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Chlorine-Free Red-Burning Pyrotechnics

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Abstract: *The development of a red, chlorine-free pyrotechnic illuminant of high luminosity and spectral purity was investigated. Red-light emission based solely on transient $SrOH_{(g)}$ has been achieved by using either 5-amino-1H-tetrazole or hexamine to deoxidize the combustion flame of a Mg/$Sr(NO_3)_2$/Epon-binder composition and reduce the amount of both condensed and gaseous SrO, which emits undesirable orange-red light. The new formulations were found to possess high thermal onset temperatures. Avoiding chlorine in these formulations eliminates the risk of the formation of PCBs, PCDDs, and PCDFs. This finding, hence, will have a great impact on both military pyrotechnics and commercial firework sectors.*

Red-burning pyrotechnic flares are of paramount importance for distress and tactical signals in both civilian and military environments. These formulations typically contain a metallic fuel such as magnesium, strontium nitrate ($Sr(NO_3)_2$) as the oxidizer, an organochlorine compound such as poly(vinyl chloride) (PVC), an organic binder, and sometimes auxiliary chlorine sources such as potassium perchlorate ($KClO_4$).[1] Upon combustion, these compositions produce magnesium oxide ($MgO_{(s)}$), strontium(I) chloride ($SrCl_{(g)}$), and strontium(I) hydroxide ($SrOH_{(g)}$). The last two species both yield a distinct emission pattern in the red spectral wavelength range,[2] while condensed MgO greatly assists in obtaining a high luminous intensity I_λ.

Unfortunately, the combustion of chlorinated organic materials such as PVC, as well as mixtures of hydrocarbons with perchlorates, are suspected to lead to the formation of highly carcinogenic polychlorinated aromatic compounds such as polychlorinated dibenzodixins (PCDDs), polychlorinated dibenzofuranes (PCDFs), and polychlorinated biphenyls (PCBs).[3] Although there is a debate as to the exact quantities of PCDDs, PCDFs, and PCBs formed during the combustion process of chlorine-containing pyrotechnics,[4,5] current research efforts are generally directed towards eliminating any chlorine from pyrotechnic formulations in an effort to increase environmental compliance.

It has long been assumed that highly saturated ($\Sigma \geq 76\,\%$) red-burning flare formulations with a dominant wavelength $\lambda_d \geq 600$ nm would require the presence of significant amounts of $SrCl_{(g)}$. $SrOH_{(g)}$, although identified to be present in Sr-based red flames, was for decades believed to be an inferior emitter in terms of quantum efficiency,[1,6a–d] and was even considered to be detrimental to a saturated red flame (sic!).[6e] Hence, red-burning flare formulations based on the emission of atomic lithium (Li_g) were also examined in the past. Although this approach produced acceptable results,[7] the use of new ingredients in energetic materials requires extensive testing, as outlined in NATO STANAG 4147, and may lead to the ultimate rejection of new ingredients.[8]

Although chlorine-free variants of green- and blue-light-emitting pyrotechnic compositions have been reported,[9,10] the development of a chlorine-free red-light-emitting flare of both high luminosity and deep saturation has remained elusive.

In the present study, it was hence sought to omit PVC from the current US Army in-service M158 red star cluster formulation **A** (Table 1). As a consequence of environmental concerns associated with the Laminac binder system, the epoxy "drop-in" formulation **B** (Table 1) and chlorine-free formulations **C**–**E** were prepared and evaluated to provide relevant data points for further experimentation. As detailed in Table 2, formulation **B** yielded a longer burn time and lower luminosity than the control formulation (**A**), as has been observed previously when, all other factors being held constant, the epoxy replaced the Laminac binder system.[11]

Table 1: In-service M158 formulation **A**, its epoxy “drop-in **B**, and the PVC-free formulations **C**–**E**.

Component	A	B	C	D	E
$Sr(NO_3)_2$	48	48	63	55.5	48
Mg 30/50	33	33	33	40.5	48
PVC	15	15			
Laminac 4116/Lupersol	4				
Epon 813/Versamid 140		4	4	4	4

However, the chlorine-free formulations **C**–**E** failed to achieve the necessary requirements and gave a rather red-orange light with dominant wavelengths of $\lambda_d = 593$–598 nm and insufficient saturations of $\Sigma = 54$–$65\,\%$. Thermochemical calculations (see the Supporting Information) show these compositions to have very high combustion temperatures (ca. 3000 K) and high concentrations of both condensed $MgO_{(s,l)}$

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Table 2: Performance of the control and formulations **A**–**D**.

Formulation	BT[a] [s]	LI[b] [kcd]	LE[c] [kcd s g^{-1}]	λ_d[d] [nm]	Σ[e] [%]
requirement	8.5 ± 2.0	30.0	N/A[f]	620 ± 20	76.0
A	9.2	32.3	15.5	613	86.3
B	9.7	27.9	14.2	612	88.1
C	7.3	37.7	13.9	593	54.2
D	6.0	52.1	15.7	596	59.2
E	5.3	60.5	16.1	598	65.4

[a] BT = burn time. [b] LI = luminous intensity. [c] LE = luminous efficiency. [d] λ_d = dominant wavelength. [e] Σ = saturation. [f] Not specified.

and $SrO_{(l)}$.[12] This excessive incandescence explains the observed low color saturation. In addition, the calculations reveal high amounts of $SrO_{(g)}$, which is known to produce an orange emission at $\lambda = 595$ nm. It was hence decided to reduce the amount of both gaseous and condensed $SrO_{(g/l)}$ by introducing hydrogen and/or carbon monoxide to deoxidize the flame. The concomitant release of nitrogen was also aimed to increase the luminous intensity of the flame, as had been shown recently to be beneficial with formulations emitting in the mid-infrared region.[13]

