

# Metal Monochloride Emitters in Pyrotechnic Flames — Ions or Neutrals?

Barry Sturman

6 Corowa Court, Mount Waverley, Victoria 3149, Australia

## ABSTRACT

*Twelve English-language books on pyrotechnics were surveyed for the authors' views on the nature of the metal monochlorides that are associated with the emission of colored light in pyrotechnic flames. Three of the ten authors stated that the emitters were metal chloride ions ( $MCl^+$ ), five that they were neutral metal chloride molecules ( $MCl$ ), and two took no clear position. A study of the references cited in these books establishes that the emitters are neutral monochlorides. The idea that they are  $MCl^+$  ions is traced to a book published in 1965, which cited only one reference (published in 1949), and that reference clearly stated that the emitters are neutral molecules.*

**Keywords:** colored flame, emitter, spectra, monochloride, ion, neutral

## Introduction

A survey of 12 English-language books on pyrotechnics published since the early 1960s revealed a difference of opinion as to the nature of the metal-chlorine species that contribute to the colours of pyrotechnic flames containing chlorine (Cl) and barium (Ba), calcium (Ca), copper (Cu), or strontium (Sr). Some authors stated that the emitters are neutral monochlorides,  $MCl$ , while others indicated that the emitters are singly-charged positive monochloride ions,  $MCl^+$ . This review traces the development of this difference of opinion and attempts to establish which of the two points of view is correct by analyzing the information in the references cited in the books. Accordingly, this review has three main parts. It begins with a summary of the positions presented in the 12 books, followed

by a summary of the information contained in the references cited in those books. Finally, there is a discussion of that information and of some additional material from more recent publications.

## Results of the Book Survey

The following quotes show what each author wrote:

### 1. Ellern 1961<sup>[1]</sup>

“Except for the line spectra of the substances usable for colored lights, there is very little literature available on the theoretical aspects and quantitative relations of colored flames. Dr D. Hart<sup>[2]</sup> refers to the red flame as due to molecular bands in the red region, caused by molecular strontium oxide and chloride, and diluted with other lines and bands from incandescent particles. He refers to the green flame as being due to bright blue (*sic*) bands from copper and barium chloride in the 4000 to 5000 and 5000 to 5500 angstrom region.” (p 81)

“Barrow and Caldin<sup>[3]</sup> have measured the luminous intensities of flare compositions at constant temperature”. (p 98)

### 2. Shidlovskiy 1964 (English translation 1974)<sup>[4]</sup>

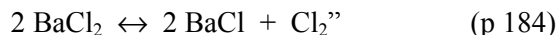
“At high temperatures, strontium chloride dissociates, forming strontium monochloride and splitting off free chlorine:



“In practice, red flare compositions are formulated only on the basis of the emission of strontium oxide or strontium monochloride, the emission of the latter being more intense, and in addition, closer to the extreme red portion of the

spectrum. This accounts for the effort to introduce chlorine into all the formulations of red flare compositions.” (p 183)

“Barium chloride dissociates in a flame, forming barium monochloride and splitting off free chlorine:



“The emission spectrum of BaCl consists of numerous bands in the green portion of the spectrum.” (p 185)

“The production...of an adequate, pure green flame can be achieved in practice only by using the emission of barium monochloride. Hence, compounds containing chlorine must of necessity be introduced into green flare compositions.” (p 185)

“Blue flames are obtained mostly on the basis of cuprous chloride CuCl...The blue emission of cuprous chloride can be obtained only in the reducing zone of the flame and at temperatures not in excess of 1000-1200 °C.” (p 186)

“A description of the formulas and technology of German signal-flare compositions used during World War II is given by Eppig.<sup>[5]</sup>” (p 186)

### 3. Cackett 1965<sup>[6]</sup>

“Spectra of illuminating and coloured signal flames are composed of three distinct elements. There is a general temperature continuum derived from the thermal excitation of solid and gaseous products of combustion and which is the main source of the white light that is always present. Next, there are complex systems of band spectra derived from molecular emitters such as ionized oxides and chlorides” (p 30)

“Blue flames rely for their colour on the band-system of CuCl<sup>+</sup> ranging from 4200 Å to 4600 Å and to weaker systems in the blue-green and green regions which are simultaneously developed” (p 32)

“All red signal compositions rely on the formation of SrCl<sup>+</sup> and SrO<sup>+</sup> ions in the flame to produce their characteristic spectral bands. In practice attention is focussed on developing the SrCl<sup>+</sup> ions to a maximum as the SrO<sup>+</sup> ions are always present in the flames.” (p 53)

“Green signal compositions, that have really good green flames, are difficult to produce because of the unsaturated hue which is the result of diluting the BaCl<sup>+</sup> spectral band with white temperature-continuum and with orange and red spectral bands from BaO<sup>+</sup> and from strontium salts as impurities.” (p 56).

