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VISIBLE SPECTRA OF STANDARD NAVY COLORED FLARES

HENRY A. WEBSTER III

15 August 1983

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SUMMARY

The visible spectra, color data and output powers from standard Navy red, green and yellow signal flares are presented. The spectra were taken under essentially identical conditions on actual in-service Navy devices. The dominant emissions accounting for the output power in the flares are from the molecular bands of the alkaline earth oxides, hydroxides and chlorides in the red and green flares and from atomic sodium in the yellow flare.

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INTRODUCTION

A recent search of the open pyrotechnics literature has shown the unavailability of the visible spectra of common in-service military colored flares. The visible spectrum of a highway red flare, similar in composition to the military red flare, has been published by Douda.¹ A new book by McLain has no visible spectra.² The most recent book in the field of pyrotechnics by Shimizu presents block diagram spectra of pyrotechnic flame emitters but no actual flare spectra.³ Earlier studies have presented emission studies of special selected pyrotechnic flames but none of actual pyrotechnic devices.^{4,5}

The purpose of this report is to present the actual flame spectra of in-service Navy pyrotechnic colored flares. These spectra were all taken on the same spectrograph under essentially identical conditions.

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1. B. E. Douda, *Am. J. Optom. and Arch. Am. Acad. Optom.* 49, 415 (1972).
 2. J. H. McLain, "Pyrotechnics," (Franklin Institute Press, Philadelphia, 1980).
 3. T. Shimizu, "Fireworks: The Art, Science and Technique," (Takeo Shimizu, Tokyo, Japan, 1981).
 4. B. E. Douda, *J. Opt. Soc. Am.* 55, 787 (1965).
 5. R. F. Barrow and E. F. Caldin, *Proc. Phys. Soc.* (London), B62, 32 (1949).

EXPERIMENTAL*

The flares burned in these experiments were standard Navy colored flare units. The red flares were Mk 124 Mod 0 Marine Smoke and Illumination Signals (MSIS). The green flares were Mk 117 Mod 0 Marine Smoke and Illumination Signals. The yellow flares were Mk 118 Mod 0 Marine Smoke and Illumination Signals. The flare compositions for these signals are given in Table 1. Data were taken for ten to twenty flare burns.

The flares were burned face-down at a distance of four meters from the spectrograph. No attempt was made to isolate any specific area in the flame. Visible spectra were taken with a Spex Model 1802 one-meter grating spectrograph. This spectrograph has a 1200 groove/mm grating blazed at 500 nm and gives a dispersion of 0.8 nm/mm in the first order in the region from 400 - 680 nm. Kodak Type 1-F and 103-F spectrographic plates were used for recording the spectra. The spectra were scanned and digitized on an Optronics S-2000 densitometer, and the film density was converted to radiant and luminous power readings using standard techniques.

Measurements of dominant wavelength, purity and candlepower were made with the Hunter tri-stimulus colorimeter currently used for all colored flare testing programs. This instrument

*In order to specify procedures adequately, it has been necessary occasionally to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the Navy, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

TABLE 1 - NAVY COLORED FLARE COMPOSITIONS

	<u>Mk 124</u> <u>RED</u>	<u>Mk 117</u> <u>GREEN</u>	<u>Mk 118</u> <u>YELLOW</u>
Magnesium, MIL-M-382	24.4	21.0	30.3
Potassium Perchlorate, MIL-P-217	20.5	32.5	21.0
Strontium Nitrate, MIL-S-20322	34.7	----	----
Barium Nitrate, MIL-B-162	----	22.5	20.0
Polyvinyl Chloride, MIL-P-20307	11.4	12.0	----
Sodium Oxalate, JAN-S-210	----	----	19.8
Copper Powder, MIL-C-768	----	7.0	----
Asphaltum, MIL-A-356	9.0	----	3.9
Binder, MIL-STD-708	----	5.0	5.0

has four filter/detector combinations designed so that the filter plus detector response curves match as closely as possible the CIE color-matching functions \bar{x} , \bar{y} and \bar{z} . Measurements from each detector then give the tri-stimulus values X, Y and Z which are defined as:

