

Blue Flame Pyrotechnic Compositions: A Concise Review

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Abstract: *A brief historical background to the development of effective pyrotechnic blue flame compositions, including strobing formulas, from the 19th century to the present day, is presented. The latest prevailing theories on blue flame generation are discussed and a list of some effective modern formulations is given.*

Keywords: *Pyrotechnic illumination, blue flame, copper salts, copper oxides.*

Introduction

Despite the continuous development of improved green, red and yellow fire compositions due to an increasingly demanding fireworks and distress-signals market, there is nothing more fascinating to some pyrotechnic chemists than a long-lasting, intense, deep blue pyrotechnic flame. Regrettably, blue flame compositions have not been exploited to the same extent as other colours, primarily because the human eye is more sensitive to longer wavelengths of the visible spectrum, notably yellow, green and red, which are the colours of choice for military and civilian signalling. As a consequence, blue flame compositions are now almost exclusively employed in the production of ground and aerial fireworks and mostly in the form of pellets ('stars') of blue-light producing composition. Although a badly formulated blue firework may still be described as 'beautiful' by the average unskilled observer, those skilled in the art would agree that the creation of a saturated, deep blue flame 'still represents a challenge to the pyrotechnic chemist' as stated by Conkling,¹ because of the required delicate balance between ingredients purity, flame temperature and the concentration of the right copper-based molecular emitter.

This paper aims to present a concise review of the main developments of blue-light producing pyrotechnic formulations throughout the last century and to highlight the latest theories on blue flame generation.

Historical background

The Ruggieri brothers, famous Italian pyrotechnists of the early 18th century, seem to have been the first who tried to impart blue and green hues to their black powder-based stars and other aerial effects by adding ammonium chloride and copper sulphate.² However the history of 'modern' blue flame compositions is invariably linked to the discovery of potassium chlorate. Thus, the likely first reference to the manufacture of more effective blue lights dates back to 1836, when a Belgian artillery officer published a pyrotechnics treatise including a section devoted to a composition based on 'chlorate of potash, ivory, bismuth, alum, zinc and copper sulphate...'² Following this early work, an English pyrotechnician disclosed³ in 1878 a compilation of formulae for blue stars and blue lancework which were also based on potassium chlorate whereas the copper-containing ingredient was copper oxychloride. It is likely that similar or more effective compositions had already been in use as early as the late 18th century, particularly in France, where potassium chlorate had been first prepared in 1786 by C. L. Berthollet, during one of his fabric-bleaching experiments involving aqueous potassium hydroxide and chlorine gas.⁴

Apart from fireworks, a number of civilian (railway) signalling devices⁵ including blue lights were also developed during the late 19th century in the US and Europe. These did not always contain conventional oxidisers and may not be classed as pyrotechnic illuminating devices in the modern

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sense i.e. mixtures of oxidiser, fuel and coloured light producing agent. For example, a patent⁶ was filed in 1895 describing the manufacture of a 'pyrotechnic' blue signal based on a mixture of zinc powder, selenium and carbon disulphide. Due to the absence of an oxidiser, the intensity of the signal, which was designed to be lit in the open air in slurry form, would not have been comparable to that of the fiercer chlorate-based blue compositions that would have been used in firework displays by some pyrotechnicians of the time.

Despite the early beginnings, the first scientifically rigorous publications concerning blue lights were not to appear until the 1950s, long after the discovery of the more stable perchlorates and the development of modern spectroscopic methods for flame emission observation.⁷⁻¹³ At this time two classic text-books of military pyrotechnics^{14,15} also dealt with the chemistry and physics of coloured flames including blue ones. Arguably, some of the blue light compositions developed during this time were still dangerous to manufacture. For example, Shidlovskiy¹⁵ describes an 'improved' blue flare of good colour purity containing a pressed mixture of potassium chlorate, sulphur and basic copper carbonate to neutralise the acidity of the sulphur. Other Russian workers were active developing blue formulations during the 1960s, their research eventually culminating in a series of patents describing improved blue flares based on ammonium perchlorate, hexamine, copper(I) chloride, copper(II) oxide, copper(I) thiocyanate and stearic acid.¹⁶⁻¹⁸ These mixtures, which exhibited low impact sensitivity, were capable of producing blue emission of high spectral purity, due to the presence of ammonium perchlorate. A few years after the Russian patents had been published, the American army developed a blue-burning tracer composition capable of providing a smoke trail after the blue flame was no longer visible.¹⁹ As the composition contained metal fuels, it was not capable of producing a saturated, deep blue emission. One mixture is reported to have contained potassium perchlorate, magnesium powder, anhydrous copper(I) chloride, barium nitrate, sulphur and hexachlorobenzene. Nevertheless, modern tracer compositions rely on green and red flames, to which the human eye is far more sensitive.