### 4. Ellern 1968<sup>[7]</sup>

“Color in a flame, as used in pyrotechnics, results from the spectra of excited gaseous metal atoms, molecules or ions <sup>[8,9]</sup>. Salts of a certain limited number of metals are vaporized and the gaseous molecules or their first partial dissociation products lead to band spectra. On further splitting to neutral atoms of the metal, atomic lines are produced, and eventually metal ions create ionic spectral lines. The latter are undesirable for color production in the flame. So-called C-type chemiluminescence, wherein a small number of molecules emit an abnormally large amount of radiation, plays an important part in the colored emission of red or green flares. An excellent discussion of the mechanisms of pyrotechnic color production is found in reports by Douda.<sup>[10,11,12]</sup>” (p 97).

### 5. Lancaster 1972,<sup>[13]</sup> 1992,<sup>[14]</sup> and 1998<sup>[15]</sup>

“Strontium monochloride, barium monochloride and cuprous chloride are the three compounds required for the color production and the excess of chlorine has to be present to ensure their formation”.<sup>[13]</sup> (p 60)

This statement was repeated in the two subsequent editions of this book.<sup>[14,15]</sup>

### 6. McLain 1980<sup>[16]</sup>

“Green flares derive their color from the BaCl<sub>2</sub> emission band. As the temperature rises, the BaO<sup>+</sup> emission band increasingly contributes colors in the orange-to-red portion of the spectrum” (p 89)

“Blue is the most difficult color to achieve and bleaches severely when intensity is raised. The blue color comes from the CuCl<sup>+</sup> emission band.” (p 89)

## 7. Shimizu 1981<sup>[17]</sup>

"The important emitters of firework flames are molecules with the exception of Na atoms. The molecules are produced in quite different forms from the original colour producing materials mixed into the composition. The chemical combination of the emitters are relatively simple and in general are outside the ordinary valency law. For example, they are written as SrCl, BaCl, CuCl, etc. and not SrCl<sub>2</sub>, BaCl<sub>2</sub>, CuCl<sub>2</sub> etc." (p 57)

Pages 59–61 show flame spectra of Sr, Ba, Ca and Cu with and without Cl<sub>2</sub> or HCl. Atomic lines and molecular bands are identified. Figure 47 on page 63 shows the relevant molecular emission bands in relation to the CIE chromaticity diagram.

## 8. Shimizu 1974<sup>[18]</sup> (English translation 1983)<sup>[19]</sup>

"Strontium spectra:

"Strontium salts (carbonate, nitrate, oxalate, etc.) yield the strontium line (4607 Å)..., the SrOH band (5995–6130 Å)..., and the SrCl band ( $\alpha$  = 6170–6230 Å;  $\beta$  = 6270–6350 Å;  $\gamma$  = 6400–6460 Å)". (p 75)

"The strontium line is a fairly intense purple-blue. The SrOH band is an intense red-orange, and it is very important for a red colored flame. Chlorine or hydrogen chloride in the flame lowers the intensity of the SrOH band, because the molecule SrOH is changed into SrCl. The  $\alpha$  and  $\beta$  bands in the SrCl band are bright red and are the most important components of a good red flame. The  $\gamma$  band is very weak and not important. Chlorine or hydrogen chloride in the flame strengthens the SrCl band. Generally hydrogen chloride has a greater effect than chlorine. If the flame has no chlorine or hydrogen chloride, there will be no SrCl band." (p 76)

"Barium spectra:

"Barium salts (carbonate, nitrate, oxalate, chloride etc.) give the following: barium lines at 5535.5 Å (weak yellow-green), 5778 Å (very weak yellow), and 6100 Å (weak orange)...; BaO band at 4854–6330 Å (very complicated shape, ranging from greenish-blue to red); and the BaCl band at 5505 Å to about 5350 Å (deep green). There are three intense bands:  $\alpha$  (5110–5150 Å),  $\beta$  (5245–5280 Å) and  $\gamma$  (5305–5330 Å)

...The barium lines are so weak that they have hardly any effect on the flame color. The BaO band is the most important white light source for illumination. It is reduced by the presence of chlorine or hydrogen chloride in the flame, by changing BaO into BaCl. The BaCl band is the most important green light source, but it is only present if chlorine or hydrogen chloride are in the flame. As with strontium, the effect of hydrogen chloride is greater than that of chlorine." (p 76)

"Copper Spectra

"Copper salts (sulfate, arsenite, Paris green, etc.) and powdered copper metal give a purple-blue band (4026–4058, 4071–4105, 4123–4164, 4201–4219, 4229–4252, 4269–4277, 4290–4323\*, 4340–4343, 4355–4399\*, 4417–4432, 4438–4481\*, 4496–4513, 4526–4560\* Å. ... There is also a band from blue to yellow-green (4590–4608, 4630–4658, 4678–4698, 4724–4747, 4769–4781, 4801–4838, 4850–4863, 4888–4928, 4950–4966, 4989–5037, 5056–5074, 5092–5120, 5151–5169, 5190–5225, 5263–5304, 5285–5429, 5503–5531, and 5628 Å ...). There is another band at 5263–5531 Å... The group of purple-blue bands is the most important factor in the production of a blue flame. The asterisks (\*) denote the most intense bands. The group of bands from blue to yellow-green is very weak and unimportant. These two groups comprise the CuCl band and become very clear when chlorine or hydrogen chloride are in the flame. The CuCl band appears weaker at temperatures of 2500 °K (2227 °C) and higher because of the decomposition of the CuCl molecule. The other band (5263–5531 Å) comes from CuOH molecules. This is visible when there is no excess chlorine or hydrogen chloride in the flame, and it appears as a weak green color, detracting from a blue flame. Generally our blue flames had a red tip. This is attributable to the copper atom or CuO ... the red emissions are very weak and not noteworthy." (p 76)

