



Novel yellow colored flame compositions with superior spectral performance



Ramy Sadek, Mohamed Kassem, Mohamed Abdo, Sherif Elbasuney*

School of Chemical Engineering, Military Technical College, Kobry El-Kobba, Cairo, Egypt

ARTICLE INFO

Article history:

Received 4 November 2016
Received in revised form
6 December 2016
Accepted 15 December 2016
Available online 26 December 2016

Keywords:

Pyrotechnics
Colored flames
Yellow tracer
Atomic spectroscopy
Color quality

ABSTRACT

The production of colored flames is the primary purpose of military signaling, projectile tracing, and illuminating devices. Certain elements and compounds when heated to high temperature have the unique property of emitting lines or narrow bands in the visible region (380–780 nm). This study, reports on the development of novel yellow colored flame compositions with enhanced spectral performance in terms of luminous intensity, and color quality to standard Russian yellow tracer. The light intensity and the imprint spectra of developed yellow flares were measured using digital luxmeter and UV–Vis. spectrometer respectively. The main giving of this study is that the light intensity, and color quality of Russian yellow tracer were improved by 287%, and 170% respectively. This was accomplished by means of optimizing the ratio of novel binder to color source using aluminum metal fuel. Aluminum-based formulations were found to maximize the formation of yellow reactive emitting specimens, and to eliminate any interfering incandescent emission resulted from MgO. Quantification of yellow color emitting specimens in the combustion gaseous products was achieved using chemical equilibrium thermodynamic code named ICT (Institute of Chemical Technology in Germany, Virgin 2008); in an attempt to judge the light quality. This improvement in yellow flare performance established the rule that the emission intensity increases as the reaction temperature increases. In the meantime upper limit of temperature was avoided to maximize the color quality.

© 2017 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Pyrotechnic compositions have wide range of applications including gas generator, smoke, noise, heat, and colored flame [1–5]. The production of bright light with single wave length is the primary purpose of colored flame compositions [6–8]. Certain elements and compounds when heated to high temperature have the unique property of emitting lines or narrow bands of light in the visible region (380–780 nm) [9–13]. These elements are called the color source, for instance strontium (red), barium (green), copper (green or blue), and sodium (yellow) [14–17]. Strontium, barium, and copper emit color by forming their halides; this emission type is known as molecular emission which is characterized by broad band emission [18]. In the meantime, atomic emission is characterized by sharp discrete wave length [19,20]. The production of a

vividly colored flame is a challenging problem which need a delicate balance between different factors including [21,22].

- 1) An atomic or molecular species that emit the desired wavelength.
- 2) The emitting species must be sufficiently volatile to exist in the vapor state.
- 3) Sufficient heat should be created to produce the excited emitter.
- 4) Heat is necessary to volatilize and excite the emitter.

The combustion wave of colored flame was demonstrated to consist of five distinctive zones as demonstrated in Fig. 1 [23–25].

The vapors of the atomic or the molecular emitting species are excited by the thermal energy of the secondary luminous combustion zone [26]. The excited levels of atoms, or molecules relaxed to the ground state with the emission of the visible light. Yellow flame presents no color problem considering the very strong atomic emission from excited sodium atoms [15,27]. The wavelength of sodium light actually consists of two wavelengths called D lines (D_1 and D_2) [28]. The sodium spectrum is dominated by the

* Corresponding author.

E-mail addresses: s.elbasuney@MTC.edu.eg, sherif_basuney2000@yahoo.com (S. Elbasuney).

Peer review under responsibility of China Ordnance Society.

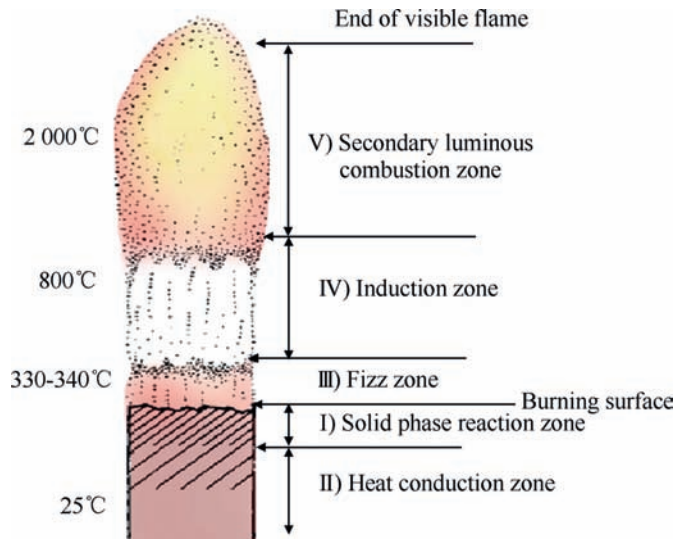


Fig. 1. Distinctive combustions zones of colored flames.

