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Chlorine-Free Pyrotechnics: Copper(I) Iodide as a "Green" Blue-Light Emitter**

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Abstract: *The generation of blue-light-emitting pyrotechnic formulations without the use of chlorine-containing compounds is reported. Suitable blue-light emission has been achieved through the generation of molecular emitting copper(I) iodide. The most optimal copper(I) iodide based blue-light-emitting formulation was found to have performances exceeding those of chlorine-containing compositions, and was found to be insensitive to various ignition stimuli.*

The generation of a blue flame in pyrotechnics is very challenging and requires the exact tuning of different parameters such as the specific ratio of the ingredients, reactivity, and combustion temperature.[1] Blue flame colors are obtained by using copper or copper-containing compounds, which in the presence of a chlorine source, produce the blue-emitting species copper(I) chloride (CuCl). This light-emitting species is currently believed to be the best emitter in the blue region of the visible spectrum, ranging from 435 to 480 nm. A series of bands in the region from 428 to 452 nm with additional peaks between 476–488 nm are obtained from this molecular species.[1,2] It has been hypothesized that CuCl is an especially unstable species, and that decomposition occurs at temperatures above 1200 °C. The decomposition is believed to occur in an oxygen-rich flame, producing copper(II) oxide (CuO) and copper(I) hydroxide (CuOH). While CuOH emits in the green region from 525 to 555 nm, CuO emits bands in the red region, which is often observable at the top of blue flames.[3] The theory as to whether CuCl decomposes at 1200 °C has been disputed in a theoretical sense by Sturman. He carried out thermodynamic modeling investigations using the NASA-CEA code revealing that excellent blue flame colors can be obtained at much higher temperatures.[4]

Potassium perchlorate and ammonium perchlorate oxidizers are often employed as the chlorine source in blue-light-emitting flames. Unfortunately, the use of perchlorates in today's pyrotechnic formulations is discouraged due to environmental concerns.[5] To encourage the production of CuCl, polychlorinated organic compounds such as polyvinyl chloride are commonly employed in blue-light-emitting formulations to provide a large excess of chlorine.[1] In the literature, there are contradictory opinions concerning the amount of toxic polychlorinated organic compounds generated during the combustion of chlorine-containing pyrotechnic formulations. Such toxic compounds include the highly carcinogenic polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). Although Fleischer et al.[6] state that low concentrations of PCBs, PCDDs, and PCDFs are generated following fireworks displays, Dyke and Coleman[7] found significantly higher concentrations of these carcinogenic materials following such displays. Given the presence of perchlorates and chlorinated organic compounds in blue-light-emitting compositions, it was of interest to develop formulations of this color that are entirely devoid of these materials.

It was hypothesized that copper(I) iodide (CuI) could serve as an environmentally benign alternative in blue-light emission. Spectroscopically, CuI is known to emit in the blue region at 460 nm,[8] though this emitter has not been known to form a blue light of high quality in pyrotechnic formulations. Presumably, with a CuI-based blue flame, the formation of polyiodated bisphenyls (PIBs) is likely. Fortunately, PIBs are not believed to be associated with health hazards; these materials are also used as contrast agents for radiological purposes in medicine.[9]

In the design of a chlorine-free blue flame, copper iodate ($Cu(IO_3)_2$) was believed to be a suitable oxidizer in CuI-based formulations, as it also can form this light emitter during the combustion process. $Cu(IO_3)_2$ is easy to prepare from potassium iodate and copper nitrate,[10] and is insensitive towards various ignition stimuli. Formulations based on CuCl as a blue-light emitter have been reported to yield a blue flame of the highest quality.[11]

To investigate blue-light-emitting formulations based on copper iodate as the oxidizer and colorant without any additional chlorine-containing compound, we chose Shimizu's blue-light-emitting formulation[11a] consisting of 68 % potassium perchlorate, 15 % copper, 17 % polyvinyl chloride, and 5 % starch as the control (Table 1), and reinvestigated it using our equipment.

Table 1: Shimizu's chlorine-containing blue-light-emitting formulation.

	$KClO_4$ [wt %]	Cu [wt %]	PVC [wt %]	Starch [wt %]
Control	68	15	17	5

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Table 2: Performance and sensitivity of the chlorine-containing control.

	BT [s]	DW [nm]	SP [%]	LI [cd]	LE [cdsg^{-1}]	IS [J]	FS [N]	T_{dec} [°C]
Control	4	475 (552)	61	54	360	8	324	307

The performance of the chlorine-containing control **A** is summarized in Table 2. The burn time (BT), dominant wavelength (DW), spectral purity (SP), luminous intensity (LI), and luminous efficiency (LE) have been determined. The impact sensitivity (IS) and friction sensitivity (FS), as well as the decomposition temperature (T_{dec}) were measured. Although the control yielded an intense blue flame during the combustion process, two dominant wavelength values were detected appearing at 475 nm in the blue region and at 552 nm in the green region. The latter band can be attributed to the formation of CuOH during the combustion process. A spectral purity of 61% and a luminous intensity of 54 cd were obtained. The control was relatively insensitive toward various ignition stimuli, revealing an impact sensitivity of 8 J, a friction sensitivity of 324 N, and a decomposition temperature of 307 °C.