"Calcium spectra

"Calcium salts such as calcium carbonate give a CaOH band and a CaCl band. The CaOH band... has two portions: an intense red (6105–6270 Å) and intense yellow-green (5500–5580 Å). The CaCl band has four parts: weak red (6294–6360 Å), intense red-orange (6030–6078 Å),

intense orange (5915–5986 Å), and slightly weak yellow (5803–5838 Å). The CaOH band occurs in flames in which no chlorine or hydrogen chloride is present. It is not used by itself for producing colored flames. The CaCl band is used as an orange light source. Chlorine or hydrogen chloride intensify the CaCl bands.” (p 77)

These quotes were taken from Chapter 7, which consists of 40 pages entirely devoted to colored flames. There are 4 pages of flame spectra. Figure 49 on page 823 shows the relevant molecular emission bands in relation to the CIE chromaticity diagram.

## 9. Conkling 1985<sup>[20]</sup>

“The best flame emission in the red region of the visible spectrum is produced by molecular strontium monochloride, SrCl...The SrCl molecule emits a series of bands in the 620–640 nanometer region – the “deep red” portion of the visible spectrum... Strontium monohydroxide, is another substantial emitter in the red and orange-red regions<sup>[10,17]</sup>. The emission spectrum of a red flare is shown in Figure 7.1...the primary emitting species are SrCl and SrOH molecules in the vapor state”.<sup>[21]</sup>

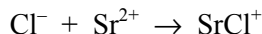
“Pyrotechnic compositions containing a barium compound and a good chlorine source can generate barium monochloride, BaCl, in the flame and the emission of green light will be observed. BaCl –an unstable species at room temperature – is an excellent emitter in the 505–535 nanometer region of the visible spectrum –the ‘deep green’ portion<sup>[10,17]</sup> ... The emission spectrum of a green flare was shown in Figure 4.1 ... molecular BaCl in the vapor state, typically the primary emitter of green light”.<sup>[21]</sup>

“The best flame emission in the blue region of the visible spectrum (435–480 nanometers) is obtained from copper monochloride, CuCl. Flame emission from this molecular species yields a series of bands in the region from 428–452 nanometers, with additional peaks between 476–488 nanometers.”<sup>[10,17]”</sup>

## 10. Akhavan 1998<sup>[22]</sup>

“Red light is produced by adding strontium compounds to the pyrotechnic mixture. At high temperatures the strontium compound breaks

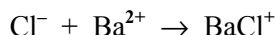
apart and reacts with the chlorine from the oxidizer [i.e. perchlorate ( $\text{ClO}_4^-$ ) molecule] to form  $\text{SrCl}^+$  as shown in Reaction 8.1.



“It is the  $\text{SrCl}^+$  molecule which emits light in the red region of the electromagnetic spectrum, ie. 600–690 nm. Green light is produced by adding barium compounds to the pyrotechnic mixture. Green light is emitted from the  $\text{BaCl}^+$  molecule at 505–535 nm. Blue light is achieved by reacting copper compounds with potassium perchlorate to form  $\text{CuCl}^+$  which emits light in the blue region of the visible electromagnetic spectrum, ie. 420–460 nm”. (p 156)

## 11. Russell 2000<sup>[23]</sup>

“Under the influence of heat, oxidisers such as potassium perchlorate decompose into the chloride and oxygen.... At higher temperatures (>2500 °C) the KCl ionises and the chlorine that is liberated reacts with fragments from barium compounds to form light-emitting species such as BaCl in accordance with...



The main species responsible for the green color of barium flames is BaCl, while contributions are also made from BaO and BaOH as shown in Table 8.1.” (p.70)

(This table, on page 71, shows Ba,  $\text{Ba}^+$ , BaOH, BaO, and BaCl).

“Reference to Table 8.1 shows that in the absence of chlorine-containing species the visible emission is dominated by BaOH, in spite of the fact that the equilibrium concentration of BaOH is many orders of magnitude smaller than that of BaO. The reason for this is that the hydroxide is formed directly in an excited state in a process known as chemiluminescence, as shown by reaction...

