensitivity Data. 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 $360\ N > \times > 80$ N, very sensitive <80 N, extreme sensitive <10 N. Electrostatic discharge was measured with an OZM small-scale electrostatic spark X SPARK 10. ESD: sensitive <0.1 J, insensitive >0.1 J. The thermal stability was carried out using an OZM Research DTA 552-Ex Differential Thermal Analyser with a heating rate of $5\,^{\circ}C\,min^{-1}$ [1].

3 Results and Discussion

The white-smoking compositions consisted of only four ingredients: 30% TA and the remaining 70% of various ratios of potassium chlorate, hexamine and MCPH. In detail, this testing protocol was outlined by Domanico [28]. The different ratios of the underlying fuel mixtures are illustrated in Figure 1. Starting from the eight preliminary formulations **W1** to **W8**, only **W3**, **W4** and **W6** resulted in a thick, white smoke cloud. Surprisingly, only 30% TA within the mixture

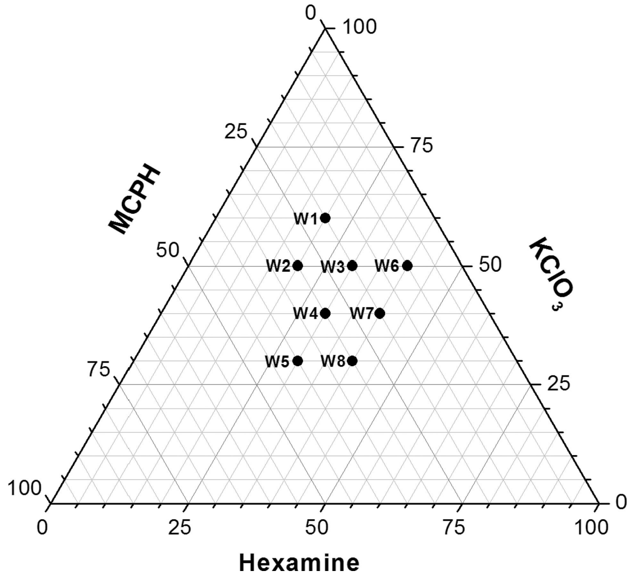

Figure 1. Triangle diagram of the underlying fuel mixtures of the smoke formulations **W1** to **W8**. See ESI for an exact listing of weight percentages. An explanation of triangle diagrams is given by Kosanke in [31].

was sufficient for a dense smoke generation [6,8–9]. However, **W3** and **W4** formed sparkles during the whole burn. The slightly higher percentage of hexamine in **W6** weakens this observation due to its deoxidizing effect on the combustion flame [19]. It seems to be advantageous to use lower contents of MCPH in order to ensure higher burning temperatures, since the sublimation point of TA is 402 °C [32]. For this reason, it is expected that the underlying pyrotechnical system in **W6** (40% hexamine, 50% KClO$_3$, 10% MCPH) provided enough energy for sublimation, but on the same time avoiding the formation of sparkles.

In analogy to the literature and – if applicable – to further optimize the smoke yield, the amount of TA was gradually increased from 30% to 60% in 5% steps. The other components were each uniformly reduced, since the composition in **W6** was the basis for the formulations **W9–W14** (Table 1).

The best visual performance in terms of smoke thickness and burning behavior was observed in **W11** (45% TA) and **W13** (55% TA). It is noticeable, that an even higher amount of TA (60%) in **W14** suffered from low smoke generation. Because of the relatively low content of other ingredients within this mixture, there are only few components left, which could promote the underlying redox reaction.

Table 1. Formulations **W9** to **W14** based on **W6** with increased TA contents.

Formulation	TA [wt-%]	Hexamine [wt-%]	KClO$_3$ [wt-%]	MCPH [wt-%]
W9	35.0	26.0	32.5	6.5
W10	40.0	24.0	30.0	6.0
W11	45.0	22.0	27.5	5.5
W12	50.0	20.0	25.0	5.0
W13	55.0	18.0	22.5	4.5
W14	60.0	16.0	20.0	4.0

For a more detailed characterization of smoke performance according to burning behavior, optical properties and yield, formulations **W6**, **W11** and **W13** were compared to literature-known references based on [16] (Table 2). The compositions of these white-smoking reference formulations are shown in the supporting information. In detail, **Ref-W1** applied a mixture of sucrose and 5-AT as fuel combination, while **Ref-W2** only contained 5-AT as main fuel. Thus, these formulations are suitable to investigate the effect of different fuels on the obscuration properties of white smokes. Moreover, both formulations contained stearic acid, which is commonly used as minor fuel and temperature regulator in pyrotechnics [33]. Another difference was the coolant. While **Ref-W1** also contained MCPH, the much stronger sodium bicarbonate was applied in **Ref-W2** [30].