More recent developments

Despite these initial breakthroughs, the first systematic study of new, less sensitive and less toxic blue formulations was not published until 1980,²⁰ when the flame colour and intensity of a series of compositions based on potassium perchlorate mixed with copper powder, cupric oxide or basic copper carbonate were compared with those of a standard composition based on Paris green (copper acetoarsenite), an excellent blue light-colouring agent which was widely used at the time but known to be highly toxic. In that work the chlorinated polymers PVC (polyvinylchloride), Parlon (chlorinated isoprene) and hexachlorobenzene were explored as suitable chlorine carriers. The author did not assess the quality of the new compositions using conventional spectroscopic techniques, relying instead on his and his colleagues' naked eye, which was described as the 'best sensor for identifying subtle differences in the blue light colour' when in a dark room. This work demonstrated that each of the alternative blue colour-producing agents (with the exception of copper powder) was able to yield as good an effect as Paris green and that the burning rates and ignition characteristics were satisfactory. A series of effective purple flame compositions were also developed.

An interesting more recent development in blue flame technology came about in the 1990s in the form of 'strobing' formulations. The strobing effect is caused by the cyclical or oscillating combustion of the composition due to the formation and then co-existence after ignition, of a smoulder- and a flash-type reaction. To give a practical example, a pressed pellet of a composition containing magnesium and a sub-stoichiometric amount of ammonium perchlorate in the presence of a metal sulphate can ignite and self-sustain flameless combustion whilst accumulating heat in the slag layer. When the temperature in the slag reaches the melting point of the sulphate, which can now also act as a second oxidiser, the mixture bursts into a brilliant auto-extinguishing flash, but one which is not violent enough to extinguish the 'dark' smoulder reaction. The process repeats itself with frequencies varying between 3 and 10 Hz, depending on the stoichiometric ratio and particle size of the ingredients, until the composition is

consumed. Several compositions are known to be capable of strobing²¹ and an excellent review of strobe chemistry has been published.²²

Among first strobe pioneers, it was Jennings-White who developed low smoke, high-performance blue strobes²³ based on ammonium perchlorate, copper metal and either guanidinium nitrate or tetramethylammonium nitrate (TMAN). Because of the high nitrogen content, these compositions, which were suitable for pressing into stars, produced excellent colour purity and strobed reliably during combustion. More work followed by McCaskie, who published a method²⁴ for the production of blue strobe stars capable of flashing at 10 Hz. The new compositions were based on guanidinium nitrate, ammonium perchlorate, PVC and a copper(I) oxide.

Although no further reports on blue strobes have appeared since McCaskie's work, research into continuous-burning blue lights for improved fireworks continues to this day in many countries, including China,²⁵ the Czech Republic,²⁶ the Netherlands,²⁷ the US^{28,29} and Russia.³⁰ A whole variety of high-nitrogen ingredients are currently being explored, among which are simple energetic organic compounds like nitroglycerin (NG), diethylene glycol dinitrate (EGDN),

nitroguanidine (NGu) and nitrocellulose (NC). Some of these formulations have been patented on the grounds of the reduced smokiness and good luminous intensities. However, during scale up operations involving nitroglycerin there would be safety issues as some of these formulations require up to 10 wt% of NG.³⁰