bright doublet known as the sodium D-lines at 584 ± 2 and 588 ± 1 nm [29]. The transition which gives rise to the doublet is from the 3P to the 3S level [30,31]. The 3P level is split into states with total angular momentum $j = 3/2$ and $j = 1/2$ by the magnetic energy of the electron spin in the presence of the internal magnetic field caused by the orbital motion; this effect is called the spin-orbit effect [32]. The difference in energy for the $3P_{3/2}$ and $3P_{1/2}$ is 0.0021 eV (Fig. 2).

Magnesium metal fuel is broadly used in many colored flame compositions. In an oxidizing flame, magnesium is converted to magnesium oxide (MgO), which is an excellent white light emitter by incandescence which may lower the color purity [10,33–36]. In yellow flares the emission intensity at D₁ and D₂ lines increases as the reaction temperature is raised; there is no molecular emitting species to decompose. However, there is an upper limit of temperature that must be avoided for maximum color quality (5000 K) as demonstrated in Fig. 3 [14,37,38].

The chromaticity diagram describes colors in terms of rectangular x and y dimensionless coordinates, further details can be found in the following reference [39]. The pure colors are ranged along the upper edge of the diagram, their wavelengths indicated in

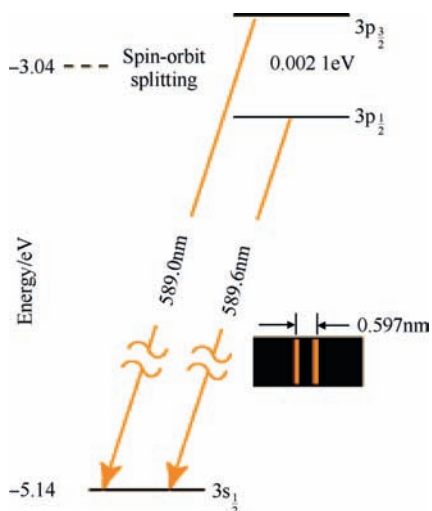


Fig. 2. The sodium doublet energy level diagram.

nm. The colors displayed by sources of blackbody radiation at different temperatures (in kelvin) lie along a line that extends into the center of the diagram [38,40]. As the temperature increases the yellow color fades until 5000 K, above 5000 K the flame becomes white.

The main purpose of this study is to develop yellow flares with enhanced performance, in terms of color quality, color intensity, and duration time. It was possible to enhance light intensity, and color quality of reference flare (Russian yellow e flare) by 287% and 170% respectively. This was achieved mainly by optimizing the ratio of binder to color source using aluminum as a fuel. Quantification of combustion gasses and combustion temperature was accomplished using chemical equilibrium computer program named ICT Thermodynamic Code (Institute of Chemical Technology in Germany, virgin 2008).

2. Experimental work

2.1. Chemicals and materials

The main constituents for yellow flare composition include: oxidizer, metal fuel, color source, binder, and color intensifier. One constituent can have a dual function; NaNO_3 can act as a color source and oxidizer. Table 1 tabulates a list of chemicals used in this study.

2.2. Formulation of yellow colored flame compositions

Russian yellow fire flare was employed as a reference [41] “(see Table 2)”. A systematic study to develop enhanced yellow flare was conducted; this study includes the following main steps:

- 1) Fuel rich/stoichiometric formulations ($F_0 - F_1$).
- 2) Type of binder ($F_2 - F_3$).
- 3) Type of fuel (F_4).
- 4) Fuel to oxidizer ratio ($F_5 - F_8$).
- 5) Binder to color source at different fuel types ($F_9 - F_{12}$).

Table 2 summarizes the chemical composition of different investigated formulations.

Manufacture technology should emphasize mixing of different ingredients to the molecular level, good homogenization, and accepted mechanical properties [3]. In this study, the yellow flares were developed through five steps including: sieving of solid particles, intimate mixing, granulation to ensure homogeneity, filling, and pressing. The employed equipments in yellow flare preparation and spectral measurements are scheduled in Table 3.

2.3. Spectral measurements

Photometric tunnels are widely employed to measure the spectral performance of different pyrotechnic devices including: flares, signal, tracer, etc. The employed photometric tunnel dimensions were 8 m (L) \times 2 m (H) \times 0.5 m (W). The distance between the specimen holder and the spectrometer photodetector was 7 m. A schematic of the employed photometric dark tunnel is represented in Fig. 4.