Table 2. Burn time (BT), burn rate (BR) and yield factor *Y* of formulations **W6**, **W11**, **W13** and the references **Ref-W1** and **Ref-W2**.

Formulation	BT[a] [s]	BR[b] [g s^{-1}]	Y[c] [%]	RH[d] [%]
W6	19	0.35	32	31
W11	38	0.26	35	31
W13	40	0.20	28	30
Ref-W1	28	–	27	66
Ref-W2	28	–	24	61

[a] Burn time (2.0 g scale). [b] Burn rate (10.0 g scale). [c] Yield factor. [d] Relative humidity.

W6 has the highest burn rate of 0.35 g s^{-1}, followed by **W11** (0.26 g s^{-1}) and **W13** with 0.20 g s^{-1}. These values were also confirmed by the observed burn time: **W6** burned down very fast in 19 s, while **W11** and **W13** achieved almost similar time periods (38–40 s). As a result, it is possible to modify the burn rate and burn time by varying the TA content, while observing almost constant yields. For the references, no burn rates were given in the literature, however, it can be assumed by the burn times of 28 s that it would be in between **W6** and **W11**.

Unfortunately, the yield of the references **Ref-W1** and **Ref-W2** were determined at a humidity of 61–66%, while the novel hexamine-based compositions were measured at 30–31%. It is noticeable, that the yield of hexamine-based mixtures is significantly higher in comparison to the references considering the difference in humidity. **W6** with only 30% TA content could provide a yield of 32%. As expected, the increased amount of TA (45%) in **W11** entailed an improvement of yield to 35%. Nevertheless, the observed yield of formulation **W13** was reduced again to 28%. The 5-AT-based reference **Ref-W2** led to a low yield of 24%, while a fuel mixture of sugar and 5-AT in **Ref-W1** resulted in 27%.

Moreover, the characterization of optical properties of **W6**, **W11**, **W13** as well as **Ref-W1** and **Ref-W2** are summarized in Table 3. For discussion, the measurement carried out over a time period of 6 min for the transmittance at 555 nm is illustrated in Figure 2. The transmittance over time of **Ref-W1** changed drastically from 18% to nearly 90% in just 6 min. This means, that the smoke screen does not last long. In contrast, **Ref-W2** remained almost constant in the range of 15–23% resulting in a well-dispersed, more persistent smoke cloud [16]. Comparing this to the hexamine-based formulations, a similar trend to **Ref-W2** was observed. At the beginning of each measurement (0 s), the transmittance is in the range of 4–8% for all three evaluated compositions. After 6 min of measurement, all three hexamine-based formulations were still in a range of 27–39%, however, the transmittance increased slightly faster compared to **Ref-W2**. Finally, the transmittance over the whole time period of measurement was averaged for further comparison resulting in the values depicted in Table 3. Over the whole 6 min, **W13** achieved the lowest averaged transmittance of 15%, while **W6** is slightly higher (25%) and **W11** was in between. The averaged transmittance of **Ref-W1** performed the worst with 59%, however, the 5-AT-based **Ref-W2** (22%) is in the same range as **W6**. As expected, the mass-based figure of merit FM_m of **Ref-W1** was even lower ($0.20\ \mathrm{m^2\,g^{-1}}$) according to its yield and transmittance observed. The other formulations were all in a similar range of $0.52–0.70\ \mathrm{m^2\,g^{-1}}$. **Ref-W2** has a FM_m of $0.58\ \mathrm{m^2\,g^{-1}}$ fitting in between **W6** ($0.52\ \mathrm{m^2\,g^{-1}}$) and **W11** ($0.66\ \mathrm{m^2\,g^{-1}}$), while **W13** achieved the highest value of $0.70\ \mathrm{m^2\,g^{-1}}$. In conclusion, **W11** and **W13** resulted in similar efficiency.

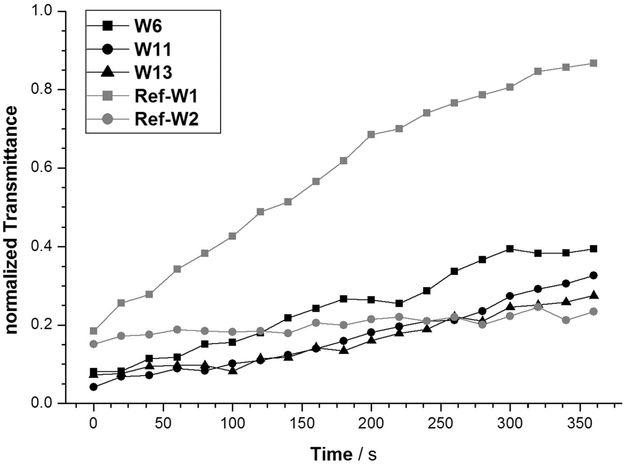

Figure 2. Normalized transmittance over time at 555 nm of formulations **W6**, **W11**, **W13** and the references **Ref-W1** and **Ref-W2** for a time period of 6 min. The spectrum was normalized to a reference spectrum.