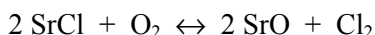


“Here, [BaOH]\* is the excited molecule that releases energy ... that corresponds to the green region of the visible spectrum.” (p 72)

“Strontium chloride has a melting point of 870 °C and exerts a considerable vapour pressure above this temperature. The boiling point of SrCl<sub>2</sub> is 1250 °C and at temperatures above this it dissociates forming strontium monochloride and chlorine...



“At still higher temperatures (the following) reaction ...predominates:



“An excess of chlorine... causes a shift to the left and an improvement in the flame saturation of strontium monochloride. Table 8.3 shows the main emission bands/lines for a red star.” (p 73)

*(This Table, on page 73, shows Sr, SrOH, SrCl, and SrO.)*

“The main species responsible for the blue colour in copper flames is cuprous chloride, CuCl... In order to produce a good blue, the temperature must be controlled to ensure that the largest possible amount of vaporised CuCl is present in the flame. A typical spectrum shows wavelength peaks in the region 420–500 nm attributable to CuCl band spectra, a peak at 770 nm due to atomic potassium from the oxidizer, together with CuOH band spectra between 535 and 555 nm.” (pp 84–85).

## 12. Hardt 2001<sup>[24]</sup>

“Many ionized species exist in the gaseous phase as bi- and tri-atomic molecules which give off molecular band spectra that arise from the ability of the molecule to absorb vibrational and rotational energy. Because molecules have fixed masses, sizes and interatomic spacing their rotational and vibrational energies are also quantized and so can take up and emit energies in discrete wavelengths. To the extent that these band spectra are in the visible range, they are of interest to pyrotechnics... The molecular species that give the best colours are the halides of the alkaline earths and copper” (p 40)

Table 6-2 (p 41) lists a number of metal monohalides, monoxides and monohydroxides

and the wavelengths of some of their visible emission bands. All are neutral. The reference is to Herzberg.<sup>[25]</sup>

## Summary of the Book Survey

The “neutral molecules” opinion is taught by Ellern<sup>[1,7]</sup>, Shidlovskiy<sup>[4]</sup>, Lancaster<sup>[13,14,15]</sup>, Shimizu<sup>[17,19]</sup> and Conkling.<sup>[20]</sup> The “ions” opinion is taught by Cackett<sup>[6]</sup> and Akhavan.<sup>[22]</sup> McLain<sup>[16]</sup> teaches “ions”, but also says that green flames are coloured by the emission band of neutral barium dichloride. Russell<sup>[23]</sup> teaches “neutral molecules”, but gives an equation for the formation of BaCl that shows the formation of BaCl<sup>+</sup>, as if there were no difference. Hardt<sup>[24]</sup> specifically refers to emitters as “ionized species (that) exist in the gaseous phase as bi- and tri-atomic molecules”, but presents a table of emitters that consists entirely of neutral molecules.

Several authors mention the contribution of metal monohydroxides and monoxides to flame colours; this is clearly an important issue in any discussion of coloured flames. It will not be pursued here, however, because it is not relevant to the question of whether or not the metal chloride emitters are ions or neutrals.

## References Cited by the Authors of the Books

### 1. Ellern 1961<sup>[1]</sup>

Ellern cited two references that are relevant to the present subject.<sup>[2,3]</sup>

The writer has not seen the 1953 encyclopedia article by Hart.<sup>[2]</sup> The 1949 paper by Barrow and Caldin<sup>[3]</sup> is very much more important than might be guessed from Ellern’s remarks. Here is a part of what Barrow and Caldin wrote:

“Blue flames. These rely for their colour on emission of the spectrum of CuCl. Most of the light comes from the D and E systems in the range 4200–4600 Å.<sup>[26]</sup> the blue-green systems B and C, and the green system A, are much weaker”. (p 33)

“Green flames. BaCl, which gives rise to a well-known band system at 5050–5350 Å, is the obvious choice for a green emitter and it is in fact

generally used... The spectrograms of such flames...invariably show the extensive band system of BaO (4000–8000 Å). There is also strong emission from the near infra-red system of BaCl<sup>[27]</sup> which, however, lies beyond the visible region of the spectrum. Other discrete bands in the region 7000–7600 Å. have not yet been identified.” (pp 33–34)

“Red flames. Strontium compounds are used to colour the red flames, but there are still some obscure features in the spectra. The simultaneous presence of strontium and chlorine compounds in the compositions leads to strong emission of the red system of SrCl (the violet system also appears weakly). However there are also present two closely-spaced sequences degraded to the violet which do not belong to the SrCl system. The long wavelength edges of these sequences are at 6884.5 and 6114.2 Å. In strontium flames containing no chlorine these heads are more strongly developed, and, in addition, the region between them can be seen to be filled with a very close pattern of what appear to be rotational structure lines. The most likely emitter would seem to be SrO, and it is some support for this suggestion that a heavy-current positive-column discharge through SrO contained in a silica tube leads to the production of the same bands.” (p 34)

Barrow and Caldin, who were academic spectroscopists, clearly teach that the emitters are neutral molecules. The writer has not seen the 1941 edition of Pearse and Gaydon’s book<sup>[26]</sup> that was cited by Barrow and Caldin, but the following quotes from the 1963 edition<sup>[28]</sup> are highly relevant:

