Review of

Selected Pyrotechnic Publications of Dr. Takeo Shimizu, Part 3: Studies on Fireworks Colored-Flame Compositions

Dr. Takeo Shimizu

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This latest volume in the Pyrotechnic Literature Series presents a series of papers on work done by Dr. Shimizu in 1958 at the Hosoya Fireworks Company. Originally published in the *Journal of the Industrial Explosives Society, Japan*, the papers have been translated into English for this publication. Dr. Shimizu himself translated all but one of them. Even though this work is about 40 years old, it is by far the most complete and authoritative on the subject. This extensive volume (120 pages) will be of great interest for anyone wanting to acquire a scientific understanding of colored pyrotechnic flames. Those of a more practical inclination will find many formulas for colored flame compositions, nearly always with extensive detail on the effects of varying the proportions of the ingredients.

The work begins with a theoretical discussion of the line-reversal method of measuring the temperature of a flame. Unfortunately a typographical error in the initial explanation of the method will be confusing to those new to the subject. No doubt this will be corrected in future printings. The diagram on page 2, which illustrates this section, is correct.

In the following chapter, Dr. Shimizu presents the results of applying the line-reversal method to the measurement of the flame temperatures of burning firework compositions. The conclusions of this work have been published briefly elsewhere;[1a] this paper gives all the detail that is so characteristic of Dr. Shimizu's work.

Dr. Shimizu next discusses the spectra of colored pyrotechnic flames. The first paper in this section focuses on the spectral features observed in the flames of compositions without added color-producing agents. These background spectra contribute to the color of the flame, usually to its detriment. Dr. Shimizu identifies the intense yellow emission from sodium (present in impurities) and continuous "black body" spectra from incandescent particles as the main background features that detract from the color of pyrotechnic flames. The spectral backgrounds of the various flames are discussed in detail and approaches to reducing the backgrounds are explained.

The next paper treats red, yellow and green firework flames. Spectra of flames from compositions containing salts of strontium, sodium, barium and calcium are presented and discussed. At the time this work was being done academic spectroscopists were studying colored flames with the aim of identifying the molecules responsible for the characteristic spectral features. In an author's note, Dr. Shimizu relates the findings of one such study[2] to his own observations and his earlier conclusions. The spectral bands he originally attributed to gaseous strontium monoxide (SrO) turned out to come instead from strontium monohydroxide (SrOH) and strontium monochloride (SrCl). Dr. Shimizu correctly identified the main species responsible for the green color of barium flames as barium monochloride (BaCl). He correctly points out that gaseous barium monoxide (BaO) produces emission bands over most of the visible spectrum, coloring the flame white.[3a] Gaseous barium monohydroxide (BaOH, not mentioned by Dr. Shimizu) has green emission bands that overlap those of BaCl and extend further towards the blue end of the spectrum.[4] Presumably, their presence would not detract from the color of a green flame. In practice, the production of a clear green flame entails maximizing the emission of BaCl and minimizing that of BaO. Dr. Shimizu notes that pyrotechnic flames colored with calcium compounds can range from nearly red to yellowish. The color depends on the relative intensities of the red and orange bands from calcium monochloride (CaCl) and the green and orange bands that Dr. Shimizu attributes to calcium monoxide (CaO) but which spectroscopists have shown to come from calcium monohydroxide (CaOH).[3b,5]

Flames colored with sodium salts derive their yellow color from the pair of sodium atomic emission lines at 589.0 and 589.6 nanometers. The color is strongly influenced by the presence of a background of continuous radiation. In high temperature flames this can be so intense that the flame is a yellowish-white color. In cooler flames containing potassium salts, the flame appears reddish yellow; with ammonium perchlorate, "the flame looks pure yellow".

Dr. Shimizu devotes an entire chapter to blue firework flames. He begins with a description of what happens when a copper wire is introduced into the flame of a gasoline burner, with and without the introduction of hydrogen chloride or chlorine gas. Three colors are seen: blue, light green and red-orange. The last, writes Dr. Shimizu, "always appears at the tip of the flame. Therefore it may be caused by CuO due to the oxygen in the air". The correctness of this suggestion is supported by the spectroscopy literature, which lists a series of bands from CuO in the orange-red region of the spectrum.[3c] Dr. Shimizu writes, "It is well known that blue flames come from CuCl band spectra. However where does the light green come from? Perhaps the emitter has a different structure from that of the blue." Once again Dr. Shimizu's suggestion is confirmed by the spectroscopists, who attribute the green emission to CuOH.[6] The problem of creating a satisfactory blue flame is essentially that of maximizing the intensity of the CuCl spectrum in the flame. Dr. Shimizu demonstrates how this can be done with compositions using ammonium perchlorate and potassium perchlorate, and he explains the great superiority of the former. The effect of various chlorine donors is also discussed, and the difficulty of achieving a satisfactory blue flame with high-temperature compositions based on magnesium is explained.