The illuminance (E) was measured using Miltronics DL 1076 digital luxmeter and converted into luminous intensity (I) in candela (cd), by substituting the distance (d) between the light source and the detector in Equation (1) [42]

$$I_{cd} = E_{lx} \times d_m^2 \quad (1)$$

The average luminous intensity (cd/s) was retrieved by

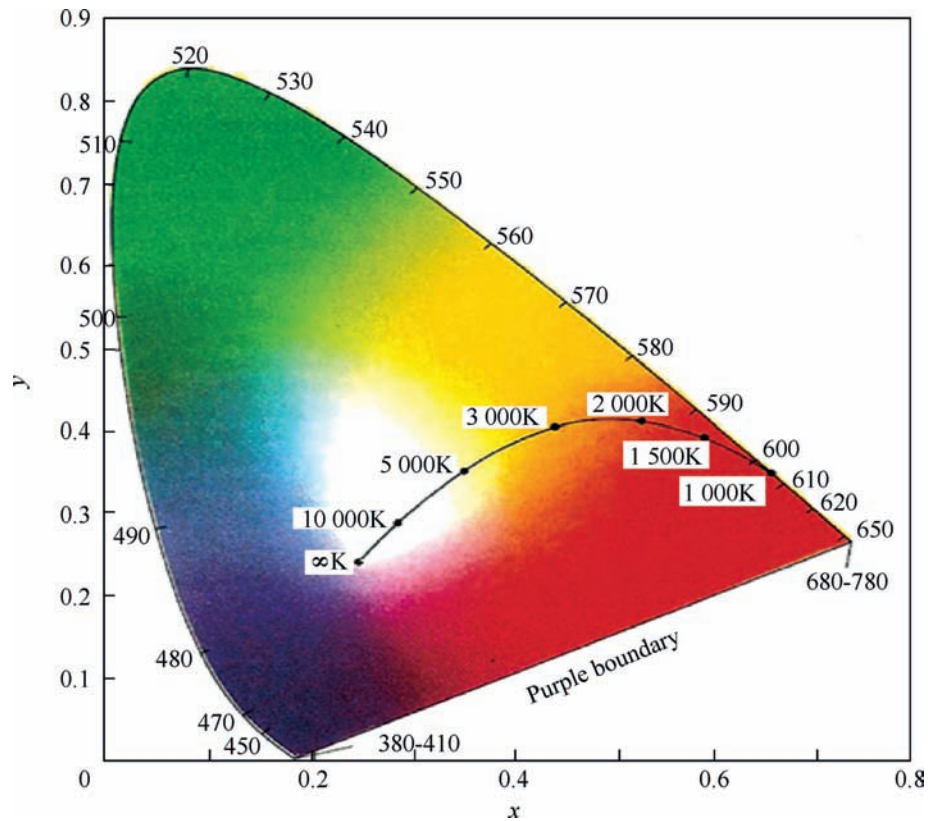


Fig. 3. Chromaticity diagram.

Table 1
The function and structure of different used chemicals.

Chemicals	Function	Structure	Grade	Supplier
Sodium nitrate	Oxidizer & color source	NaNO ₃	Analytical grade	Alpha chemika
Magnesium	Fuel	Mg	98%, ribbon	Alpha chemika
Aluminum	Fuel	Al	99%, fine powder	Alpha chemika
Polyvinyl chloride	Binder & color intensifier	(C ₂ H ₃ Cl) _n	Analytical grade	Alpha chemika
Arabic gum	Binder	(C ₁₆ H ₇ N ₂ O ₃) _n	Analytical grade	Alpha chemika
Shellac	Binder	(C ₃₀ H ₅₀ O ₁₁) _n	Analytical grade	Alpha chemika

Table 2
Chemical composition of developed yellow flares.

F.	NaNO ₃ /Wt %	Mg /Wt %	Al /Wt %	PVC /Wt %	Shellac /Wt %	Arabic Gum /Wt %	Comment
F ₀	56	27	—	17	—	—	Reference
F ₁	67.8	15.2	—	17	—	—	Stoichiometric
F ₂	56	27	—	—	17	—	Binder type
F ₃	56	27	—	—	—	17	
F ₄	55	—	28	17	—	—	Fuel type
F ₅	62	21	—	—	—	17	Fuel to oxidizer ratio
F ₆	59	24	—	—	—	17	
F ₇	62	—	21	—	—	17	
F ₈	59	—	24	—	—	17	
F ₉	66	27	—	—	—	7	
F ₁₀	61	27	—	—	—	12	
F ₁₁	66	—	27	—	—	7	
F ₁₂	61	—	27	—	—	12	

integrating the total area under the curve, the total luminous intensity (I), in candela (cd) divided by the action time. The main drawback of such measurement is that it cannot provide information about color quality. Color quality was evaluated, using ocean

optics USB 4000 spectrometer; over the yellow band from 575 to 600 nm [14,43]. Spectral measurement was conducted every 30 s. The average luminous intensity (cd/s) and spectrometer response (counts/s) over the yellow band (575–600 nm) for the developed

Table 3
Employed Equipments for yellow flare preparation and spectral measurements.