$$X = k \int I(\lambda) \bar{x}(\lambda) d\lambda$$

$$Y = k \int I(\lambda) \bar{y}(\lambda) d\lambda$$

$$Z = k \int I(\lambda) \bar{z}(\lambda) d\lambda$$

where k is a normalization constant and $I(\lambda)$ is the intensity of the source at wavelength λ . The chromaticity coordinates, x and y, can be calculated using X, Y and Z. The values of dominant wavelength and purity are then determined by a standard graphical method after plotting the chromaticity diagram.⁶ The average experimental error in dominant wavelength is ± 2 percent and in excitation purity is ± 5 percent. The Hunter cell which gives the tri-stimulus value of Y is calibrated against an NBS traceable standard lamp to give the value of candlepower. The experimental error in candlepower is ± 7 percent.

RESULTS

The visible radiant power spectra of the Mk 124 MSIS red flare, the Mk 117 MSIS green flare and the Mk 118 MSIS yellow flare are shown in Figures 1, 2 and 3, respectively. Each spectrum is normalized to a value of one at its maximum. Approximately five spectra were taken during each flare burn.

6. D. B. Judd and G. Wyszecki, "Color in Business, Science, and Industry," Third Edition, (John Wiley and Sons, Inc., New York, 1975), pp. 170-172.

