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Illuminating pyrotechnic compositions and their specific features

DOCTORAL DISSERTATION

Natural sciences,
Chemistry (N 003)

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FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRAS

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Apšviečiameji pirotechniniai mišiniai ir jų specifinės savybės

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List of original papers by PhD candidate

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Paper 2 D. Juknelevicius, P. Alenfelt, A. Ramanavicius, The Performance of Red Flare Pyrotechnic Compositions modified with Gas Generating Additives, Propellants Explos. Pyrotechn., 2020, 45: 671-679.

Paper 3 D. Juknelevicius, T. M. Klapötke, A. Ramanavicius, Blue Strobe Pyrotechnic composition based on Aminoguanidinium Nitrate, Propellants Explos. Pyrotechn., 2019, 44: 1466-1471.

Paper 4 D. Juknelevicius, A. Dufter, M. Rusan, T. M. Klapötke, A. Ramanavicius, Study of Pyrotechnic Blue Strobe Compositions Based on Ammonium Perchlorate and Tetramethylammonium Nitrate, Eur. J. Inorg. Chem., 2017, 7: 1113-1119.

Papers published before the start of the PhD studies

Paper 5 D. Juknelevicius, R. Kubilius, A. Ramanavicius, Oxidizer Ratio and Oxygen Balance Influence on the Emission Spectra of a Green-Colored Pyrotechnic Flames, Eur. J. Inorg. Chem., 2015, 33: 5511-5515.

Paper 6 D. Juknelevicius, E. Karvinen, T. M. Klapötke, R. Kubilius, A. Ramanavicius, M. Rusan, Copper(I) Bromide: An Alternative Emitter for Blue-Colored Flame Pyrotechnics, Chem. Eur. J., 2015, 21: 15354–15359.

Paper 7 D. Juknelevicius, L. Mikoliunaite, S. Sakirzanovas, R. Kubilius, A. Ramanavicius, A Spectrophotometric Study of Red Pyrotechnic Flame Properties Using Three Classical Oxidizers: Ammonium Perchlorate, Potassium Perchlorate, Potassium Chlorate, Z. Anorg. Allg. Chem., 2014, 640: 2560-2565.

Author's contribution to the original papers relevant to the PhD

Paper 1	Conceptualization, investigation, data analysis, writing - original draft.
Paper 2	Conceptualization, methodology, investigation, data analysis, validation, writing & editing.
Paper 3	Conceptualization, methodology, investigation, data analysis, writing - original draft.
Paper 4	Supervision, conceptualization, methodology, investigation, review & editing.

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LIST OF ABBREVIATIONS

5-AT	5-aminotetrazole (anhydrous)
AGN	Aminoguanidinium nitrate
AP	Ammonium perchlorate
BCC	Basic copper carbonate (malachite)
CP	Chlorinated paraffin
CR	Chlorinated rubber
Cu	Copper powder (electrolytic)
CuOCl	Copper oxychloride, $Cu_2Cl(OH)_3$
Dex	Dextrin
DTA	Differential thermal analysis
GN	Guanidinium nitrate
HCB	Hexachlorobenzene
I_v	light intensity
IR	Infrared region
L_{sp}	Specific luminous intensity or efficiency ($cd \cdot s \cdot g^{-1}$)
NC	Nitrocellulose powder
MgAl	Magnalium powder (Mg and Al alloy 50:50)
p_e	Color purity or saturation
PVC	Polyvinyl chloride
RH	Relative humidity
TMAN	Tetramethylammonium nitrate
VIS	Visible region
Ω	Oxygen balance

INTRODUCTION

The pyrotechnic illuminants are known for their ability to burn producing brilliant colored flames. With brightness sometimes exceeding 50000 cd and having a distinct flame color, such pyrotechnic compositions have been applied in several utilitarian fields throughout the years.