As for other coloured lights, the latest trend in blue light research involves developing smokeless compositions³¹ capable of highly saturated emission, which may be used for indoor and special effects fireworks. These typically require the addition of insensitive fuels of very high nitrogen content (typically ≥ 80 wt%) which often have a highly positive heat of formation but low impact and friction sensitivity. The larger volume of nitrogen released during combustion and the increased burn rate when compared to ordinary fuels (like red gum or hexamine) act to enhance colour purity by reducing broadband emission. Promising high-nitrogen fuels include 3,6-dihydrazino-1,2,4,5-tetrazine (or some of its salts),³² 5,5'-bis-1*H*-tetrazole and bis(1*H*-tetrazol-5-yl)amine monohydrate (or some of their salts)³³, 1-methyl-5-nitraminotetrazole³⁴ and 5-amino-1*H*-tetrazole (or some of their salts).³⁵ The chemical structures of these neutral compounds are shown in Figure 1. Their copper salts have also

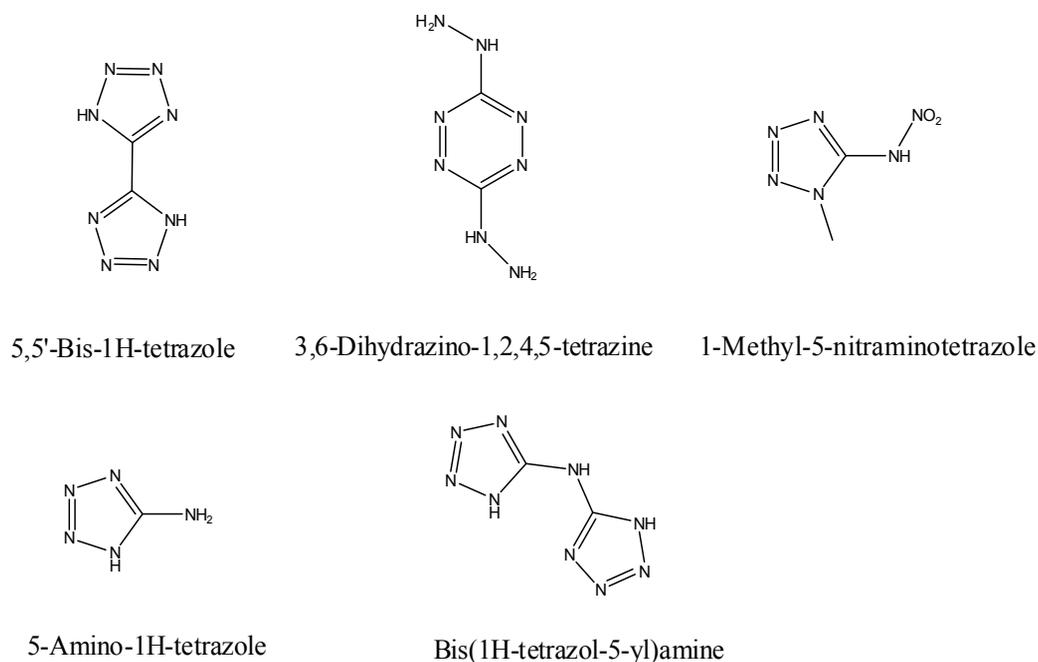


Figure 1. Structures of selected high-nitrogen fuels.

been investigated as substitutes for conventional blue colour producing agents. For example, the copper salt of bis(1*H*-tetrazol-5-yl)amine has been reported³³ to produce intense, deep blue colour in an area of the spectrum not previously observed using conventional colouring agents.

Although most of the above-mentioned high-nitrogen fuels are expensive or laborious to prepare other than on a small laboratory scale,³³ 1-methyl-5-nitraminotetrazole and 5,5'-bis-1*H*-tetrazole would seem good choices at present, as their synthetic procedure appears to be less involved.^{31,34} In addition to these two compounds, a series of relatively inexpensive metallic and organic salts of 5-aminotetrazole has been recently synthesised and these may also be ideal high-nitrogen fuels and excellent reviews describing the chemical and physical properties are available.^{36,37} Hydrazinium 5-aminotetrazolate is the latest addition at the time of writing (2009).³⁸ Easily and safely synthesised from 5-aminotetrazole and hydrazinium hydrate, with a calculated enthalpy of formation of +373 kJ mol⁻¹, but with low sensitiveness to impact, friction and electrostatic discharge, this compound would seem a promising candidate fuel for new smokeless blue light formulations.

