Metal–Fluorocarbon Pyrolants. XV: Combustion of two Ytterbium–Halocarbon Formulations

Ernst-Christian Koch,*[a,b] Volker Weiser,[c] Evelin Roth,[c] Sebastian Knapp,*[c] Joost van Lingen[d] and Jacco Moorhoff[d]

[a] NATO Munitions Safety Information Analysis Center (MSIAC), Boulevard Leopold III, B-1110 Bruxelles, Belgium

[b] Technische Universität Kaiserslautern, Erwin-Schrödinger-Str. 52, D-67663 Kaiserslautern, Germany

[c] Fraunhofer Institut für Chemische Technologie, Joseph-von-Fraunhofer-Strasse 7, D-76327 Pfinztal, Germany

[d] TNO Technical Sciences, Lange Kleiweg 137, 2288 GJ Rijswijk, Netherlands

Abstract: *Binary pyrolants based on ytterbium and either polytetrafluoroethylene or hexachloroethane yield a broad stable combustion regime with intense luminous flames. Combustion temperatures have been determined spectroscopically for both pyrolant types. The temperature correlates with the burn rate of the pyrolant. The UV-Vis spectra of the fuel rich pyrolants have been measured and were converted into x,y-color values in the 1931 CIE color diagram. The color obtained with both pyrolant types produce shorter dominant wavelength emission and higher saturation than common BaCl BO_2 emitters.*

Keywords: *Ytterbium, Polytetrafluoroethylene, PTFE, Pyrolant, Burn rate, Combustion Temperature*

Introduction

Some time ago it was reasoned by Sturman that the rare earth metals and their compounds should in principle function as flame color agents.[1] The reason for his assumption was the observation that the individual elements give distinct emissions when introduced as aqueous salt solutions into inductively coupled plasma. Earlier Dumont had found that lanthanum acetylacetonate when used as fuel in an ammonium perchlorate based formulation yields a white flame.[2] Mischmetall and cerium acetylacetonate when used in perchlorate based formulations both yield a faint orange flame.[3] Another important prediction made by Sturman was that either the rare earth metals or their alloys should also yield sparks with colours other than those typically found on the black-body curve. That is, distinct red and green emissions should be accessible at best through use of some of these elements. However apart from the above work the potential of rare earth metals in pyrotechnic formulations has never been investigated.

Recently we have shown that the lanthanide metals samarium (Sm), europium (Eu), thulium (Tm) and ytterbium (Yb) can burn in the vapor phase.[4] This is due to compliance of these metals with Glassman's criterion which requires vaporization temperatures of the metals to be lower than the dissociation temperatures of the corresponding oxides.[4,5] Powdered ytterbium undergoes vapour phase combustion in oxygen and with halogen based oxidizers.[6] A narrow range of ternary mixtures of Yb with polytetrafluoroethylene and Viton® yields extended luminous flames which radiate intensely in the infrared spectral range and outperform standard infrared decoy flare payloads based on Magnesium/PTFE/Viton® (MTV)[7a] in a certain spectral band.[8] In view of the unexpected results of ytterbium based formulations we decided to investigate the combustion behaviour of binary mixtures of ytterbium with polytetrafluoroethylene and hexachloroethane, the latter being the preferred oxidizer in obscurant formulations.[9]

Article Details	***Article No: - 0093***
Manuscript Received:-22/03/2012	***Final Revisions:-10/07/2012***
Publication Date:-11/07/2012	***Archive Reference:-1469***

Experimental details

Warning

Metal–fluorocarbon pyrolants are explosive materials inherently sensitive to electrostatic discharge, heat, flame and impact. These materials when alight yield intense radiation sufficient to cause severe skin burns. In the unconsolidated state the material can undergo deflagration and even shock up to low order detonation in larger quantities (>1 kg).[7b]

All preparations must be conducted in accordance with appropriate national safety regulations. In particular the personnel involved should wear flame-resistant personal protection equipment such as overalls and balaclava made from NOMEX® -III or aluminized PBI® with a facial heat shield. The personnel must be grounded by conductive protective shoes and a wristband, and all equipment and tooling must be grounded as well.[7c]