Equipment	Function
Cizeta 20 ton electronic press	<ul style="list-style-type: none"> Pressing the mixture forming a coherent homogenized final product for transportation, handling, and testing.
Die	<ul style="list-style-type: none"> A steal body with the required dimensions for flare pressing.
Digital light meter	<ul style="list-style-type: none"> For luminous flux density measurements.
DL 1076 digital luxmeter, Miltronics, (Country)	<ul style="list-style-type: none"> The unit of measurement is the Lux. (also known as luxmeter). By unit conversion we get the light intensity in candlepower.
UV–Vis. Spectrometer	<ul style="list-style-type: none"> For wavelength and intensity measurements.
USB 4000 spectrometer, ocean optics, USA	<ul style="list-style-type: none"> For wavelength and intensity measurements. It is responsive from 200 to 1100 nm (UV– Visible - NIR). Maximum intensity is 65000 counts. Gives the output spectrum of the sample. Detector response for a selective wavelength band.
Edmund industrial optics with lens holder	<ul style="list-style-type: none"> To avoid spectrometer saturation with high intensity light.

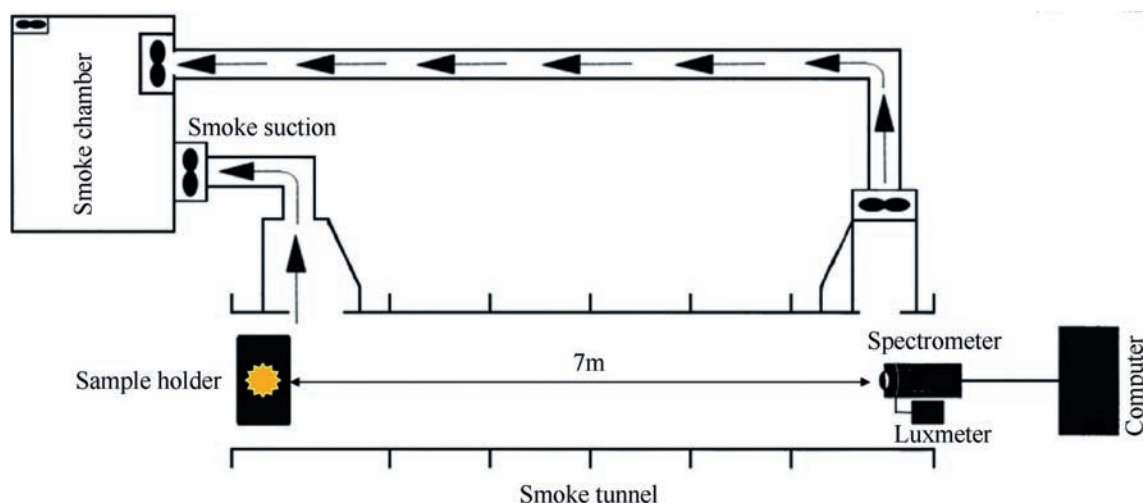


Fig. 4. Schematic for spectra measurements of developed yellow flares.

flares to reference flare were measured.

3. Results and discussion

3.1. Effect of binder type

The binder itself could have a significant impact on the reaction temperature and yellow flare performance. Arabic gum was found to be an effective binder in terms of enhanced light intensity and color quality by 38% and 1% respectively, relative to reference yellow tracer based on PVC (Fig. 5).

PVC as a binder could suppress the formation of Na vapors via the formation NaCl; this action could deteriorate yellow color production. Shellac (F₂) didn't improve the intensity due to the low combustion temperature. High temperature is mandatory to produce the excited state of light emitting species [3]; this was confirmed through thermochemical calculations using ICT code.

3.2. Effect of fuel type

Magnesium is the most commonly used fuel in colored flame compositions [37]. However, the formation of MgO as black body emitter can broaden the generated spectra, and deteriorate the color quality [44]. This is why, the metal fuel (Mg) of reference yellow flare was replaced by Al in an attempt to improve the color quality [45]. The employed binder was arabic gum which was found

to be effective binder. F₄ exhibited an imprint spectrum with sharp intense d-line peaks [46,47] (Fig. 6).