“Without exception, flame bands have been found to belong to molecules which are electrically neutral, but very frequently the molecules are not stable in the chemical sense...” (p 322)

“BaCl Green System

“Occurrence. Barium chloride in carbon arc or flame”. (p 77)

“(BaCl) Infra-red System

“Occurrence. In the flame of pyrotechnic compositions.” (p 78)

“BaO

“Occurrence. When barium salts are introduced into carbon arc or flame”. (p 82)

“BaOH

“The strong green coloration of flames containing barium salts has recently been shown to be due to the triatomic hydroxide, not the oxide.” (p 82)

“CuCl

“Occurrence. Five systems have been observed in flames, in fluorescence and in absorption. They also appear when CuCl is introduced into active nitrogen, and in an arc. The bands frequently occur as impurities in flame spectra, especially of CO...The group of pairs of bands formed by systems D and E is quite characteristic. See Plate 10.” (p 152)

“SrCl

“Occurrence. When strontium chloride is introduced into an arc or flame”. (p 294)

“SrO

“Strontium salts give bright red banded radiation in flames and arcs, but the flame bands are mostly due to SrOH.” (p 298)

“SrOH

“These bands are responsible for the strong red colour of flames and fireworks containing strontium.” (p 299)

Pearse and Gaydon<sup>[28]</sup> often give details of the electronic transitions that are associated with the various bands in spectrum of each molecule, with references to the primary spectroscopic literature from the late 1920s to the late 1950s.

Barrow and Caldin’s paper,<sup>[3]</sup> especially when supplemented by the information in Pearse and Gaydon’s book<sup>[28]</sup>, provides very strong support for the neutral molecule position and none whatsoever for the ion position.

## 2. Shidlovskiy 1964 (English translation 1974)<sup>[4]</sup>

Shidlovskiy did not cite specific reference for his statements on the nature of the flame emitters. The writer has not seen the report on German signal flare compositions<sup>[5]</sup> mentioned by Shidlovskiy.

### 3. Cackett 1965<sup>[6]</sup>

Cackett, who was the first to present the “ion” opinion, cited but one reference in his discussion of coloured flames: Barrow and Caldin.<sup>[3]</sup> Cackett did not mention that his identification of the emitters as positive metal monochloride ions was at odds with his cited reference, and he offered no justification for his new identification of the emitters.

### 4. Ellern 1968<sup>[7]</sup>

The two relevant references cited in Ellern’s 1961<sup>[1]</sup> book are cited again in this book, but in a different context. Hart’s encyclopaedia article<sup>[2]</sup> is mentioned as “an authoritative article on military pyrotechnics” in the section covering the literature of pyrotechnics (p 10) but there is no mention of his views on colour emitters. Barrow and Caldin<sup>[3]</sup> are cited in the chapter on colored lights in support of the statement that blue signal lights “seem to be somewhat maligned and deprecated, apparently not so much on optical grounds but because it is difficult and perhaps impossible to create a blue pyrotechnic flame of great depth of color.” (p 123) The contribution of these authors in identifying the emitters is not mentioned.

Ellern also cited five works by Douda.<sup>[8–12]</sup> One of these<sup>[8]</sup> refers to another of Douda’s works<sup>[10]</sup> for a discussion of the theory of coloured flames and one of the others<sup>[9]</sup> is a patent of no direct relevance to the present subject.

Of the remaining three works by Douda, the first<sup>[10]</sup> is a monograph covering all aspects of coloured flame production. It includes references to 18 sources, including five that discuss ionization in flames. Douda attributed the red colour of Sr flames to SrCl and SrOH, and the green of Ba flames to BaCl and BaOH. He explained that addition of halogen to the flame is expected to increase the concentration of the metal hydroxide, and he continued: “In both instances, because the pyrotechnic compositions are usually saturated with the metal and halogen, a very substantial amount of the metal halide will be present in the flame in addition to the hydroxide. The halide formation with barium and strontium is not objectionable because these molecules fortunately also emit energy as de-

fined by their molecular band spectrum in the desired wavelength.” (p 18).

Referring to flames containing copper, Douda wrote “As in the case of barium and strontium, the halogen combines with hydrogen to form the halide acid, thereby causing an OH excess which, in turn, contributes to the formation of more CuOH. Also, as in the case of barium and strontium, although more metal hydroxide is formed, the metal halide is formed in even greater amounts. Because the strontium and barium halides emit in desirable wavelengths, the net result is a quantitative increase of emission in desirable wavelengths. In the case of copper, however, the increase in CuOH is out weighed by the increase in copper halide formation, thus resulting in a shift from CuOH green emission to blue copper halide emission.” (p 22).