Another recent development towards new smokeless blue lights involves the synthesis³⁹ of a nitrogen-rich copper complex derived from 1-(chloroethyl)-5-nitriminotetrazole (Figure 2), which effectively contains its own source of molecular chlorine as well as a single energetic nitrimine group. Although not oxygen-balanced, the compound essentially possesses the necessary ingredients for blue fire generation, i.e. the blue colouring agent, a nitrogen-rich fuel and an oxidising moiety. When admixed with a secondary oxidiser, this compound may serve well for the intended task. However, although easily prepared in good yields, the starting material, 1-(2-chloroethyl)-5-nitriminotetrazole, would appear to be shock and friction sensitive, which may preclude future industrial application.

In line with the increasing global awareness for health and safety policies, coloured light-producing fireworks, including blue devices, have been identified⁴⁰ as generators of polychlorinated dibenzodioxins and dibenzofurans. As such, conventional formulations are not entirely safe

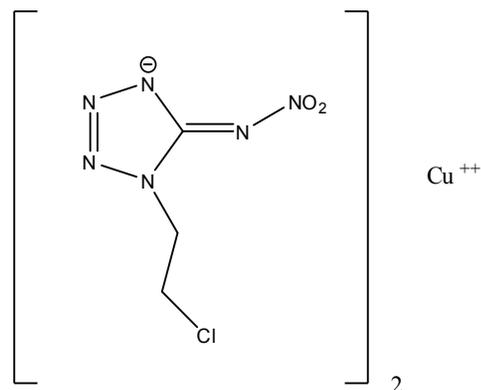


Figure 2. Structure of the (anhydrous) copper complex of 1-(2-chloroethyl)-5-nitriminotetrazole.

from an operational and environmental point of view if the devices are designed to function indoors. Since the presence of chlorine in the composition is required to produce deep coloured light, it is unlikely that the use of chlorine carriers will be completely phased out in future. However the use of low-carbon, high-nitrogen fuels should drastically reduce the formation of toxic airborne chlorinated species. Future efforts in blue (and other colours) light research may therefore benefit from combining high-nitrogen, insensitive oxidisers with high-nitrogen fuels. New continuous-burning and blue strobe compositions of high spectral purity may be accessed by systematically screening the performance, ageing profile and sensitivity of a number of such new formulations.

Oxidisers for blue light compositions

Although ammonium and potassium perchlorate are currently universally-favoured choices for both continuous-burning and strobe formulations due to the relatively low price and inherent thermal stability, high energy, appreciable chlorine content and good compatibility with organic and metallic fuels, these oxidisers have been identified as water pollutants exhibiting high residence times in lakes and rivers. Perchlorates in particular are known to inhibit iodide uptake by the thyroid gland and their presence in drinking water causes concern.³⁹

Despite the high cost and potential scale-up safety concerns, new 'green oxidisers' may be accessed by admixture of the nitrogen-rich, hygroscopic ammonium dinitramide (ADN)⁴¹ with relatively

small amounts of established insensitive energetic molecules of lower hygroscopicity but high-nitrogen content and relatively high oxygen balance (~20%) such as guanylurea dinitramide (FOX-12), 1,1-diamino-2,2-dinitroethene (FOX-7) and 3-nitro-1,2,4-triazol-5-one (NTO). These should act as hydrogen-bonding donors for the ADN, thus minimising its affinity for atmospheric moisture. It is the intention of the author to investigate the oxidising effectiveness of such mixtures in blue flame compositions.