Ytterbium ingot and powder (99.9% rare earth oxide (REO)), volume median diameter $D[v, 0.5]$ = 3.19 µm, polytetrafluoroethylene, $D[v, 0.5]$ = 7.5 µm and hexachloroethane were all purchased from ALFA AESAR and used without further treatment. The ytterbium ingot was rasped down with a rasp to yield a coarse powder of ~150 µm mean diameter. 5 g batches of the pyrolants were prepared by dry mixing of the components in a 25 ml spherical mixing container made of conductive polypropylene for 30 min at 120 rpm in a tumbling blender. All pellets were pressed at 10 MPa pressure applied for 10 s in a 5.6 mm cylindrical die under safety precautions. Typical sample weight ranged between 1800 and 2000 mg. Pellets were firmly wrapped in transparent adhesive Tesa®-film to protect the lateral surface from flame spreading but to keep the burn front visible. The cylinders were glued with cyanoacrylate glue on small ceramic squares (20 × 20 × 4 mm). The pellets were transferred into a fireproof fumehood with constant venting and ignited with a non-luminous propane torch flame.

For the temperature determination Near infrared-(NIR) spectra were recorded with a PGS-NIR-Spektrometer 2.2 (Carl Zeiss AG, Germany) in the wavelength range λ = 1.0–2.1 µm and calibrated with a technical blackbody heated to 2000 K. Using proprietary ICT-BaM-Code calculated spectra were fitted to the experimental spectra with a least squares fit.[10] The UV-Vis spectra were recorded with a spectrograph Shamrock A-SR-500i-B2 with Andor DU920P-UV-DD-detector (both purchased from Andor Inc. USA). A diffraction grating with 150 lines/mm was used.

The combustion process was recorded with a Panasonic HDC-HS20 with the following settings; aperture: 16; exposure time: 1/8000 s. The accuracy of the burn rate determination is limited by the frame rate of the video camera which is 28 frames/second.

Results and discussion

Pressing densities (ρ_{exp}) greater than 90% Theoretical Maximum Density (TMD) were achieved for Yb/PTFE-compositions containing up to 82 wt% Yb. At higher ytterbium contents the mixtures do not consolidate in the same manner and yield densities of around 87% TMD (Fig. 1). Stable combustion of Yb/PTFE is observed from 62–95 wt% Yb. In this range the combustion rate increases exponentially from about 1 mm s^{-1} to 26 mm s^{-1} at ξ(Yb) ≈ 90 wt% and 87% TMD. With further increasing Yb content the combustion rate decreases again to around ξ(Yb) ≈ 95 wt% as is depicted in Fig. 2. Below 62% Yb ignition of the pyrolant occurs but is followed by rapid

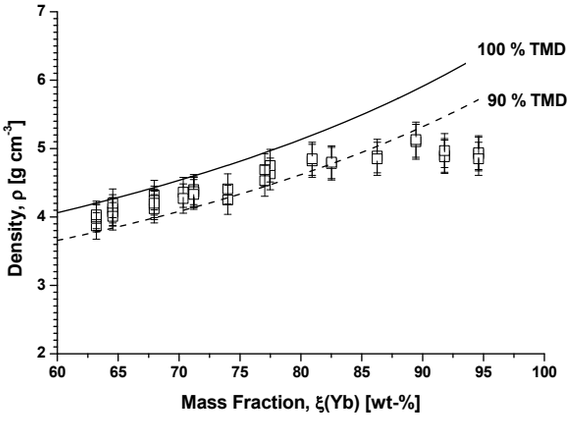

Figure 1. *Experimental density of ytterbium/ polytetrafluoroethylene pyrolants and theoretical maximum density (TMD).*

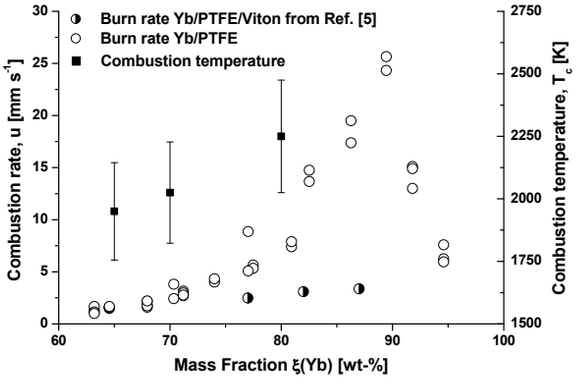

Figure 2. *Combustion rate of Yb-based pyrolants and combustion temperature with bars indicating the scatter of measured data.*