Formulations using copper iodate and several different fuels such as 5-aminotetrazole, guanidinium nitrate, copper, and starch have been investigated; however, they did not burn efficiently. Either the formulations glowed or they did not yield blue light.

Although 5-aminotetrazole as the sole fuel source did not produce the energy necessary for a combustion reaction, magnesium was added in an effort to raise the formulation's combustion temperature and to facilitate efficient propagation. The compositions of these formulations are summarized in Table 3. Formulation **1**, containing only 53% copper iodate, exhibited a poor burning behavior, and blue light was not observed. Formulations **2**–**4** burned with a blue flame, with smoke and residues being observed. While formulations **2**–**4** exhibited a reasonable sensitivity to ignition stimuli, the quality of these flames was poor, as all spectral purities were lower than those of the control (Table 4).

Table 3: Formulations **1**–**4**.

	$Cu(IO_3)_2$ [wt%]	5-At [wt%]	Mg [wt%]	Epon 828/Epikure 3140 [wt%]
1	53	35	5	7
2	65	15	15	5
3	75	5	15	5
4	75	12	8	5

Table 4: Performance and sensitivity of formulations **2**–**4**.

	BT [s]	DW [nm]	SP [%]	LI [cd]	LE [cdsg^{-1}]	IS [J]	FS [N]	Grain size [μm]	T_{dec} [°C]
2	5	468 (546)	58	45	375	10	>360	<100	164
3	5	480 (555)	51	76	633	10	>360	<100	167
4	6	465 (532)	56	80	800	8	>360	<100	170

Table 5: Formulations **5**–**8**.

	$Cu(IO_3)_2$ [wt%]	5-At [wt%]	Mg [wt%]	CuI [wt%]	Urea [wt%]	Cu [wt%]	Epon 828/ Epikure 3140 [wt%]
5	65	7	15	8	–	–	5
6	65	7	5	18	–	–	5
7	65	7	5	10	4	–	5
8	65	–	13	10	–	7	5

Compared to these formulations, formulations **5**–**8** contain copper iodide as an additional colorant, with formulation **7** containing urea, and formulation **8** containing copper powder in lieu of 5-aminotetrazole (Table 5). Although the luminous intensities of these formulations were below those of the chlorine-containing control, formulations **6** and **8** were observed to have better spectral purities than the control, with a dominant wavelength in the blue-light-emitting region (Table 6). The large excess of CuI employed in formulation **6** contributed to its enhanced spectral purity. Unfortunately, the composition suffers from a moderate sensitivity to impact.

Table 6: Performance and sensitivity of formulations **5**–**8**.

	BT [s]	DW [nm]	SP [%]	LI [cd]	LE [cdsg^{-1}]	IS [J]	FS [N]	Grain size [μm]	T_{dec} [°C]
A	4	475 (552)	61	54	360	8	324	307	307
5	4	470 (555)	59	67	447	10	>360	<100	173
6	4	473 (555)	65	42	280	5	>360	<100	161
7	3	480 (527)	56	32	160	5	>360	<100	167
8	4	470 (551)	60	41	273	5	>360	<100	170

Jennings-White reported a blue-light-emitting formulation, consisting of 50% guanidinium nitrate, 20% parlon, 15% copper, and 15% magnesium.[12] Using this formulation as a guide, we prepared and investigated compositions containing copper iodate and guanidinium nitrate (Table 7). The combination of magnesium with two further fuels—urea and copper—was tested. While formulation **9** could not be ignited, formulations **10** and **11** burned efficiently, yielding an intense blue flame. Unlike the previous formalations that provided a CuI-based blue flame, formulations **10** and **11** exhibited no smoke and no residues.

Table 7: Formulations **9**–**11**.

	$Cu(IO_3)_2$ [wt%]	Guanidinium nitrate [wt%]	Mg [wt%]	Urea [wt%]	Cu [wt%]	Epon 828/ Epikure 3140 [wt%]
9	15	50	9	21	–	5
10	20	50	10	–	15	5
11	30	35	9	21	–	5

Formulations **10** and **11** both exhibited longer burn times, higher spectral purities, and higher luminosities than the control. Formulation **10** is particularly noteworthy, as this formulation has a luminous intensity 33% brighter and

a luminous efficiency value three times better than the control formulation. Moreover, formulations **10** and **11** were found to have very low impact and friction sensitivities, with reasonably high decomposition temperatures (Table 8).

