

Pyrotechnics

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A Strontium- and Chlorine-Free Pyrotechnic Illuminant of High Color Purity

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Abstract: The development of a red-light-emitting pyrotechnic illuminant has garnered interest from the pyrotechnics community owing to potential regulations by the United States Environmental Protection Agency (U.S. EPA) regarding the use of strontium and chlorinated organic materials. To address these environmental regulatory concerns, the development of lithium-based red-light-emitting pyrotechnic compositions of high purity and color quality is described. These formulations do not contain strontium or chlorinated organic materials. Rather, the disclosed formulations are based on a non-hygroscopic dilithium nitrogen-rich salt that serves as both oxidizer and red colorant. These formulations are likely to draw interest from the civilian fireworks and military pyrotechnics communities for further development as they both have a vested interest in the development of environmentally conscious formulations.

For many, firework displays are an integral component of national or religious holidays or New Year's Eve. In the military sector, the production of colored light finds common usage for signaling purposes or for illuminating a specified area to accomplish a mission. Owing to the ubiquitous presence of colored-light-emitting pyrotechnics, it is imperative that health and environmental issues are considered when developing illuminating compositions of high performance and high color quality. Colored flames are produced mostly by burning alkali and alkaline-earth metal salts. Traditional red-light-emitting pyrotechnic formulations are based on strontium and chlorinated organic materials.^[1] These mixtures mostly contain strontium nitrate in combination with a chlorine donor, such as polyvinyl chloride (PVC), to form metastable strontium(I) chloride as the red-light-emitting species.

Although the bright red light of strontium- and chlorine-containing mixtures might seem innocuous, their use is a cause for concern. During the combustion of chlorine-containing pyrotechnic formulations, highly carcinogenic

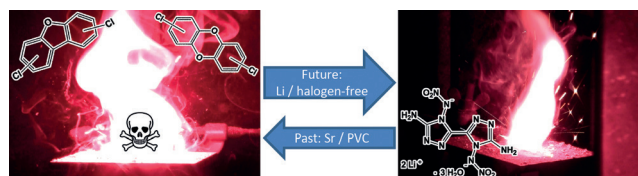


Figure 1. Comparison of a strontium/PVC-containing formulation and lithium/chlorine-free formulation B.

polychlorinated biphenyl, dibenzofuran, and dibenzo-*p*-dioxin derivatives are formed (Figure 1).^[2]

Although there are contradictory opinions in the literature concerning the amount of polychlorinated decomposition products formed,^[3,4] chlorine-free pyrotechnic formulations are desired nevertheless. In this context, chlorine-free pyrotechnic formulations yielding green,^[5] blue,^[6] and red light^[7] with good color quality and high intensity have been reported in recent years.

According to a recent report from the United States Environmental Protection Agency (U.S. EPA), strontium is potentially harmful to human health.^[8] It is reported that strontium replaces calcium in the bone, interferes with bone strength, and thus affects the skeletal development of children and adolescents. In 2014, the U.S. EPA made a preliminary decision to start regulating the amount of strontium in drinking water.^[8,9] Strontium has been detected in 99 % of all public water systems and at levels of concern in 7 % of the public water systems in the USA.^[10] Whereas U.S. military training grounds were not included in the study, these facilities may show elevated concentrations of strontium as well, given the presence of strontium in currently used red-light-illuminating signaling pyrotechnic compositions. Considering these new concerns regarding the use of strontium, a new method for generating red light of deep color purity is needed.

As an alternative to strontium, lithium-based formulations have been considered as a means to generate red light. Although lithium-based formulations have been investigated in the past, they have been plagued by high hygroscopicity and low color purity.^[11] Instead of red light, these lithium-based formulations yielded pink or orange flames. Furthermore, past lithium-based formulations utilized perchlorates as the oxidizers, and these oxidizers are no longer viewed as being acceptable from an environmental point of view.^[11,12] Certain parameters have to be complied with in order to obtain optimal color properties when using lithium as a red-light emitter. The principle emitter in lithium-based red flames is atomic lithium, and its concentration should be kept as low as possible to avoid a broadening of the lithium line