The next work of Douda cited by Ellern<sup>[7]</sup> is a technical report<sup>[11]</sup> in which Douda wrote: “Strong BaCl emissions have been reported at 524 mμ and for BaOH at 527 mμ.” (p 6)

“Strong SrCl and SrOH emissions occur in this region” [i.e., around 640 mμ]. (p 6)

“BaCl and BaOH dominate in green barium flames.” (p 6)

“SrCl and SrOH dominate in red strontium flames”. (p 6)

The last work of Douda cited by Ellern<sup>[7]</sup> is a paper<sup>[12]</sup> on green flares. Douda wrote:

“In the presence of chlorine, the suppression of MgO and BaO flame emission is a decreasing function of effective temperature, and the ratio BaO/BaCl is an increasing function of effective temperature accompanied by a shift of hue toward yellow and a reduction in excitation purity. By analogy with dissociation constants reported for BaF and BaOH, the dissociation energy of BaCl is estimated to be near 100 kcal/mole. Such an increased value more readily accounts for the sizable BaCl emission observed at a brightness temperature of 2200 K and an effective emitting temperature of 2700 K. Evidence concerning the contribution of BaOH is inconclusive. The 107 kcal/mole dissociation energy in comparison with the 100 kcal/mole estimated for BaCl suggests that BaOH should also be a substantial contributor.” (p 793)

## 5. Lancaster 1972,<sup>[13]</sup> 1992,<sup>[14]</sup> and 1998<sup>[15]</sup>

Lancaster did not cite specific references for his statement about colour emitters. His first edition<sup>[13]</sup> has a list of 23 references including the first (Russian, 1943) edition of Shidlovskiy, both of Ellern's books<sup>[1,7]</sup> and a 1957 Japanese-language book by Shimizu.<sup>[29]</sup> The second edition has 40 references, including all of those in the first edition. Relevant additions include both of Shimizu's books discussed above,<sup>[17,19]</sup> the books by McLain<sup>[16]</sup> and Conkling,<sup>[20]</sup> and to *Pyrotechnica*.<sup>[30]</sup> The third edition of Lancaster's book<sup>[15]</sup> has 76 references, but none of those added since the second edition appear to be relevant to the present topic.

## 6. McLain 1980<sup>[16]</sup>

McLain did not cite specific reference for his statements quoted above. His chapter on "Light" has a list of 14 references including Ellern,<sup>[7]</sup> Shidlovskiy,<sup>[4]</sup> Cackett,<sup>[6]</sup> Lancaster<sup>[13]</sup> and a work by Douda<sup>[31]</sup> that deals with the characteristics of the spectra of magnesium-sodium nitrate-binder illuminating flares. McLain adopted the ion teaching of Cackett, despite the opposing views of Ellern, Shidlovskiy, Lancaster and Douda. It is noteworthy that Douda's writings on coloured flames<sup>[10,11,12]</sup> were not cited by McLain.

## 7. Shimizu 1981<sup>[17]</sup>

Shimizu did not cite specific reference for his statements quoted above. His book has a list of 13 references including Ellern,<sup>[7]</sup> Shidlovskiy,<sup>[4]</sup> Lancaster,<sup>[13]</sup> and three of his own books.<sup>[29,18,32]</sup> He also lists *Pyrotechnica* Issues I–IV.<sup>[30]</sup>

## 8. Shimizu 1974<sup>[18]</sup> (English translation 1983)<sup>[19]</sup>

In this work Shimizu listed 11 references concerning flame spectra. These include Pearse and Gaydon's book,<sup>[28]</sup> along with 10 references to the primary spectroscopic literature. Many of these refer to oxide and monohydroxide emitters, but four deal specifically with the spectra of neutral metal monohalides.<sup>[33–36]</sup>

## 9. Conkling 1985<sup>[20]</sup>

As indicated above, Conkling cited specific references for his statements. As well as works of Douda<sup>[10]</sup> and Shimizu<sup>[17]</sup> that have already been discussed, Conkling cited a 1983 report by Webster.<sup>[21]</sup> The writer has not seen this report, but Webster published a paper<sup>[37]</sup> having the same title in 1986 and this presumably contains much the same information. It includes emission spectra of red, green and yellow flares. Webster wrote:

"The primary emitting species in the red flare are SrCl and SrOH. Emission bands from the SrCl  $A^2\Pi \rightarrow X^2\Sigma^+$  system are observed at 661.4 nm, 662.0 nm 674.5 nm and 675.6 nm. Emission from the SrCl  $B^2\Sigma \rightarrow X^2\Sigma^+$  system is observed at 623.9 nm, and 648.5nm. The band in both these systems show sharp band heads and are degraded to the violet. ...Bands from the SrCl  $C^2\Pi \rightarrow X^2\Sigma^+$  system were observed at 393.7 nm, 396.1 nm and 400.9 nm. Molecular emission from the SrOH band system (was) observed...at 605.0 nm, 646.0 nm, 659.0 nm, 667.5 nm and 682.0 nm. The bands at 646.0 nm, 659.0 nm and 667.5 nm overlap the SrCl bands at these wavelengths. This makes the SrCl bands appear stronger and more diffuse than would normally be expected." (p 2)