Table 8: Performance and sensitivity of formulations **10** and **11**.

	BT [s]	DW [nm]	SP [%]	LI [cd]	LE [cdsg^{-1}]	IS [J]	FS [N]	Grain size [μm]	T_{dec} [°C]
A	4	475 (552)	61	54	360	8	324	307	307
10	6	477 (555)	64	80	1067	> 40	> 360	< 100	198
11	6	476 (525)	63	78	780	> 40	> 360	< 100	180

In addition to the experimental evidence, the CIE chromaticity diagram of formulations **10** and **11** show them to be suitable blue-light emitters (Figure 1).

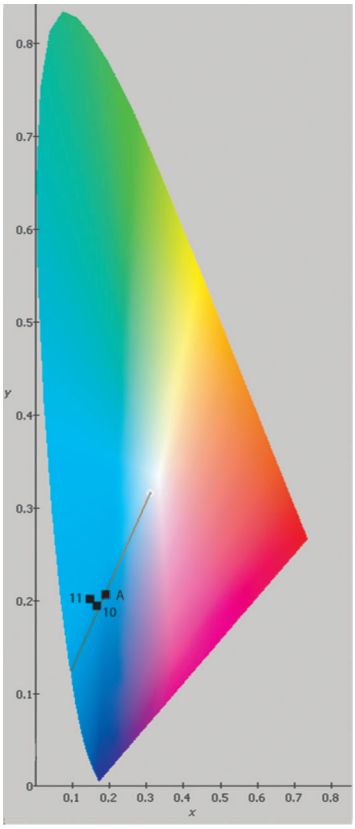

Figure 1. CIE 1931 chromaticity diagram of formulations **A**, **10**, and **11**.

Several blue-light-emitting formulations based on copper(I) iodide as the molecular emitter have been investigated. $Cu(IO_3)_2$ was determined to serve as a suitable oxidizer for achieving blue-light emission based on molecular copper(I) iodide. Only formulations containing magnesium in addition to various high-nitrogen-containing fuels displayed a useful and practical burning behavior. The best results were achieved for mixtures containing copper iodate/magnesium/guanidinium nitrate, with urea or copper serving as an additional fuel source (formulations **10** and **11**). Formulation **10** exhibited the best performance, with a burn time, spectral purity, and luminous output greatly exceeding those of the chlorine-containing control. It can be concluded that for the generation of blue-flame colors, CuCl is not the only suitable blue-light emitter. CuI can also serve this purpose in a properly tuned formulation. This is advantageous from the "greener" pyrotechnics perspective, as the potential formation of highly toxic PCBs, PCDFs, and PCDDs is avoided.

Experimental Section

CAUTION! The mixtures described here are potential explosives, which are sensitive to environmental stimuli such as impact, friction, heat, and electrostatic discharge. While we encountered no problems in handling of these materials, appropriate precautions and proper protective measures (safety glasses, face shields, leather coats, Kevlar gloves, and ear protectors) should be taken when preparing and manipulating these materials.

Copper iodate was purchased from abcr. Copper, potassium perchlorate, urea, 5-aminotetrazole, nitroguanidine, guanidinium nitrate, polyvinyl chloride, magnesium, and copper iodide were purchased from Aldrich, Fluka and Acros, and were used as received. The pyrotechnical compositions were prepared by rigorously grinding all substances in a mortar with a pestle. The mixtures were introduced to Epon 828/Epikure 3140 binder system, mixed by hand with a plastic spatula for 15 min, and ground in a mortar again. Pellets, each 0.6 g, were pressed in one increment using a consolidation dead load of 2000 kg. The pellets were dried overnight in an oven at 60 °C. The controlled burn was filmed with a digital video camera recorder (SONY, DCR-HC37E). The performance of each composition was evaluated with respect to color emission, smoke generation, and the amount of solid residues. Spectrometric measurements were performed using a HR2000 + ES spectrometer with an ILX511B linear silicon CCD-array detector and included software from Ocean Optics with a detector–sample distance of 1 m. The dominant wavelength (DW) and spectral purity (SP) were measured based on the 1931 CIE method using illuminant C as the white reference point. Luminous intensities (LI) and luminous efficiencies (LE) were determined using pellets each weighing 0.6 g. Five samples were measured for each formulation and all given values are averaged based on the full burn of the mixture. Decomposition points were measured with a Linseis PT10 DSC apparatus using heating rates of 5 °C min^{-1}.[13] The impact and friction sensitivities were determined using a BAM drophammer and a BAM friction tester.[14–18] The sensitivities of the compounds are indicated according to the U.N. Recommendations on the Transport of Dangerous Goods (+):[19] 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, extreme sensitive < 10 N.

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