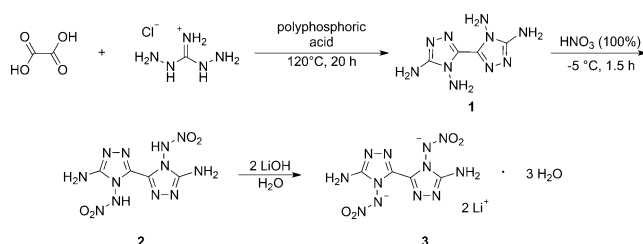
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width.^[12c,13,14] In contrast to strontium-containing formulations, a reductive flame atmosphere is essential to achieve red light with lithium.

A practical red-light-emitting formulation based on lithium must be of deep color purity and must be based on a lithium material that is not moisture-sensitive. To achieve a reductive flame atmosphere, it is important to prevent oxidation processes in the outer part of the flame that are accompanied by the formation of unwanted LiOH, LiO, and condensed compounds such as Li₂O. These species lower the amount of atomic lithium present, and reduce the color purity. The release of high amounts of nitrogen was believed to be beneficial owing to its favorable energy release and metal-free combustion. One suitable candidate, the dilithium salt of 3,3'-diamino-4,4'-dinitramino-5,5'-bi-1,2,4-triazolate, Li₂ANAT (**3**; Scheme 1), was synthesized. Compound **3** was found to have a high decomposition temperature as well as non-hygroscopic behavior. It was thus investigated in pyro-



Scheme 1. Synthesis of dilithium 3,3'-diamino-4,4'-dinitramino-5,5'-bi-1,2,4-triazolate trihydrate (**3**).

technic formulations. Colorant **3** was synthesized in a simple three-step reaction (Scheme 1). 4,4',5,5'-Tetraamino-3,3'-bi-1,2,4-triazole (**1**) and 5,5'-diamino-4,4'-dinitramino-3,3'-bi-1,2,4-triazole (**2**) had been synthesized previously.^[15] Deprotonation of **2** with LiOH gave the dilithium salt **3**.

The dilithium salt **3** was extensively characterized by multinuclear NMR and vibrational spectroscopy as well as by X-ray techniques (see the Supporting Information). Compound **3** is both an oxidizer and a colorant at the same time, which is beneficial for reducing the number of components in pyrotechnic mixtures, and was tested for its suitability as a component of pyrotechnic formulations and compared to a chlorine-free strontium-based formulation on a 1 g scale.^[7] Two formulations **A** and **B** (Table 1) were investigated. Both formulations consist of **3**, magnesium, hexamine, and nitrocellulose as fuels, and were prepared with the Epon 813/Versamid 140 (1:1) binder system (Table 1). Although the lithium salt contained crystal water, there were no problems related to hygroscopicity. As the control, the chlorine-free strontium-based formulation containing strontium nitrate, magnesium, 5-aminotetrazole (5-AT), and the binder system Epon 813/Versamid 140 (4:1) was employed (Table 1).^[7] The burn time (BT), the dominant wavelength (DW), the luminous intensity (LI), the spectral purity (SP), the friction (FS), impact (IS), and electrostatic discharge sensitivity (ESD), as well as the decomposition temperature (T_{onset}) were determined.

Table 1: Components of formulations **A** and **B** and the strontium-containing control.

Formulation	Control	Weight [%]	
		A	B
Sr(NO ₃) ₂	48	–	–
Li ₂ ANAT (3)	–	51	48
Mg 50/100 mesh	33	31	15
nitrocellulose	–	2	4
hexamine	–	12	26
5-AT	12	–	–
epoxy binder	7	4	7

Formulations **A** and **B** burned with a red flame, and no smoke was observed. The performance of both formulations is summarized in Table 2. The two formulations exhibited longer burn times than the control and dominant wavelengths

Table 2: Performance of the strontium-containing control and the lithium-based formulations **A** and **B**.