It is clear that the average luminous intensity per time (cd/s) and detector response (counts/s) of F₄ is much greater than F₀ over the yellow band (575–600 nm). It was clear that Al greatly improved the light intensity by 206%; and the color quality was also improved by 107% to the reference. The content of main yellow color emitting specimen (Na atom) in the combustion flame was increased by 70.7% and the incandescent emissions from MgO were no longer present in the reaction products using ICT code. This findings confirmed that aluminum fuel has a positive impact on color quality.

3.3. Optimization of color source to binder

The optimum ratio of color source NaNO₃ to binder (Arabic gum) was optimized at different fuel types (Mg & Al). The dramatic finding and superior change in yellow flare performance was achieved with arabic gum at 12 Wt % with Al fuel. Yellow flare (F₁₂) exhibited the highest average luminous intensity (cd/s) as demonstrated in Fig. 7.

F₁₂ with highest average luminous intensity (cd/s), could exhibit high color quality due to the intense formation of sodium atoms in the flame zone and the elimination of any incandescent emission due to MgO. Furthermore, F₁₂ demonstrated the highest combustion temperature. Quantification of combustion temperature and

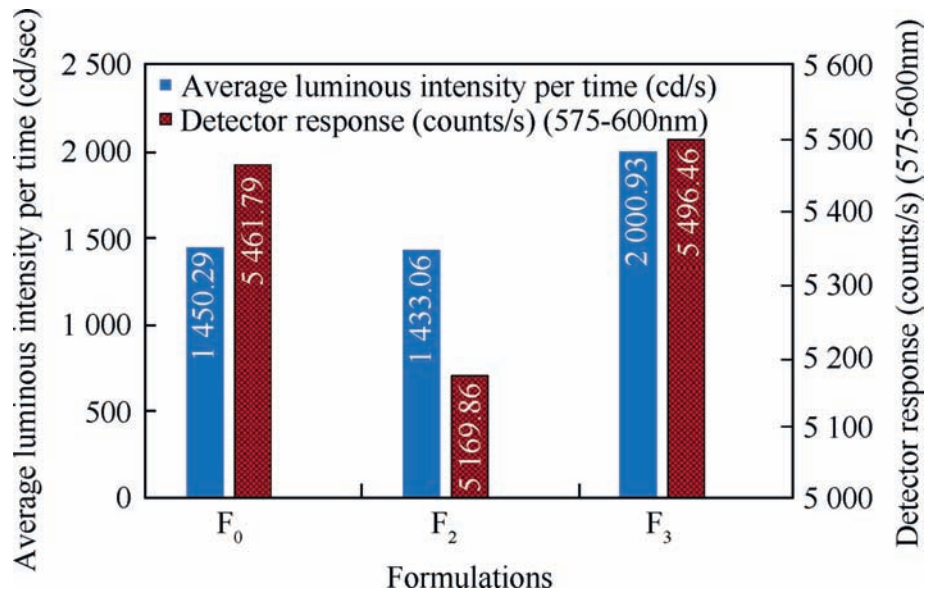


Fig. 5. Effect of binder type on the luminous intensity in (cd/s).

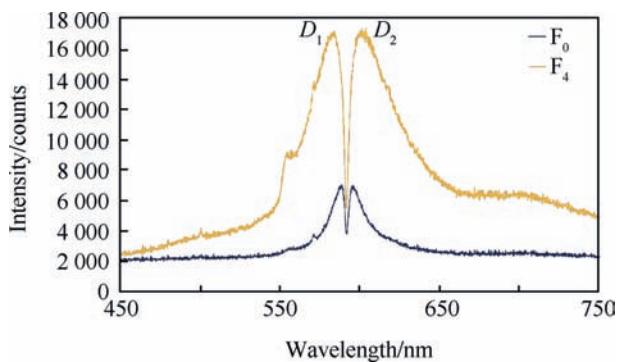


Fig. 6. The impact of fuel type on the imprint spectrum yellow flares.

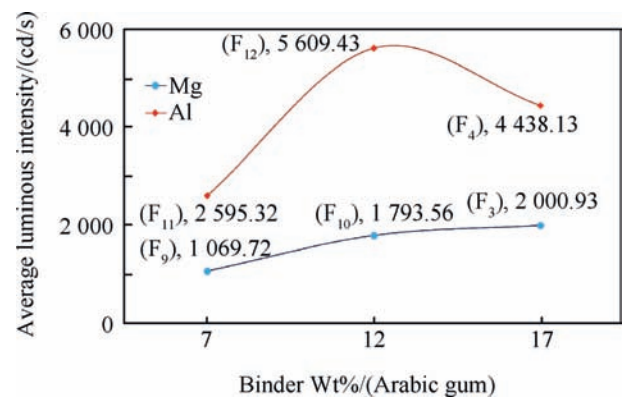


Fig. 7. Effect of color source to binder on the luminous intensity in (cd/s).

gaseous decomposition products were investigated using ICT code (Table 4).