Chemistry of pyrotechnic blue flame

Pyrotechnically-generated coloured light is the result of electronic excitation and the subsequent photonic decay of specific metal monochlorides (molecular emitters) which are transiently formed in the flame.^{1,42} It has long been accepted that emission of blue light requires the formation of electronically excited copper(I) monochloride, CuCl,⁴³ which decays to the ground state emitting in the visible region of the electromagnetic spectrum between approximately 430 and 450 nm. However, there are significantly-intense emission lines well beyond 450 nm with weaker lines tailing to 550 nm (detailed analyses of the emission lines of CuCl have been published).^{9,11,44} This results in CuCl being only 88% pure in its emission in contrast to the preferred emitters for the non-blue colours which are at or near 100% purity, which makes 'the production of a high purity blue flame much more difficult (and from a practical standpoint perhaps impossible) than producing the other colours'.⁴⁵

CuCl is formed by the reaction of atomic copper or copper oxide with radical chlorine or HCl, which derive primarily from combustion and/or pyrolysis of the chlorine carrier (or donor), which may be a chlorinated polymer or non-polymeric compound. Commonly used polymers include polyvinylchloride (PVC) and chlorinated polyisoprene (Parlon). Examples of non-polymeric chlorine carriers, which are used less frequently than the polymers, include hexachloroethane (HCE) and hexachlorobenzene (HCB), although the latter is now forbidden as it violates regulations on persistent organic pollutants. Despite intuition, thermodynamic modelling demonstrates that, with the exception of ammonium perchlorate, the production of radical chlorine from potassium

perchlorate is minimal, as the reaction is not favoured energetically. In early times, chlorates worked well without a chlorine carrier because they were used in combination with sulphur, whose reaction with KClO₃ does indeed release chlorine gas.⁴⁴

As for the source of copper, this is normally introduced with the colour light-producing agent in the form of a salt (copper sulphate or basic copper carbonate), an oxide (cupric oxide, cuprous oxide or copper oxychloride), a sulphide (copper sulphide), an organic compound (like copper acetoarsenite, 'Paris green'²⁰, which is now considered obsolete due to its toxicity) or even as copper metal powder.

It is generally assumed that in the strongly oxidising environment of a pyrotechnic flame, at temperatures above 1500 K, CuCl decomposes to CuO and CuOH,^{1,15} which emit in the green region of the visible spectrum between 500–530 nm. Since the green light contaminates the blue emission of copper chloride, a temperature value of ~1500 K has for years been accepted as the upper limit for effective blue light generation. This statement has recently been disputed in two papers^{46,47} which focussed on the nature of the blue emitter in pyrotechnic flames.

In the first paper,⁴⁶ the identity of the emitter has been reassessed as the trimeric form of copper monochloride, or Cu₃Cl₃. This conclusion was based on an extensive review of previous work involving mass spectrometric detection^{48,49} of the headspace gases found above sealed, heated (700–1800 K) crucibles containing CuCl or above the solid surface of laser-ablated CuCl targets.⁵⁰ It was shown that below 1360 K virtually no gaseous CuCl was present, with only the trimeric and tetrameric species being detected. As the temperature was increased, the concentration of 'monomeric' CuCl also increased, eventually predominating over the trimeric species above 1900 K (~1630 °C). Although undoubtedly informative, this review was based on experimental observations of simple *non-pyrotechnic* systems. The fact that the gas phase above molten CuCl or above a laser-ablated surface of solid CuCl is rich in trimeric and tetrameric CuCl does not guarantee that at similar temperatures, the same species would be thermodynamically favoured in a highly oxidising

pyrotechnic flame, where a number of reactive radicals exist.

Not surprisingly, the hypothesis of the trimeric nature for the blue emitter was challenged in a second publication.⁴⁷ This work employed a thermodynamic code developed by NASA to model the calculated adiabatic temperature and mole fraction of the copper species predicted to form at equilibrium in the flames generated by eight continuous-burning compositions taken from the literature. For all of the compositions, the calculated equilibrium concentrations of CuCl turned out to be much higher than those of Cu₃Cl₃, which was predicted to form only in trace amounts, indicating that CuCl would be the main emitter. In addition, the calculated adiabatic flame temperatures were all above 1500 K which further discredited statements that flame temperature

must be kept below 1500 K to generate CuCl effectively. Whilst the modelling results indicated that substantial amounts of CuCl can still be generated at ~2500 K, it was stated that at these higher temperatures broadband radiation from incandescent solid and liquid particles would interfere with the weaker blue emission of copper chloride, which may explain the often reported inefficacy of ‘hot’, metal-based blue formulations. In addition, it must be remembered that any trace impurity, and in particular sodium-containing impurities, in the fuel(s) and/or oxidiser is likely to contaminate the blue emission with the D line emission of elemental sodium (589 nm), to which the human eye is far more sensitive than blue light.