For safety of life at sea several varieties of pyrotechnic articles are used to attract attention in the case of an accident. Such articles are cheap, reliable and produce a bright flame that is visible from a long distance. The importance of a bright flame becomes even more pronounced at extreme weather conditions such as storm, rain or fog.

In fireworks bright color flames of high purity are used extensively. The first colored flame fireworks became available since the discovery of $KClO_3$ in the late 18th century. However, they weren't particularly bright, since only later on metallic fuels such as Mg and Al were adopted in pyrotechnics. Nowadays, a variety of colored flame compositions are used that yield virtually any color and some that are modified for strobe burning or an additional spark effect.

Aim of this study

To increase the efficiency of illuminating pyrotechnic compositions, while maintaining high flame color purity, chemical stability and compatibility.

Objectives of this study and scientific novelty

1) To investigate how far the amount of Mg in a hand-flare composition can be increased, while maintaining a low burn rate of $<2,1$ mm/s without a loss in color purity or light intensity and to asses other additives, which can increase the flare's performance.

Novelty: While some materials that increase the performance of a flare composition have been reported, there was still no work done in order to design an efficient and slow burning composition.

2) To identify the best additive, which can increase the performance of a Mg-rich flare composition and to determine critical amounts of additive that can be tolerated.

Novelty: The three-component flare composition of $Sr(NO_3)_2/Mg/PVC$ *is known for a long-time, and only few of its modifications are used. The main goal was to determine other additives that at higher ratios (at over 10 wt.-%) can increase the performance of the Mg-rich flare composition.*

3) To overview and to identify the best blue flame compositions presented in the literature that are known for their high color saturation and good overall performance. To compare the best blue flame compositions with respect to their flame light intensity, efficiency, saturation, emission spectra and CIE coordinates and dominant wavelength.

Novelty: This kind of experimental examination has not been done to date, wherein a rather diverse range of blue flame pyrotechnic compositions are examined quantitatively using a spectrometer. Very few researchers in general have reported CIE coordinates with p_e, I_v, L_{sp} *values for blue flames. In addition, some old-fashioned ingredients were tested to demonstrate that arsenic-containing ingredients (Paris Green) offer no benefit in the color purity, and other, more novel, compositions show better performance.*

4) To evaluate what kind of pyrotechnic systems are suitable for a blue strobe pellet that would function and possess moderate chemical stability and to analyze some other strobe moderators and catalysts.

Novelty: Blue strobes are a notoriously rare pyrotechnic effect that has not been much examined due to very limited number of compositions suitable to produce these strobes and their expensiveness, however, they are very desired for the fireworks. Such systems are complex and very few compositions are presented that work and are chemically stable at the same time.

Statements of defense

1. Combination of rounded Mg powder and gas generating additives yields a high-performance flare composition (>22 kcd s/g) that has a distinct red flame (p_e >90%) and burn rate that is <2.1 mm/s.
2. Guanidinium nitrate (GN) is a suitable additive for red flare compositions, when used in the range of 0-15 wt.-%. Resulting mixture can reach up to 60% higher efficiency (L_{sp}) in comparison to a similar GN-free composition.
3. Blue flame compositions with relatively high color saturation (p_e >50%) can be obtained without the use of arsenic-containing compounds that have been used in the past, such as “Paris green”.
4. Blue strobe composition can be designed with the use of aminoguanidinium nitrate as a strobe moderator.

1. LITERATURE REVIEW

1.1. Pyrotechnic compositions

A pyrotechnic composition is meant to describe at least two component containing heterogeneous solid mixture, that is capable of reacting in a self-sustained exothermic reaction[1]. The reaction produces heat, light (glow, flame, sparks), sound, smoke (physical and chemical) that has found its use in many utilitarian fields[2]. By this definition, pyrotechnics are distinguished from explosives and propellants, which are molecular compounds that have fuel and oxidizer functional groups in the same molecule, for example, nitro ester (oxidizer) groups in nitro glycerine.