Table 4. Sensitivity data of formulations **W6**, **W11**, **W13** and the references **Ref-W1** and **Ref-W2**.

Formulation	IS[a] [J]	FS[b] [N]	ESD[c] [J]	T_{dec}[d] [°C],
W6	7	360	0.5	203
W11	10	360	0.6	203
W13	20	360	1.0	204
Ref-W1	35	360	1.0	164
Ref-W2	35	360	1.0	172

[a] Impact sensitivity. [b] Friction sensitivity. [c] Electrostatic discharge sensitivity. [d] Decomposition temperature.

Table 3. Averaged transmittance over time *T* and mass-based composition figure of merit FM_m of **W6**, **W11**, **W13** and the references **Ref-W1** and **Ref-W2**.

Formulation	T[a] [%]	FM_m[b] [$\mathrm{m^2\,g^{-1}}$]	RH[c] [%]
W6	25	0.52	33
W11	17	0.66	34
W13	15	0.70	32
Ref-W1	59	0.20	27
Ref-W2	22	0.58	23

[a] Averaged normalized transmittance over a time period of 6 min at 555 nm. [b] Mass-based figure of merit. [c] Relative humidity.

Finally, an overview of the determined sensitivity data is given in Table 4. All tested white-colored smoke formulations were insensitive towards friction and electrostatic discharge. The reference mixtures were classified as less sensitive towards impact stimuli, while all hexamine-based compositions were moderate sensitive towards impact. The decomposition temperatures of hexamine-based smoke mixtures were in the range of 203–204 °C, while the decomposition temperatures of the references **Ref-W1** and **Ref-W2** were lower in the range of 164–172 °C. The slightly higher decomposition temperature of hexamine-based compositions could explain the higher yields observed, since more dye should be sublime. Although the mixtures should be handled with care and caution, since they are potentially sensitive energetic materials and can easily be ignited [34].

4 Conclusions

Hexamine was investigated as alternative main fuel for white smoke compositions. Therefore, simple four ingredients mixtures were prepared consisting of only potassium chlorate, hexamine, TA and MCPH. As a consequence, three different white-smoking formulations were evaluated according to their burning behavior, yield as well as optical and energetic properties. For comparison, literature-known white-colored compositions based on 5-AT and a fuel mixture (sucrose/5-AT) were considered.

As a result, the newly developed hexamine-based formulations achieved always higher yields than the 5-AT- and sugar-based references. An explanation could be the significant higher decomposition temperature in the range of 203–204 °C, since it promotes the sublimation of TA rather than combustion. Further, the effect of increasing the TA content within a consistent mixture was studied. A slightly increase led to higher yields; a modification of burn time and burn rate is possible (**W6** and **W11**). However, an even higher TA percentage within the mixture (**W13**) worsens the yield, since the underlying redox reaction is suppressed.

The optical performance is one of the most important characteristic of white smoke. Therefore, the transmittance and mass-based figure of merit were determined to classify the optical properties. The transmittance of hexamine-based formulations was in the range of 4–8 % at the start of the measurement, which is significant lower compared to 5-AT. After 6 min of detection, the transmittance only increased to 15–17 % in comparison to the 5-AT (22 %) and sugar (59 %) mixture. For this reason, the hexamine-based formulations guarantee improved obscuration properties. All tested formulations were insensitive towards friction and ESD. However, the hexamine-based mixtures were slightly impact sensitive in comparison to the chosen references. Finally, the hexamine-based pyrotechnical compositions could serve as a low-cost alternative to 5-AT-based formulations due to the similar optical performance observed and at the same time higher yields.

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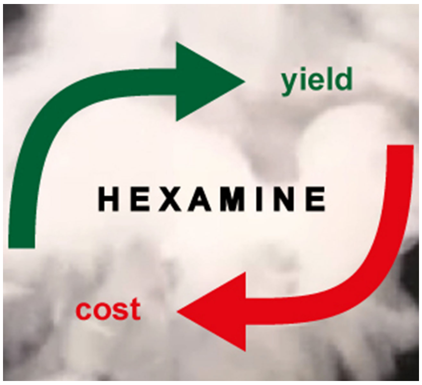
The effect of applying hexamine as the only main fuel in a known TA-based white smoke formulation is discussed.



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Combining Higher Efficiency with Lower Costs: an Alternative Hexamine-Based White Smoke Signal