Component (parts by weight)	Compositions								
	1	2	3	4	5	6	7	8	9
	CB	CB	CB	CB	S	S	S	CB	CB
Ammonium perchlorate	—	—	—	—	55	40	25	—	46.25 to 49.50
Potassium perchlorate	64.7	66.1	75.1	67.3	—	—	—	—	—
Microcrystalline nitrocellulose	—	—	—	—	—	—	—	87	—
Potassium nitrate	—	—	—	—	—	—	—	5	—
Paris green	11	—	—	—	—	—	—	—	—
Hexachloroethane	—	—	—	—	—	—	—	4	—
PVC	6	—	—	—	—	—	7.5	—	—
Accroides resin (red gum)	15	9.8	11.5	10	—	—	—	—	—
Glutinous rice starch	5	4.5	4.8	4.5	—	—	—	—	—
Cupric oxide	—	13.4	—	—	—	—	5	4	—
Parlon	—	10.7	3.8	9.1	—	—	—	—	—
Copper powder	—	—	9.6	—	15	10	7.5	—	—
Basic copper carbonate	—	—	—	13.6	—	—	—	—	—
Tetramethylammonium nitrate (TMAN)	—	—	—	—	30	—	—	—	—
Ammonium sulphate	—	—	—	—	—	10	—	—	—
Guanidine nitrate	—	—	—	—	—	25	55	—	—
Magnalium 50:50	—	—	—	—	—	15	—	—	—
3,6-Dihydrazino-1,2,4,5-tetrazine	—	—	—	—	—	—	—	—	46.25 to 49.50
Copper salt of 5,5'-bis-1H-tetrazole dihydrate	—	—	—	—	—	—	—	—	1.0 to 7.0

CB = continuous-burning type; S = strobing type. Composition 1: Shimizu’s excellent reference, but toxic blue.²⁰ Composition 2: Shimizu’s CuO blue.²⁰ Composition 3: Shimizu’s Cu powder blue.²⁰ Composition 4: Shimizu’s basic copper carbonate blue.²⁰ Composition 5: Jennings-White’s TMAN-based best blue.²³ Composition 6: Jennings-White’s best ammonium sulphate-based blue strobe.²³ Composition 7: McCaskie’s best blue strobe.²⁴ Composition 8: Nickel’s ultra-low smoke blue.²⁹ Composition 9: Hiskey’s low smoke high nitrogen blue.³¹

Examples of blue flame compositions

Table 1 lists a selection of continuous-burning and strobing blue flame compositions taken from the modern literature (1980–2009). During screening, particular emphasis was given to insensitiveness and low toxicity (with the exception of composition 1 which contains Paris green). All formulations were developed to function as pressed pellets (stars). The particle size of the components can be found in the individual references to which the formulae refer. Composition 9 was taken from the patent literature. Although it was also our intention to include a high-nitrogen blue recipe based on the copper salt of 5-aminotetrazole, no actual formula could be found in the relevant patent,³⁵ which listed only examples for other colours. The list should provide a simple and useful reference guide for practising pyrotechnic chemists and teachers of pyrotechnics.

Conclusions

Although modern pyrotechnic compositions that generate continuous or strobing blue light have undoubtedly come a long way from the days of the dim bluish stars made by the Ruggieri brothers, there is still much scope for improvement. Most current effort in blue-light research seems to be devoted towards the development of new smokeless, high-nitrogen compositions capable of producing deeply saturated blue flames. Because of the environmental and health & safety concerns of our time, we can expect this trend to continue for next decade and beyond.

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