The complexity of pyrotechnic reactions lies in the chaotic behavior that is associated with them. There are three states of matter always involved in any pyrotechnic reaction. First the reacting surface is pre-heated by the reacting composition. Some components are melted before reacting. Then at the ignition point decomposition occurs generating heat. Products are formed, which can be gases, solids and liquids. In case the ionization potential is reached, some elements get ionized as well. Both kinetic and thermodynamic factors affect the reaction equilibrium.

The 20th century authors G.W. Weingart[3], B.E. Douda[4], A.A. Shidlovski[1], J.H. McLain[5], A. Hardt[6], R. Lancaster[7], T. Shimizu[8–10], J.A. Conkling[11], have contributed significantly with their books on pyrotechnics from scientific, technical and artistic standpoints.

In more recent years, specific areas of pyrotechnics have been investigated. One of which is illuminants.

1.2. Illuminants (White, Red, Green, Yellow)

Illuminating pyrotechnics stretches into a specific branch of such reactions where the chemical reaction produces exclusively strong electromagnetic radiation in comparison to other pyrotechnic reactions. The main two areas of practical use are VIS radiation for signaling and entertainment (fireworks, special effects) and IR for military countermeasures.

The sources of such strong emissions come from excitation of atomic species, ionic species (plasma), molecules and incandescence emission by a high temperature flame that is usually in the range of 1200 – 3600 °C.

Illuminating compositions are mainly comprised of an alkali or alkaline earth metal nitrate, which serves as both oxidizer and emitter source, a metallic fuel such as Magnesium, Aluminum, Zirconium, and additional components such as chlorinated organics, binders, gas generators, burn rate moderators, stabilizers (Fig. 1).

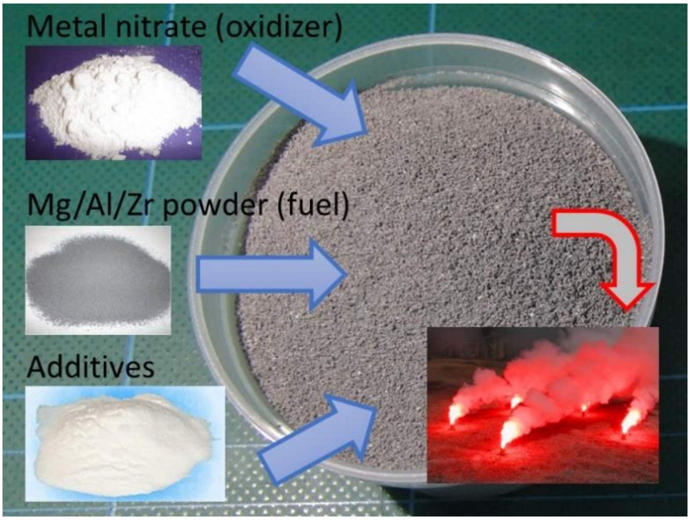


Fig. 1. The main components of an illuminating flare composition.

Magnesium is an important component used since the late 19th century, but it was not until the period between the World Wars that price and availability enabled a more extended production and development of high temperature, magnesium fueled, illuminating pyrotechnic products[12].

Before and during the Second World War products like hand-flares, signal ammunition and parachute-flares were improved to a similar level of efficiency as we see today. A lot of work was done to deepen the understanding of the underlying phenomena during 1950s to 1960s[4], though without affecting much of the products already in use. The main development driving force in recent years has been focused on eliminating certain unwanted ingredients and to a certain degree improving flame color depth[13–23].

Although having problems with corrosion induced by moisture[24] and being a relatively expensive ingredient, Mg is absolutely indispensable for the production of illuminating flares and the emission of high intensity colored light in both military and civil applications. The reason for this is a couple of unique chemical properties of Mg that distinguishes it from all other possible fuels for high temperature colored light production in pyrotechnics. First of all, the oxidation of magnesium produces large amounts of heat, which directly relates to a high number of excited molecules in the flame[25]. As a result, the flame is very luminous and spectral emitters like $SrCl_{(g)}$, $SrOH_{(g)}$, $BaCl_{(g)}$, $BaOH_{(g)}$, $Na_{(g)}$ can produce flames that have high color saturation. Secondly, Mg has a low vaporization temperature, 1107 °C, which is much lower than its oxide's decomposition temperature of ~3200 °C. This satisfies the Glassman criteria for metal vapor phase combustion[26], which results in extended vapor phase diffusion combustion zone, which allows for a large radiative area.