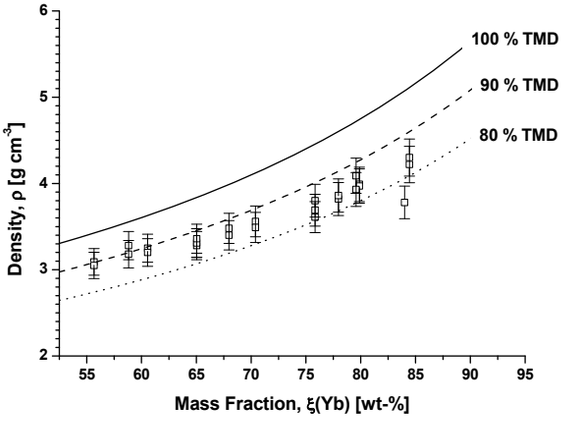

Figure 3. *Experimental density of ytterbium/ hexachloroethane pyrolants and theoretical maximum density (TMD).*

extinction. Above ~95 wt% Yb no cigarette-type burn is observed but the reaction proceeds with very fast glowing of the complete strand followed by delayed scattering of the material, probably due to afterburn with atmospheric oxygen. Thus no proper propagation rate could be determined. The burn rates for binary Yb/PTFE are higher than for three ternary Yb/PTFE/Viton pyrolants reported recently.[8] This is mainly due to higher porosity (eqn 1) of the present samples (φ = 10–20% as opposed to 1–2% for the samples prepared in Ref. 8) which facilitates heat transfer via filtrating combustion.[11]

$$\varphi = 1 - \frac{\rho_{\text{exp}}}{\text{TMD}} \qquad (1)$$

The spectroscopically determined combustion temperature is superimposed for 65, 70 and 80 wt% Yb each on the burn rate in Fig. 2. The measured mean temperatures (1979, 2000 and 2250 K) parallel the combustion rate. A similar behavior has been observed with other metal–fluorocarbon pyrolants recently.[12,13]

Pressing densities (ρ_{exp}) between 80–90% TMD were achieved for Yb/HC-compositions (Fig. 3). Stable combustion of Yb/PTFE is observed from 55–85 wt% Yb. In this range the combustion rate increases exponentially from about 2 mm s^{-1} to 17 mm s^{-1} at ξ(Yb) ≈ 75 wt% and 85% TMD. With further increasing Yb content the combustion rate decreases again to around ξ(Yb) ≈ 85 wt% as is depicted in Fig. 4.

Below 55% Yb ignition of the pyrolant occurred, but was followed by rapid extinction. Above ~85 wt% Yb no cigarette-type burn is observed, but the reaction proceeded with very fast glowing of the complete strand followed by delayed scattering of the material, probably due to afterburn with atmospheric oxygen. The spectroscopically determined combustion temperature is superimposed for 59 and 75 wt% Yb each on the burn rate in Fig. 4. The measured mean temperatures (1700 and 2100 K) nicely parallel the combustion rate.

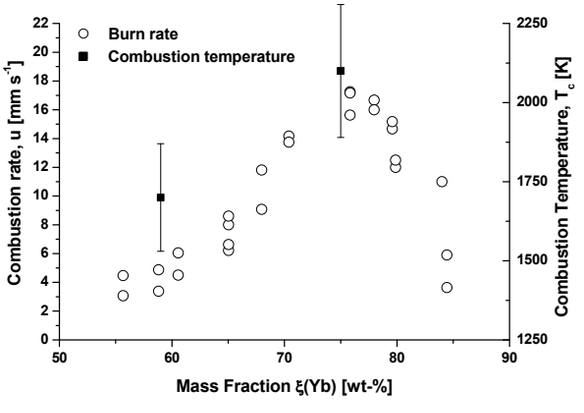

Figure 4. *Combustion rate of Yb-based pyrolants and combustion temperature with bars indicating the scatter of measured data.*

Fuel rich formulations, ξ(Yb) = 70 wt% of both Yb/PTFE and Yb/HC yield a distinct green coloration of the flame that however is partly overlapped by lateral orange soot emissions. Thus the UV-Vis spectra of both pyrolants yield a blackbody continuum superimposed from molecular emissions of Yb species Yb, YbO YbF and YbCl respectively as shown in Fig. 1 of Ref. 6. Subtraction of the blackbody curve yields the principal selective emitters as shown in Fig. 5 and 6.

Normalisation of the spectra, separate convolution with each of the three tri-stimulus color matching functions,[14] and integration yields the *X*, *Y* and *Z*-values which were converted to *x* and *y*-values as shown in Table 1 and in Fig. 7 and Fig. 8. Dominant wavelength, λ_d, given by ○, and saturation, Σ, were determined graphically.