F₁₂ exhibited the highest content of yellow color emitting specimen (Na atom) in combustion gaseous products; sodium atom was increased by 79.5% compared to reference yellow flare. The absence of MgO could secure high spectrum quality. Fig. 8 demonstrates the imprint spectrum of F₁₂ and F₄ to F₀.

Thanks to the optimum ratio of color source to binder which secured the highest intensity. The imprint spectra of F₁₂ confirmed the finding that arabic gum is a novel binder for red flare tracers. Al fuel could be the metal of choice for advanced yellow flare compositions with enhanced color quality. Furthermore, aluminum has a high chemical stability compared with magnesium fuel [33]. Aluminum surfaces are readily oxidized by the oxygen in the air, and a tight surface coating of aluminum oxide (Al₂O₃) is formed that protects the inner metal from further oxidation [48]. Hence, aluminum powder can be stored for extended periods with little loss of reactivity due to air oxidation [49]. On the other hand, magnesium is a very reactive metal. It is oxidized by moist air to form magnesium hydroxide. Consequently, yellow flare formulations based on aluminum can exhibit enhanced performance as well extended service life without loss of reactivity [50].

The optimum chemical composition of developed yellow flare

was found to be 61 Wt % NaNO₃ as both oxidizer and color source, 27 Wt % Al as fuel, and 12 Wt % arabic gum as binder. This composition secured yellow light with high intensity and high quality. Fig. 9 demonstrates digital photos of emitted yellow light for the developed yellow flare (F₁₂) to Russian reference flare. It is apparently clear that higher intensity and color quality were achieved via chemical composition optimization. Furthermore, the color broadening by MgO incandescent black body emission was eliminated.

Table 4
Impact of color intensifier to color source on yellow color emitting species.

F.	Temperature/K	Na (g) /Wt %	NaCl (g) /Wt %	NaOH (g) /Wt %	MgO (s) /Wt %	Al ₂ O ₃ (l) /Wt %
F ₀	2971.7	8.976	14.073	1.067	37.196	0
F ₃	2903.5	13.321	0	2.81	41.79	0
F ₄	3106.5	15.318	0	0.962	0	50.862
F ₉	2765.9	14.43	0	4.858	44.494	0
F ₁₀	2893.4	13.985	0	3.693	43.296	0
F ₁₁	3057.8	14.75	0	2.189	0	50.99
F ₁₂	3131.7	16.115	0	1.593	0	50.93

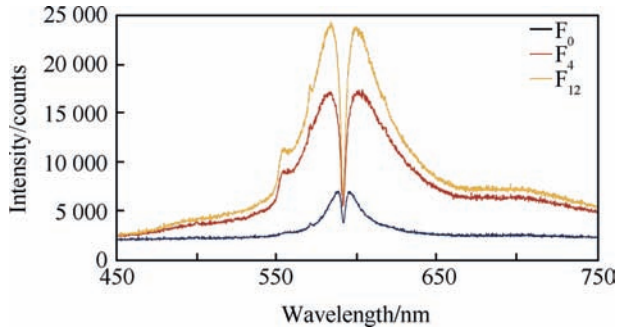


Fig. 8. Imprint spectra of developed yellow flared F_{12} and F_4 to reference yellow flare F_0 .

The tailored yellow flare F_{12} offered an increase in the luminous intensity by 287%. The color quality over the yellow band (575–600 nm) was improved by 170% to the reference. Fig. 10 summarized the average luminous intensity and detector response for all investigated formulations.

Fig. 10 demonstrated that F_{12} achieved enhanced spectral performance compared to reference yellow flare.

4. Conclusion

Arabic gum was found to be a novel binder for the development of yellow flares with superior spectral performance; as it has a dual function as a binder and prevent the formation of NaCl in the flame zone. Upon combustion, arabic gum exhibited an effective rule to support the formation of Na atom (the main yellow color emitting specimen). Al fuel was found to eliminate any incandescent emotions from (MgO). Furthermore, Al provides a higher heat of combustion which has a substantial rule to excite the Na vapors. Consequently, yellow colored flame with high intensity and quality was developed. Thanks to the optimum ratio of color source (NaNO_3) to novel binder (arabic gum) using Al fuel, this approach secured yellow tracer with superior spectral performance. It exhibited an increases the luminous intensity by 287. The yellow band spectrum (575–600 nm) was enhanced by 170% to the standard reference flare. Furthermore, yellow flare formulations based on aluminum fuel can exhibit extended service life without loss of



Fig. 9. Representative digital photographs of developed yellow flare (F_{12}) to reference flare.