A short chapter discusses the flame spectra of high-temperature compositions that contain aluminium instead of magnesium. The behavior of the two metals is very different, with aluminium tending to form sparks. Dr. Shimizu suggests that the difference is associated with the higher melting point of aluminium. The context indicates that *boiling* point is intended ("the vaporization of aluminium in the flame is not complete"). The melting points of the two metals are similar (660.4 ºC for Al, 648.8 ºC for Mg) but their boiling points are very different (2467 ºC for Al, 1107 ºC for Mg).[7] In the text the melting points are given as 1800 ºC for Al and 1100 ºC for Mg. These are incorrect, and the value quoted for Al would also be incorrect for the boiling point. Dr. Shimizu comments on the beauty of the sparks produced from some of the mixtures he tested. He notes that the best color effects were produced with lower percentages of aluminium in the composition, but "the effects are much less than when magnesium is used in the compositions". The conclusion is "it is difficult to obtain good colored flames when using aluminium as the fuel".

The final paper discusses compositions for practical use. This chapter alone would be worth the price of the book. The results of the previous chapters are summarized, and examples of effective compositions are presented. An enormous amount of work must have gone into making and testing all these compositions. In nearly every case triangle diagrams show the range of components that can produce effective results. An exception is the final composition given, that "burns with a beautiful blue when the diameter is more than 20 mm". This composition is most unusual, consisting of barium nitrate, magnesium, hexachloroethane and copper powder. A similar mix of the first three ingredients is reported to make a "very good" *green* flame.[8] It is interesting that a rather small variation, with the addition of only 5 additional percent of copper powder, can make "a superior blue".

The publication includes a biography of Dr. Shimizu, compiled by Craig Villeneuve. This, consisting largely of an autobiography that Dr. Shimizu provided to Mr. Villeneuve in response to a request for information about his life and influences, provides a nice balance to the technical material presented in the rest of the volume.

A few apparent errors were noticed. Some have already been mentioned; it is also worth noting that on page 57, column 2, paragraph 5, line 2, "strontium sulfate" appears where it seems that "strontium nitrate" was intended. Strontium sulfate is almost insoluble in water and could not be used in the preparation of strontium carbonate as described. Strontium nitrate would be perfectly satisfactory. Several of the Figures in Chapter 7 show "C_6Cl_6" (i.e., hexachlorobenzene) while the text refers to hexachloroethane (C_2Cl_6) and never to hexachlorobenzene. Presumably the Figures should show "C_2Cl_6".

Table 10, page 29, lists color agents tested with ammonium perchlorate. The list includes strontium chlorate and barium chlorate; these could well be misprints. It would be dangerous to mix chlorates with ammonium perchlorate.[1b] In the continuation of table 10 on page 30, barium chloride is listed, not barium chlorate, but sodium chlorate appears where sodium chloride was listed on page 20. It is very likely that "chloride" was intended, not "chlorate", throughout Table 10.

This publication is an important contribution to the literature of pyrotechny. It is highly recommended to all those interested in the scientific and technical aspects of colored pyrotechnic flames.

References

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2) M. Charton and A. G. Gaydon, "Band Spectra Emitted by Strontium and Barium in Arcs and Flames", *Proceedings of the Physical Society A*, Vol. 69, 1956, p 520.
3) R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, 3rd ed., Chapman & Hall, London, 1963; [a] p 82; [b] p 136; and [c] p 157.
4) C. G. James and T. M. Sugden, "New Identification of the Flame Spectra of the Alkaline-Earth Metals", *Nature*, Vol. 175, 1955, pp 333–334.
5) J. van der Hurk, Th. Hollander and C. Th. J. Alkemade, "Identification of the Emit-

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7) R.C. Weast, Ed. , *CRC Handbook of Chemistry and Physics*, 63rd ed., CRC Press, Boca Raton, FL, 1982–83.

8) *Experiments in Developing Green Flare Formulas*, U.S. Naval Ammunition Depot, Crane, Indiana. Publication AD 632 683, National Technical Information Service, Springfield, VA, 1959, p 5, formula no. 30.