Formulation	BT ^[a] [s]	LI ^[b] [cd]	DW ^[c] [nm]	SP ^[d] [%]
control	5	35 400	607	79
A	9	2130	605	70
B	16	820	606	88

[a] BT = burn time. [b] LI = luminous intensity. [c] DW = dominant wavelength. [d] SP = spectral purity.

of 605 and 606 nm, which are both within the 620 ± 20 nm region required for red light.^[7] Whereas the spectral purity of formulation **A** was below the minimum threshold of 76 %, formulation **B** showed a significantly better spectral purity of 88 %, which is also superior to that of the control. The higher magnesium content in **A** compared to **B** leads to higher luminosity but lower spectral purity owing to the increased incandescence caused by a greater amount of condensed MgO_(s,l).

Relative to the control, formulations **A** and **B** are less sensitive to impact, friction, and electrostatic discharge (Table 3). Additionally, the decomposition temperature of the better formulation **B** was measured to be higher than 200 °C. These properties allow the safe handling of the material. In Figure 2, the color points of formulations **A**, **B**, and the strontium control are shown in a CIE 1931 chromaticity diagram, illustrating that it is possible to develop a suitable red-light emitter that is free of halogens and strontium.

As can be seen, the lithium-based colorants give rise to color points that are in close proximity to that of the red strontium-based control formulation (see the Supporting

Table 3: Sensitivities of the control and formulations **A** and **B**.

Formulation	IS ^[a] [J]	FS ^[b] [N]	ESD ^[c] [J]	T_{onset} [°C] ^[d]
control	9	240	> 0.25	231
A	25	360	1.5	198
B	40	360	1	217

[a] IS = impact sensitivity. [b] FS = friction sensitivity. [c] ESD = electrostatic discharge sensitivity. [d] T_{onset} = onset temperature of decomposition.

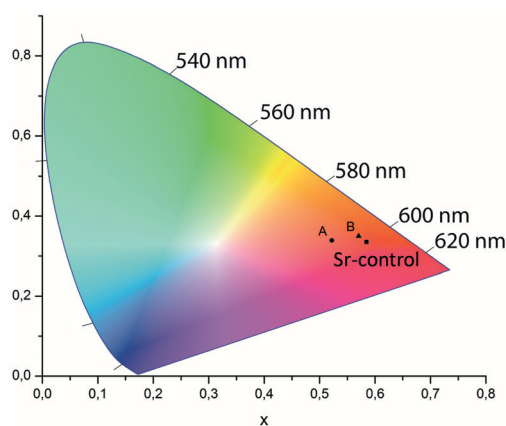


Figure 2. CIE 1931 chromaticity diagram for red formulations.

Information for details). The emission spectrum of composition **B** is depicted in Figure 3. The two atomic emission lines of lithium can be seen at 670 nm and 610 nm, respectively. As in all pyrotechnic formulations, the sodium emission at 589 nm is also present.

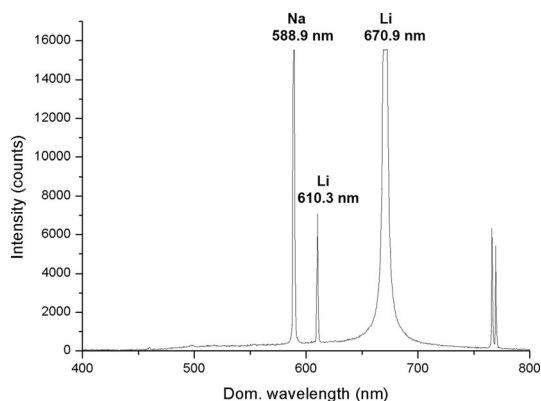


Figure 3. Emission spectrum of formulation **B**.

In conclusion, we have shown that the lithium-based nitrogen-rich compound **3** acts as both the oxidizing agent and the colorant in red-light-emitting pyrotechnic formulations. The color quality of lithium-based formulation **B** was comparable to those of chlorine-free strontium-based compositions. Whereas further optimization is still needed to improve the luminosity of lithium-based red flares, we have reported the first red-light-emitting formulation of high color quality and purity that does not contain halogen- or strontium-based materials.

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Conflict of interest

The authors declare no conflict of interest.

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