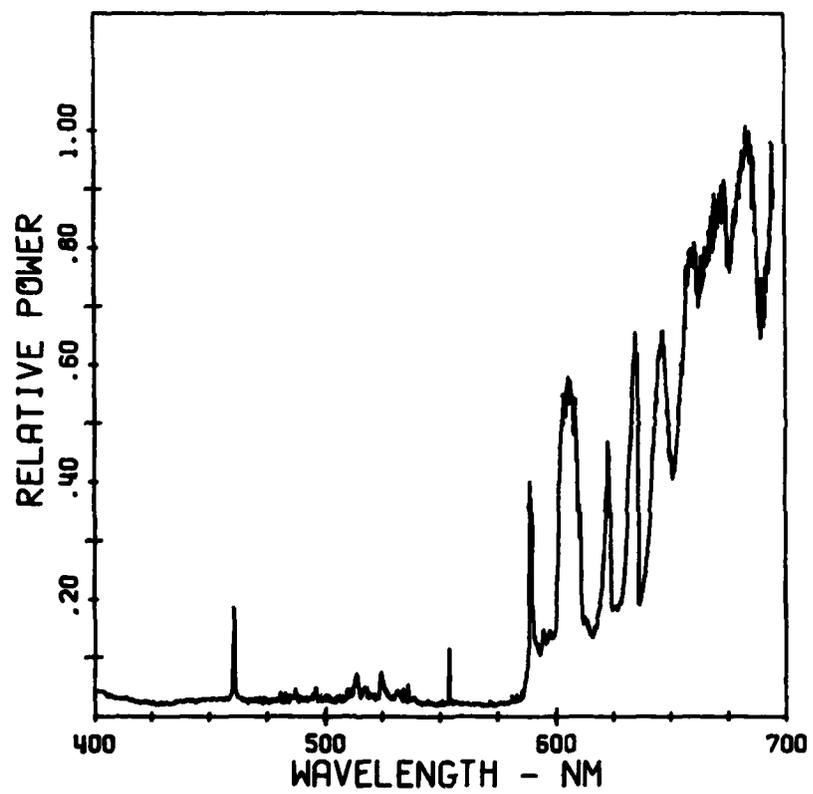


Figure 1. Radiant Power Spectrum for Mk 124 Red Flare

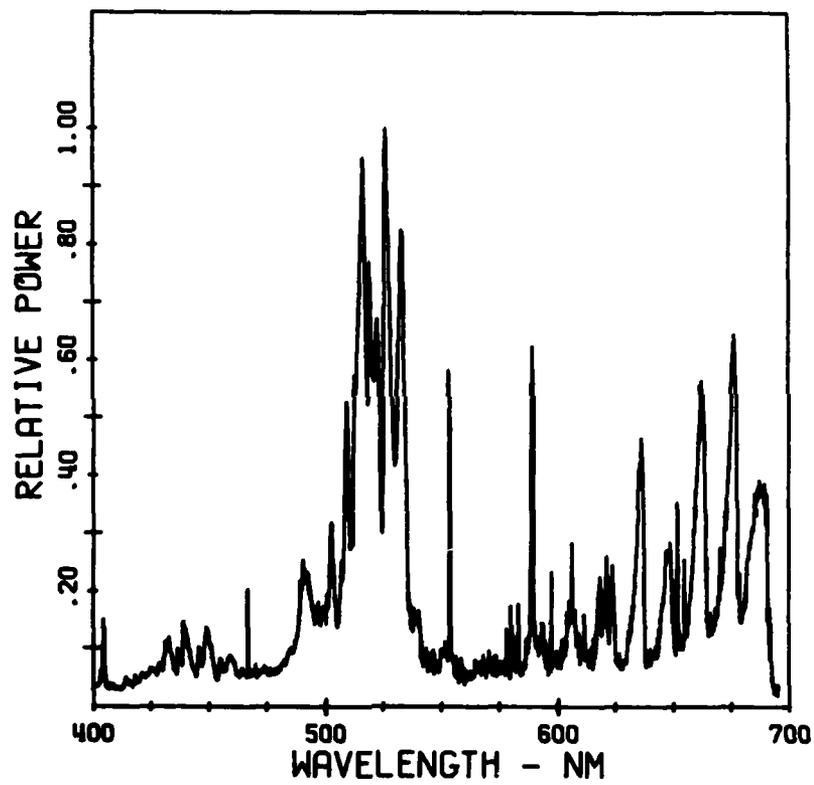


Figure 2. Radiant Power Spectrum for Mk 117 Green Flare

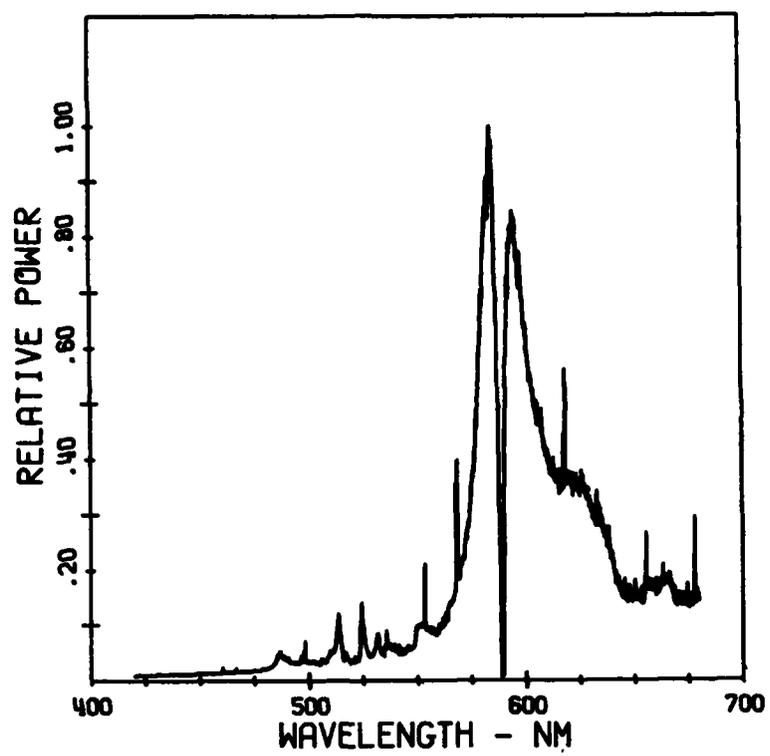


Figure 3. Radiant Power Spectrum for Mk 118 Yellow Flare

Figures 1-3 represent a single flare spectrum and were selected as being representative of the entire group of spectra taken. Little deviation was observed among individual flare spectra taken within a single burn and also among spectra from different flares.