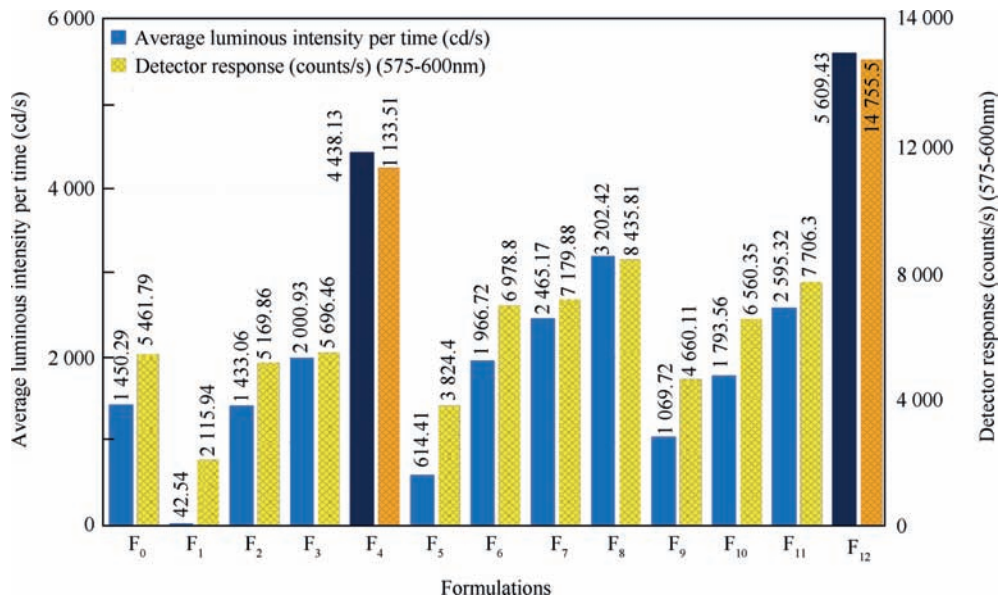


Fig. 10. Average luminous intensity and detector response for developed formulations.

reactivity in virtue of the protective oxide layer on aluminum.

Acknowledgements

Military technical college is acknowledged for funding the research project entitled “Enhanced Visible Tracers for Illumination and Tracking”.