Recently, 5-aminotetrazole (CH_3N_5, 5-AT)—a pyrotechnic ingredient known since the 1960s from gas generation and auto-ignition compositions for vehicle airbags[16]—was successfully applied in a composition for a military signaling light.[14] 5-AT has been determined to be relatively benign by the US Army Public Health Command.[15]

Unlike formulation **E**, the combustion of formulation **F** (Table 3) which contains 15 wt % 5-AT, yielded an adequate dominant wavelength and spectral purity (Table 4). The significant improvement in these performance parameters can be attributed to the addition of 5-AT at the expense of magnesium. Thermochemical calculations showed that the 5-AT resulted in a reduction of the combustion temperature, and a significant 32 % decrease in the amount of incandescent particles ($SrO_{(l)}$, $MgO_{(s)}$, $MgO_{(l)}$). Most importantly, a significant 53 % reduction in the amount of the orange-red light-emitting species $SrO_{(g)}$ was observed. Although the luminous intensity of formulation **F** was below the acceptable threshold, the use of a smaller magnesium particle size resulted in a significant improvement in luminosity without compromising the dominant wavelength and purity of the flare (Table 4, formulation **G**).

Table 3: Composition of formulations **F**–**I**.

Component	F	G	H	I
$Sr(NO_3)_2$	48	48	48	48
Mg 30/50	33	–	–	–
Mg 50/100		33	33	33
5-AT	15	15	12	
hexamine	–	–	–	12
Epon 813/Versamid 140	4	4	7	7

Table 4: Performance of formulations **F**–**I**.

Formulation	BT [s]	LI [kcd]	LE [kcd s g^{-1}]	λ_d [nm]	Σ [%]
requirement	8.5 ± 2.0	30.0	N/A	620 ± 20	76.0
control **A**	9.2	32.3	15.5	613	86.3
F	8.1	29.3	11.9	607	77.7
G	7.3	38.9	14.5	607	77.7
H	7.7	37.2	14.6	607	81.7
I	8.8	35.0	14.0	609	81.8

With formulation **G** in hand, attempts were made to further increase the spectral purity of the illuminant by increasing the binder content (Table 3, formulation **H**). Calculations indicated that a higher amount of binder releasing more hydrogen and CO could be produced, and therefore the level of SrO could be further decreased. Indeed, binder-rich formulation **H** exhibited a performance in excess of the military requirement, and a further improvement in the spectral purity was realized (Table 4). Formulation **I**, which contains hexamine ($C_6H_{12}N_4$) instead of 5-AT, resulted in an even higher dominant wavelength and similar spectral purity. The safety of formulation **H** (with regard to impact, friction, ESD, and DSC onset) was very similar to the control[17] (see the Supporting Information).

Figure 1 displays the visible emission spectrum of the combustion flame of the PVC-containing control (formulation **A**). The spectrum displays the prominent molecular bands of SrCl, SrOH, and SrH. In addition, a very weak system for $SrO_{(g)}$ as well as atomic lines arising from Na and K impurities are seen. Figure 2 shows the emission spectrum of chlorine-free composition **H**, which is dominated by unusually strong molecular bands for SrOH and SrH. Again, a weak system for $SrO_{(g)}$ is discernible. Both spectra show a slight graybody background.

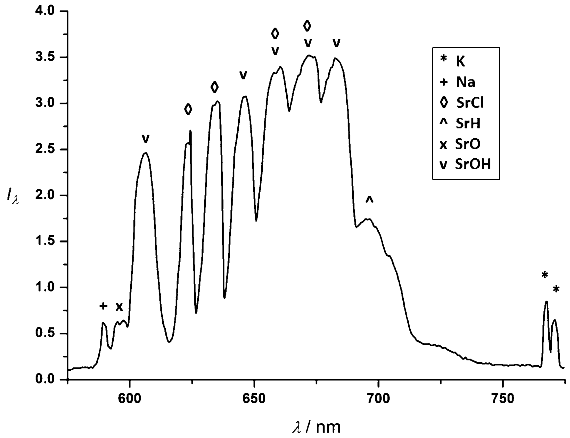

Figure 1. Emission spectrum of the combustion flame of the M158 control.

Although it was believed for decades that luminous and highly saturated red flames would require the presence of chlorine to form transient $SrCl_{(g)}$, the present study has shown that it is feasible to obtain both high intensity and highly saturated red flames exclusively based on SrOH with concomitant SrH emission.

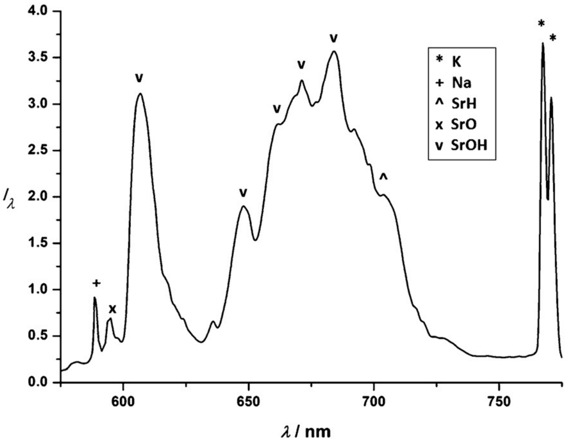

Figure 2. Emission spectrum of formulation **H**.

The use of 5-AT or hexamine lowers the combustion temperature and reduces unwanted SrO, as well as generally reducing the amount of condensed materials produced. Therefore, the first red high-intensity flare composition that doesn't require any kind of chlorine source as the color intensifier has been obtained. The de novo formation of problematic chlorinated arenes and oxyarenes for red-light-emitting illuminants can now be avoided.

Keywords: energetic materials · illumination · pyrotechnics · red flames · sustainable chemistry

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