The average luminous intensity for the Mk 124 Mod 0 MSIS was 8700 cd and the burn time was 18.5 seconds for a flare weight of 24 grams. The average dominant wavelength was 610 nm and the excitation purity was 96 percent. The flare color appeared red to the eye.

The average luminous intensity for the Mk 117 MSIS was 19400 cd and the burn time was 26 seconds for a flare weight of 140 grams. The average dominant wavelength was 558 nm and the excitation purity was 47 percent. The flare color appeared greenish-white to the eye.

The average luminous intensity for the Mk 118 MSIS was 29100 cd and the burn time was 35 seconds for a flare weight of 140 grams. The average dominant wavelength was 584 nm and the excitation purity was 82 percent. The flare color appeared yellowish-white to the eye.

DISCUSSION

Mk 124 Mod 0 MSIS Red Flare

The radiant power spectrum of the Mk 124 Mod 0 MSIS red flare is shown in Figure 1. 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, 636.2 nm, and 648.5 nm. The bands in both these systems show sharp band-heads and are degraded to the violet. Although they are not shown in Figure 1, emission 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 is observed in Figure 1 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 those wavelengths. This makes the SrCl bands appear stronger and more diffuse than would normally be expected.

Atomic emission is observed at 460.7 nm from strontium, 553.5 nm from barium and 589.0 nm and 589.6 nm from sodium. Also apparent in Figure 1 are molecular emission bands at 513.8 nm, 516.2 nm, 524.1 nm and 532.1 nm from the $C^2\Pi \rightarrow X^2\Sigma$ system in BaCl. The barium and sodium are present only as impurities. Atomic emission lines from potassium are present throughout the visible spectrum but are not strong enough to appear in Figure 1. Emission bands from SrO in the region from 400 - 470 nm are not observed.

In order to evaluate the major contributors to the perceived color of the flare it is necessary to convert the radiant power spectrum shown in Figure 1 to a luminous power spectrum. This is done by applying the CIE color-matching function, \bar{y} , to the radiant power spectrum.⁶ When this is done it is found that the primary emitter in the red flare is the SrOH molecule. The SrCl and SrOH bands above 650 nm do not contribute significantly. Their major effect is to shift the dominant wavelength to slightly longer wavelengths. The hydrogen needed to form the SrOH comes primarily from the decomposition of the polyvinyl chloride. If one wanted to increase the dominant wavelength (and thus make the light appear redder), a donor such as polytetrafluoroethylene could

conceivably be substituted for the polyvinyl chloride. The primary emitter would then be SrF which has emission bands from 628 - 688 nm. However, the success of the current composition leaves little to be desired.

This spectrum can be compared to the spectrum reported by Douda of a red highway flare used by motorists for emergency signaling.¹ The red highway flare has a formula that is typically 74% strontium nitrate, 6% potassium perchlorate, 10% sulfur and 10% grease, wax and other ingredients.⁷ The spectrum for the highway flare is similar to the spectrum obtained for the Mk 124 MSIS. The primary emission is from SrOH at 606 nm with some contribution from SrOH bands at 646 nm, 659 nm, 668 nm and 682 nm. These bands all overlap the SrCl band regions, making it difficult to determine the extent to which SrCl adds to the overall emission. The spectrum of the highway flare does show a band at 636 nm which could be assigned to SrCl. The band at 624 nm is not present in the highway flare. This fact, coupled with the very small amount of chlorine available in the formula, leads to the conclusion that emission from SrCl does not make a significant contribution to the total power obtained in the highway flare.

Mk 117 Mod 0 MSIS Green Flare

The radiant power spectrum of Mk 117 Mod 0 MSIS green flare is shown in Figure 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.

7. H. Ellern, "Military and Civilian Pyrotechnics," (Chemical Publishing Company, Inc., New York, 1968), p. 362.

The molecular BaCl emission is superimposed on less intense, but equally important BaO, BaOH, and Ba₂O₂ band emissions 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 this flare. The Mk 117 flare composition also contains copper and the resulting CuCl emissions are observed from 412-470 nm.