"The primary emitting species in the green flare are BaCl and BaO. Emission bands from the BaCl  $C^2\Pi \rightarrow X^2\Sigma^+$  system are observed at 507 nm, 514 nm 524 nm and 532 nm. The molecular BaCl emission is superimposed on less intense, but equally important BaO, BaOH and Ba<sub>2</sub>O<sub>2</sub> band emission extending from 460 nm to 678 nm. This emission, coupled with an underlying continuum from hot solid particles, is the contributing factor to the loss of color purity in the flare. The ...flare composition also contains copper and the resulting CuCl emissions are observed from 412 nm–470 nm." (p 3) Webster cited the following references: Douda,<sup>[12,38]</sup> McLain,<sup>[16]</sup> Shimizu,<sup>[17]</sup> Barrow and Caldin.<sup>[3]</sup> and Ellern.<sup>[7]</sup> All of these have already been discussed, except Douda's 1972 paper<sup>[38]</sup> on the spectrum of a red highway flare. Douda wrote:

"The dominant emitting species are strontium oxide and the flame radicals SrCl and SrOH, the radicals being strong emitters<sup>[39,28]</sup> in the red region. The strong band systems with maxima



near 606, 646, 659, 669 and 682 nanometers are due mainly to emission from SrOH and SrCl.” (pp 416–417) Reference <sup>[39]</sup> deals with magnesium-metal nitrate flares with no chlorine donors and is only marginally relevant to the present discussion.

#### 10. Akhavan 1998<sup>[22]</sup>

Akhavan cited no specific references for her statements. Her bibliography includes Conkling<sup>[20]</sup> and Ellern<sup>[7]</sup>.

#### 11. Russell 2000<sup>[23]</sup>

Russell cited no specific references for his statements. His bibliography includes Ellern<sup>[7]</sup>, McLain<sup>[16]</sup> and Lancaster<sup>[15]</sup>.

#### 12. Hardt 2001<sup>[24]</sup>

Hardt did not cite specific references for his statements, but he cited Hertzberg<sup>[25]</sup> for the information presented in his Table 6-2. Hardt’s bibliography contains over 270 references, up to the year 1999. These include 14 works by Douda but of these only one<sup>[10]</sup> is clearly relevant to the present topic. Another of the cited works of Douda<sup>[40]</sup> deals with the emission spectra of flares but is concerned only with magnesium-sodium nitrate-binder illuminating flares.

### Evidence That the Metal Monochloride Emitters Are Neutral Molecules, Not Ions

- 1) The spectra of the neutral metal monochlorides are very well known to spectroscopists. For example, in 1979 Huber and Hertzberg<sup>[41]</sup> published a volume of spectroscopic constants for all known diatomic molecules and ions, covering the literature up to 1975. They cited 14 references for data on BaCl, 14 for CaCl, 15 for CuCl and 11 for SrCl. More recently an on-line data base of references associated with the spectra of diatomic molecules<sup>[42]</sup> contained, in January 2004, 36 papers associated with the spectrum of BaCl, 61 for the CaCl spectrum, 50 for the CuCl spectrum, and 19 for the SrCl spectrum. All of these papers have been published since 1974.

- 2) The Ca, Sr and Ba monochlorides are members of a rather large family of univalent alkaline earth compounds that exist at high temperatures and that have been characterized spectroscopically in recent years.<sup>[43]</sup> The alkaline earth monohydroxide emitters are members of this same group of compounds.<sup>[43]</sup>
- 3) The electronic states of the metal monochlorides have been calculated from quantum mechanics. The predicted spectra are in good agreement with those measured experimentally. See, for example, the comparison of calculated results for the CuCl molecule with experimental results by Parekunnel et al.<sup>[44]</sup>
- 4) The number of electrons in an emitter can be determined from the characteristics of the spectrum.<sup>[45]</sup> Each electron carries half a unit of angular momentum (“spin”) that can have one of two directions, corresponding to a spin of plus or minus ½ a unit in some reference direction. If two electrons of opposite spin “pair up”, the spins cancel; if an atom or molecule has one or more unpaired electrons, the resulting electron spin interacts with the angular momentum associated with the movement of electrons around the atom or molecule and changes the energy of the electrons. If there is no unpaired electron, the electronic energy state is unaffected by electron spin. Such a state is called a “singlet”. If there is a single unpaired electron, its spin can either add to, or subtract from, the component of the angular momentum of the electronic energy states in the reference direction, with the proviso that the resulting angular momentum must always be positive. Consequently, a state having an angular momentum component in the reference direction of 1 unit is split into two, one of the new states having angular momentum of ½ unit and the other 1½ units. Such a state is called a “doublet”. Two unpaired electrons result in an electronic energy state splitting into three, called a “triplet”. In general, the *multiplicity* of a state is one more than the number of unpaired electrons. If an atom or molecule has an even number of electrons, the multiplicity of all its electronic energy levels must be odd, and conversely. An obvious example of the effect of multiplicity on an electronic

spectrum is provided by the sodium atom, which has a single unpaired electron. The “doublet” nature of the electronic energy states of atomic sodium is revealed by the familiar yellow line in the spectrum of atomic sodium actually consisting of two lines.