Due to very similar electronic transitions the

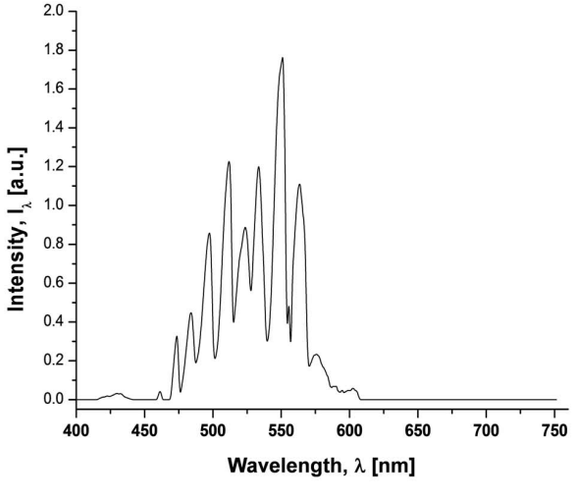

Figure 5. *UV-Vis composite spectrum from YbF, YbO and Yb.*

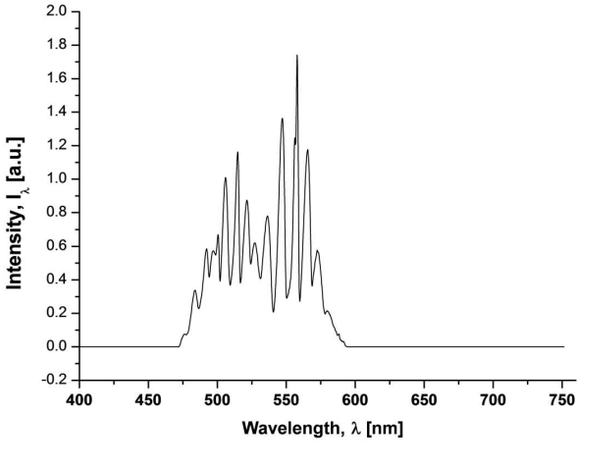

Fig. 6 *UV-Vis composite spectrum from YbCl, YbO and Yb.*

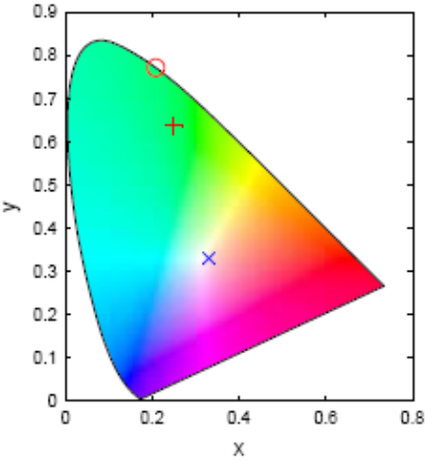

Figure 7. *Color locus of Yb, YbF, YbO composite spectrum,+, dominant wavelength, ○, and white point, ×.*

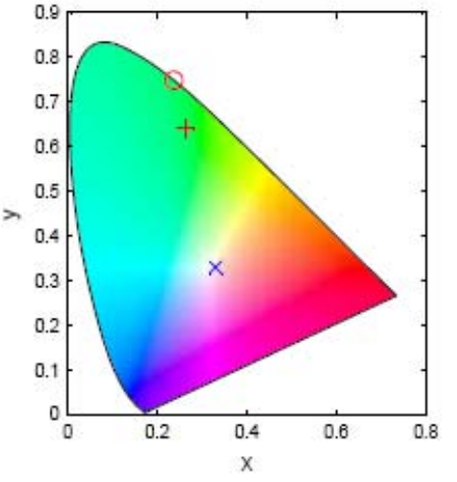

Figure 8. *Color locus of Yb, YbCl, YbO composite spectrum,+, dominant wavelength, ○, and white point, ×.*

Table 1. *Spectral properties of the composite emitter spectra based on Yb and reference data taken from ref. 19*

	Yb/PTFE	Yb/HC	$Ba(NO_3)_2$/Mg/PVC*	B/KNO_3*	B_4C/KNO_3*
λ_d (nm)	537.6	541.2	562.3	559.3	561.9
Σ (%)	69.0	73.8	61.5	55.0	52.0

* plus organic binder for each formulation

emission spectra of YbCl and YbF[15–17] are very similar and hence close color coordinates are obtained. The calculated dominant wavelengths are λ = 537.6 and 541.2 nm, the saturations are 69% and 73% respectively.