References

- [1] Bebie, J., Manual of explosives military pyrotechnics and chemical warfare agents.
- [2] Kosanke KL, et al. Encyclopedic dictionary of pyrotechnics: (and related subjects). J Pyrotech 2012. P.R.S.No. 2, Revision 4, Incorporated, section 6-7, 6-1–7-49.
- [3] Conkling JA, Mocella C. Chemistry of pyrotechnics: basic principles and theory. 2nd ed. CRC Press; 2010.
- [4] Shidlovsky A. Principles of pyrotechnics. 3rd ed. 1974.
- [5] Command USAM. Engineering design handbook: theory and application. In: Command USAM, editor. Military pyrotechnic series. Washington, DC: AMC Pamphlet; 1967. 706–185.
- [6] Ledger J. The preparatory manual of black powder and pyrotechnics. Lulu Enterprises; 2006 [Incorporated].
- [7] Johnston SF. A history of light and colour measurement: science in the shadows. CRC Press; 2001.
- [8] Shidlovskiy AA. Principles of pyrotechnics. 3rd ed. 1964. Moscow.
- [9] Hardt AP, et al. Generation of light. In: Pyrotechnics. Pyrotechnica Publications; 2001. p. 277–98.
- [10] Conkling JA, Mocella C. Basic chemical principles, in chemistry of pyrotechnics: basic principles and theory. CRC Press; 2010. p. 7–57.
- [11] Ellern H. Modern pyrotechnics. Fundamentals of applied physical. 1961.
- [12] Dillehay DR. Illuminants and illuminant research. J Pyrotech 2004;53–60.
- [13] Ellern H. Underlying phenomena. In: Military and civilian pyrotechnics. NY: CHEMICAL Publishing Company Incorporated; 1968. p. 87–98.
- [14] Conkling JA, Mocella C. Color and light production. In: Chemistry of pyrotechnics: basic principles and theory. CRC Press; 2010. p. 179–202.
- [15] Ellern H. Colored lights. In: Military and civilian pyrotechnics. NY: CHEMICAL Publishing Company Incorporated; 1968. p. 122–30.
- [16] Hardt AP, et al. Color creation. In: Pyrotechnics. Pyrotechnica Publications; 2001. p. 39–43.
- [17] Weingart GW. Pyrotechnics. Survival Press; 2001.
- [18] Tro N. Chemistry in focus: a molecular view of our world. Cengage Learning; 2015.
- [19] Kosanke KL, Kosanke BJ. Selected pyrotechnic publications of KL and BJ Kosanke. Part 1: 1981 Through 1989 J Pyrotech 1995;(2):1–22.
- [20] Meyerriecks W, Kosanke K. Color values and spectra of the principal emitters in colored flames. J Pyrotech 2003;18:1–22.
- [21] Douda B, In NADC. Theory of colored flame production. Defense Technical Information Center; 1964.
- [22] Kosanke KLKaBJ. The chemistry of colored flames. J Pyrotech 2007;25:30–48.
- [23] Bailey A, Murray SG. Pyrotechnics. In: Explosives, propellants and pyrotechnics. Brassey's; 2000. p. 115–40.
- [24] Crawford BL, Huggett C, McBrady JJ. The mechanism of the double base propellants. J Phys Colloid Chem 1950;54(No. 6):854–62.
- [25] Rice OK, Ginell R. Theory of burning of double-base rocket propellants. J Phys Colloid Chem 1950;54(No. 6):885–917.
- [26] Conkling J, Mocella C, editors. Chemistry of pyrotechnics basic principles and theory. 2nd ed. London: CRC; 2012.
- [27] Kakkar R. Atomic and molecular spectroscopy: basic concepts and applications. Cambridge University Press; 2015.
- [28] Shimizu T. Part 3. The science of fireworks, in fireworks: the art, science, and technique. Pyrotechnica Publications; 1996. p. 53–65.
- [29] Pavia DL. Introduction to organic laboratory techniques: a small scale approach. Thomson Brooks/Cole; 2005.
- [30] Herzberg G. Atomic spectra and atomic structure. Dover Publ; 2008.
- [31] Bernath PF. Spectra of atoms and molecules. Oxford University Press; 2015.
- [32] Winkler R. Spin-orbit coupling effects in two-dimensional electron and hole systems. Springer Berlin Heidelberg; 2014.
- [33] Conkling JA, Mocella C. Components of high-energy mixtures, in chemistry of pyrotechnics: basic principles and theory. CRC Press; 2010. p. 59–96. p.
- [34] Wada Y, Foster N, Yoshida T. Safety of reactive chemicals and pyrotechnics. Elsevier Science; 1995.
- [35] Defense, U.S.O. DOD Contractor's safety manual for ammunition and explosives. 2008.
- [36] Tuukkanen IM, et al. Pyrotechnic and thermal studies on the magnesium-strontium nitrate pyrotechnic system. Propellants, Explos Pyrotech 2006;31(2):110–5.
- [37] Shimizu T. Fireworks: the art, science, and technique. Pyrotechnica Publications; 1996.
- [38] Kuehni RG. Color vision & technology. Aatcc; 2008.
- [39] Schanda J. Colorimetry: understanding the CIE system. Wiley; 2007.
- [40] Malacara D, S.o.P.-o.I. Engineers. Color vision and colorimetry: theory and applications. SPIE; 2011.
- [41] Shidlovskiy AA. Principles of pyrotechnics. American Fireworks News; 1997.
- [42] Rapidtables. Online scientific and engineering resource. Lux to candela calculator. 2014. Available from: <http://www.rapidtables.com/calc/light/lux-to-candela-calculator.htm>.
- [43] Ellern H. Formulas, in military and civilian pyrotechnics. NY: CHEMICAL Publishing Company Incorporated; 1968. p. 353–87.
- [44] Ernst-Christian Koch JJS, Poret Jay C, Moretti Jared D. New pyrotechnic signal flare compositions based on cheap established and environmentally acceptable ingredients, in energetic materials: performance, safety and system applications. Germany: Fraunhofer ICT; 2015. p. 1–8.
- [45] Ellern H. Magnesium and aluminum. In: Military and civilian pyrotechnics. NY: CHEMICAL Publishing Company Incorporated; 1968. p. 328–31.
- [46] Tennyson J. Astronomical spectroscopy: an introduction to the atomic and molecular physics of astronomical spectra. World Scientific; 2010.
- [47] Mohindroo KK. Basic principles of physics. Pitambar Publishing; 1997.
- [48] Tan J, Chan KS. Understanding advanced physical inorganic chemistry: the Learner's approach. WS Education; 2011.
- [49] Lee JD. Concise inorganic chemistry. 5th ed. Wiley India Pvt. Limited; 2008.
- [50] Mohamed AK, Mostafa HE, Elbasuney S. Nanoscopic fuel-rich thermobaric formulations: chemical composition optimization and sustained secondary combustion shock wave modulation. J Hazard Mater 2016;301:492–503.