The characteristics of molecular spectra that indicate the multiplicity of the emitter are more subtle. The analysis involves careful study of the rotational structure of the various bands and is possible only with spectra recorded at very high resolution. Details are given by Gaydon<sup>[46]</sup> and by Herzberg.<sup>[25,45]</sup> Analysis of the spectra of the alkaline earth monochlorides reveals that the electronic energy states are doublets.<sup>[28,34,47]</sup> This means that there is an odd number of electrons in the emitter, which is the case for the neutral monochloride molecules but not for the ions. Similarly, the spectrum of copper monochloride<sup>[44]</sup> reveals singlet and triplet states, showing that the emitter has an even number of electrons. This is consistent with the emitter being neutral copper monochloride but not with it being the ion.

- 5) Thermodynamic modeling of the combustion of coloured flame compositions<sup>[48,49]</sup> has shown the presence of neutral metal monochlorides in the predicted equilibrium mixture of combustion products, consistent with the observed emission spectra.
- 6) The ions  $\text{CaCl}^+$ ,  $\text{SrCl}^+$  and  $\text{BaCl}^+$  would presumably have exactly the same electronic structure as the molecules  $\text{KCl}$ ,  $\text{RbCl}$  and  $\text{CsCl}$  respectively. The alkali chlorides do not exhibit visible spectra<sup>[25, 41]</sup> and it is expected that the same would be true of the alkaline earth monochloride ions.<sup>[50]</sup> Huber and Herzberg<sup>[41]</sup> and the DiRef<sup>[42]</sup> database list no spectroscopic data for  $\text{CaCl}^+$ ,  $\text{SrCl}^+$ ,  $\text{BaCl}^+$  or  $\text{CuCl}^+$ . Hildenbrand<sup>[51]</sup> measured the ionization energies of  $\text{CaCl}$ ,  $\text{SrCl}$ ,  $\text{BaCl}$  and  $\text{CuCl}$  by mass spectrometry, using electron impact ionization. Results, expressed as the appearance potential for each  $\text{MCl}^+$  ion from the corresponding  $\text{MCl}$  precursor molecule, are shown in Table 1.

**Table 1. Ionization Energies of  $\text{CaCl}$ ,  $\text{SrCl}$ ,  $\text{BaCl}$  and  $\text{CuCl}$ .<sup>[51]</sup>**

Ion	Appearance potential (eV)
$\text{CaCl}^+$	$5.6 \pm 0.5$
$\text{SrCl}^+$	$5.3 \pm 0.5$
$\text{BaCl}^+$	$5.0 \pm 0.5$
$\text{CuCl}^+$	$10.7 \pm 0.5$

The ionization energy of  $\text{CuCl}$  is so high that only a very small fraction of any population of  $\text{CuCl}$  molecules present in a flame could possibly be ionized at flame temperatures. Furthermore, only a tiny fraction of those ions would be excited at flame temperatures. The number of emitting ions at flame temperatures would therefore be exceedingly small. This consideration alone is sufficient to rule out the possibility that  $\text{CuCl}^+$  could be a significant emitter of light in a pyrotechnic flame.

## Conclusion

The metal monochloride spectra that contribute to the colours of pyrotechnic flames are emitted by neutral metal monochloride molecules,  $\text{MCl}$  where  $\text{M}$  is  $\text{Ba}$ ,  $\text{Ca}$ ,  $\text{Cu}$  or  $\text{Sr}$ . This was clearly stated by Barrow and Caldin<sup>[3]</sup> as long ago as 1949 and has been confirmed since by Douda,<sup>[8–12,39–41]</sup> Shimizu,<sup>[17–19]</sup> and Webster.<sup>[21,37,47]</sup> The idea that the emitters are singly-charged metal monochloride ions ( $\text{MCl}^+$ ) is erroneous, and can be traced to the 1965 book by Cackett.<sup>[6]</sup> At the time that Cackett wrote his book, no spectra of the monohalide ions of  $\text{Ba}$ ,  $\text{Ca}$ , or  $\text{Sr}$  had been reported in the scientific literature,<sup>[41]</sup> none have been reported since<sup>[42]</sup> and there are good reasons for expecting that these ions would not emit visible spectra.<sup>[50]</sup> Similarly, there are no reports of spectra of  $\text{CuCl}^+$ ,<sup>[41,42]</sup> the high ionization energy of this ion<sup>[51]</sup> make it most unlikely that it could exist in a flame in sufficient numbers to contribute in any significant way to the emission of light by the flame.

## A Note on Nomenclature

The neutral MCl, etc. molecules are referred to herein as “neutrals”. Douda<sup>[38]</sup> used the term “radicals” for SrCl and SrOH. This terminology was not adopted here, because Herzberg<sup>[46]</sup> used “radicals” to include all short-lived species, including molecules and ions.

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