For comparison Table 1 shows data for a conventional green star based on barium nitrate ($Ba(NO_3)_2$)/magnesium/PVC/binder, boron(B)/potassium nitrate (KNO_3)/binder and boron carbide (B_4C)/KNO_3/binder[18–20] and the tested Yb/HC and Yb/PTFE. Yb based formulations produce both lower wavelength and more saturated green than common formulations based on barium nitrate boron or boron carbide. This underlines the importance of investigating the rare earth metals as color agents in pyrotechnic flames. Investigation of organic ytterbium salts as fuels in smoke free composition is underway.

Consolidated pellets of freshly rasped coarse ytterbium (150 µm) mixed with PTFE (86/14 wt%) upon ignition with a propane torch yields a loud crackling sound and nice green sparks. A closer view actually shows that the actual sparks are white but are surrounded by areas with green chemiluminescence (Fig. 9).

Conclusion

Ytterbium/polytetrafluoroethylene and ytterbium/hexachloroethane pyrolants yield stable combustion regimes with intense luminous flames ranging from 62–95 wt% and 55–85 wt% Yb respectively. The combustion temperatures derived from NIR spectra for both pyrolant types correlate with the burn rate. The principal emitters in the UV-Vis range have been extracted and converted into *x*,*y*-color values in the 1931 CIE colour diagram. The colors obtained with both pyrolant types produce shorter dominant wavelength emission and higher saturation than common BaCl or BO_2 type emitters. Combustion of pyrolant using coarse ytterbium yields intense green sparks.

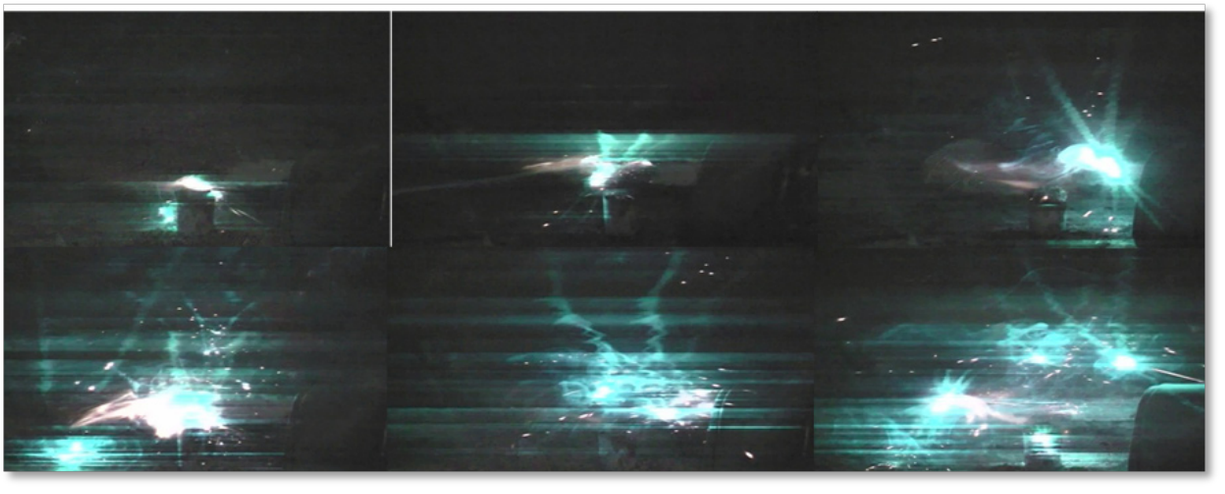

Figure 9. *Crackling combustion of Yb/PTFE (86/14) ejecting green sparks.*

Acknowledgement

Fa. Schwarze Wissenschaftliche Geräte/ Kaiserslautern is thanked for a donation of Yb ingot and powder. Dr. Arno Hahma/Diehl BGT Defence is thanked for determining the particle size distribution of Yb powder.

References

1 B. Sturman, 'The Rare Earths as Possible Flame Color Agents', *Journal of Pyrotechnics*, Vol. 9, 1999, pp. 57–61.

2 J.-L. Dumont, 'Pyrotechnic Compositions for the Production of Coloured Fireworks', EP 0 252 803 B1, 1992, France.'

3 (a) G. C. Shaw and P. S. Shadlesky, 'Smoke/Flame Pyrotechnic Marker Compositions', WASATCH Division, Thiokol Chemical Cooperation, Technical Report AFATL-TR-73-199, September 1973; (b) E.-C. Koch, unpublished work, 2000.