The most interesting part of this spectrum are the emission bands at 624 nm, 636 nm, 648 nm, 662 nm, and 675 nm. These bands are a result of SrCl emission and are not a part of any barium atomic or molecular emission system. The strontium is most likely present as an impurity in the barium nitrate. While emissions from impurity constituents are quite common in pyrotechnic flares, they are usually a negligible part of the total emission. The most common impurity is sodium which seems to be present in almost all compositions. However, even with its excellent emission properties, as an impurity it seldom accounts for more than 1% of the total power. The molecular emission from SrCl in the case of this flare accounts for almost 22% of the total radiant power. When the radiant power spectrum is converted to luminous power the significance of this added emission is greatly reduced. The added SrCl emission does, however, tend to increase the dominant wavelength and reduce the color purity further complicating the manufacture of a good green signal. It should also be pointed out that this SrCl emission is not an isolated event but is observed in all compositions containing barium nitrate and a chlorine donor.

Mk 118 Mod 0 MSIS Yellow Flare

The radiant power spectrum of the Mk 118 Mod 0 MSIS yellow flare is shown in Figure 3. The primary emitting species in the yellow flare is atomic sodium. The emission appears as the reversed and broadened sodium resonance lines at 590 nm. The broadening at half intensity is 25 nm which is theoretically consistent with a flame temperature slightly lower than the magnesium-sodium nitrate flare and a 20 percent sodium oxalate concentration.⁸

The sodium resonance lines are superimposed on a background continuum resulting from a combination of graybody emission and molecular emission from barium oxide, barium hydroxide and barium chloride (BaCl). Barium hydroxide emissions are observed at 487 nm and 512 nm. Barium chloride emissions are observed at 514 nm, 524 nm and 649 nm. The other barium oxide emissions are masked by the sodium resonance continuum. The shoulder on the long wavelength side of the sodium resonance lines ($605 < \lambda < 650$ nm) is a result of a number of barium oxide bands at 604 nm, 610 nm, 617 nm, 622 nm and 629 nm. Atomic barium lines are present at 554 nm and 660 nm. There is also emission from magnesium oxide at 500 nm.

An analysis of the formula and the visible spectrum of the standard yellow flare composition shows the reason for the lowered excitation purity in a flare which should be reasonably a much higher purity (>95%). Apparently when the yellow formula was developed it was done by simply adding sodium oxalate to a standard green flare formula. This was done

8. B. E. Douda and E. J. Bair, J. Opt. Soc. Am. 60, 1257 (1970).

primarily to keep development costs down and to hold down the cost of the item. The color and intensity are considered adequate for the signal as it now exists.

CONCLUSIONS

The output of the red flare composition used in the Mk 124 Mod 0 Marine Smoke and Illumination Signal comes primarily from SrCl and SrOH molecular species emitting at wavelengths greater than 605 nm. The flare produces 8700 cd for 18 seconds with a dominant wavelength of 610 nm and an excitation purity of 96 percent. Atomic emission from potassium, sodium and barium and molecular emission from BaCl are observed. This emission adds little to the overall output of the flare. The potassium is present from the potassium perchlorate oxidizer. The sodium and barium are present as impurities in the potassium perchlorate and strontium nitrate ingredients.

The output of the green flare composition used in the Mk 117 Mod 0 Marine Smoke and Illumination Signal comes primarily from BaCl and BaO molecular species emitting in the region from 500 nm - 540 nm. The flare produces 19400 cd for 26 seconds with a dominant wavelength of 558 nm and an excitation purity of 47 percent. Molecular emissions from BaO, BaOH, Ba₂O₂ and SrCl are also observed. These emissions, coupled with an underlying continuum from hot particles, contribute to the low color purity in this flare.

The output of the yellow flare composition used in the Mk 118 Mod 0 Marine Smoke and Illumination Signal comes primarily from atomic sodium emission at 590 nm. The flare produces 29100 cd for 35 seconds with a dominant wavelength of 584 nm and an

excitation purity of 82 percent. The sodium resonance lines are superimposed on a background continuum resulting from a combination of graybody emission and molecular emission from barium oxide, barium hydroxide and barium chloride (BaCl).

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