4 E.-C. Koch, V. Weiser, E. Roth and S. Kelzenberg, 'Consideration of some 4f-metals as New Flare Fuels – Europium, Samarium, Thulium, Ytterbium', *42nd International Annual Conference of ICT*, Karlsruhe Germany, June 28 – July 01, 2011, V-1.

5 I. Glassman, 'Combustion of Metals' in *Solid Propellant Rocket Research*, ed. M. Summerfield, Vol. 1 of *Progress in Astronautics and Aeronautics*, 1960, Academic Press, New York, p. 253.

6 E.-C. Koch, V. Weiser, E. Roth, Combustion of Ytterbium Metal, *Propellants Explosives, Pyrotechnics*, Vol. 37, 2012, pp. 9–11.

7 E.-C. Koch, *Metal-Fluorocarbon Based Energetic Materials*, Wiley-VCH, Weinheim, 2012, (a) pp. 166–173; (b) pp. 299-325; (c) pp. 294–296.

8 E.-C. Koch and A. Hahma, 'Metal-Fluorocarbon-Pyrolants. XIV: High Density-High Performance Decoy Flare Compositions Based on Ytterbium/ Polytetrafluoroethylene/Viton®', *Zeitschrift für Anorganische und Allgemeine Chemie*, Vol. 638, 2012, pp. 721–724.

9 E.-C. Koch, 'Metal Halocarbon Pyrolant Combustion' in *Handbook of Combustion*, ed. M. Lackner, F. Winter and W. Agrawal, Vol. 5, Wiley-VCH, Weinheim, 2010, pp. 355–402.

10 V. Weiser and N. Eisenreich, 'Fast Emission Spectroscopy for a Better Understanding of Pyrotechnic Combustion Behavior', *Propellants Explosives, Pyrotechnics*, Vol. 30, 2005, pp. 67–78.

11 Y. V. Frolov and V. G. Korostelev, 'Combustion of Gas-Permeable Porous Systems', *Propellants Explosives, Pyrotechnics*, Vol. 14, 1989, pp. 140–149.

12 E.-C. Koch, A. Hahma, T. M. Klapötke and H. Radies, 'Metal–Fluorocarbon Pyrolants: XI. Radiometric Performance of Pyrolants Based on Magnesium, Perfluorinated Tetrazolates, and Viton A', *Propellants Explosives, Pyrotechnics*, Vol. 35, 2010, pp. 248–253.

13 E.-C. Koch, T. M. Klapötke, H. Radies, K. Lux and A. Hahma, 'Metal-Fluorocarbon Pyrolants. XII: Calcium Salts of 5-Perfluoroalkylated Tetrazoles – Synthesis, Characterization and Performance Evaluation as Oxidizers in Ternary Mixtures with Magnesium and Viton™', *Zeitschrift für Naturforschung B*, Vol. 66b, 2011, pp. 378–386.

14 C. J. Bartleson, 'Colorimetry', in *Color Measurement, Volume 2 Optical Radiation Measurements*, ed. F. Grum and C. J. Bartleson, Academic Press, New York, 1980, pp. 33–148.

15 H. U. Lee and R. N. Zare, 'Chemiluminescent Spectra of YbF and YbCl', *Journal of Molecular Spectroscopy*, Vol. 64, 1977, pp. 233–243.

16 R. F. Barrow and C. H. Chojnicki, 'Analysis of the Optical Spectrum of Gaseous Ytterbium Monofluoride', *Journal of the Chemical Society, Faraday Transactions*, Vol. 75, 1975, pp. 728–735.

17 T. C. Melville, J. A. Coxon and C. Linton, 'High-Resolution Laser Spectroscopy of YbCl: The $A^2\Pi$-$X^2\Sigma^+$ Transition', *Journal of Molecular Spectroscopy*, Vol. 200, 2000, pp. 229–-234.

18 B. V. Ingram, 'Color Purity Measurements of Traditional Pyrotechnic Star Formulas', *Journal of Pyrotechnics*, Vol. 17, 2003, pp. 1–18.

19 J. J. Sabatini, J. C. Poret and R. N. Broad, 'Boron Carbide as a Barium-Free Green Light Emitter and Burn Rate Modifier in Pyrotechnics', *Angewandte Chemie International Edition*, Vol. 50, 2011, pp. 4624–4626.

20 W. Meyerricks and K. L. Kosanke, 'Color Values and Spectra of the Principal Emitters in Colored Flames', *Journal of Pyrotechnics*, Vol. 18, 2003, pp. 52–73.