Generally, fundamental demands for a good illuminating flare composition are: a) burning with luminous flame with maximum candlepower; b) having a distinct flame color of purity higher than 80% (e.g. red distress signal); c) preferably creating a minimum of slag, d) being chemically stable and containing chemicals of minimum toxicity. Slag formation is unwanted since long-lived burning sparks and glowing slag is always a fire hazard and could make a handheld flare dangerous to use and burn off the vanes to the canopy in a parachute suspended flare. Even more important is that a flare producing lots of slag is probably not delivering its best pyrotechnic performance (maximum light output in the case of illuminants).

1.3. Blue signals

A pyrotechnic flame with a high color saturation or color purity (p_e), is one of the biggest challenges in pyrotechnics especially for the blue color (Fig. 2). While several suitable pyrotechnic compositions can be formulated with a reasonable effort for red and green at high color purity and high luminous intensity (I_v), there are much fewer examples for blue illuminants available.

Fig. 2. A relatively dim blue flame appears above the burning surface of a 6 mm, 0.45 g blue firework star (pellet). Oxidizer: $KClO_4$.

An excellent historic perspective on colored flame development is given in the thesis by Sturman[27]. Sturman discusses the evolution of colored flames throughout the years, even from the period before the introduction of potassium chlorate into pyrotechnic compositions.

One of the first spectroscopic investigations that reported an analysis of blue flames was carried out by Barrow and Caldin[28]. Barrow and Caldin identified the emitting species as $CuCl_{(g)}$. Interestingly, mercury(I) chloride was used in these compositions as chlorine source.

Dr. Bernard E. Douda has contributed significantly to the understanding of colored flames, that includes blue flames with copper[4].

A systematic study of compositions, which are generating blue flames, was performed by Shimizu[29]. He used a self-made spectrograph containing a sample holder, a 0.04 mm slit, water prisms, lenses and a photographic plate.

The proliferation of relatively low-cost spectrometers has been helpful for studying pyrotechnic flames. Pyrotechnic compositions are assessed in a "static" way, whereby the sample is burned, and the smoke is removed well enough to ensure a free line of sight to the sample. In 2003, Brian Ingram investigated the spectra of red, green and blue pyrotechnic flames[30]. Meyerriecks and Kosanke studied the principal emitters in colored flames[31]. They utilized solutions of various chemicals in combination with a nebulizer and an oxygen/propane/acetylene flame.

Several papers have been published about the desired emitter in pyrotechnic flames comprising a copper and a chlorine source. Dolata proposed the formation of a trimer of CuCl[32]. This was quickly followed by Sturman, who provided disproof of this hypothesis[33].

While static measurements are a sound and reproducible method for characterizing compositions, such measurements are not representative of the true environment in the most of applications. In actual use, pyrotechnic compositions must burn at various airspeeds. Consequently, mixing of ambient air will alter the flame stoichiometry and temperature. Furthermore, pyrotechnic stars may extinguish in flight[25,34].

Few publications are available about "Round Robin trials" of spectral color measurements. Douda's[35] review compares results from different pyrotechnic flare testing facilities. He used 81 mm mortar flares as test objects. The test tunnels were located at the former company E.H.D. Hendrickx in Belgium, at the former government facilities at Fort Halstead, UK and at the German armed forces facilities in Meppen, Germany.

Recent efforts have been made to identify alternatives to the well-known copper-chlorine based systems. Some of us have published work on copper(I) bromide, and compared it to copper(I) chloride[13]. The work includes the 1931 CIE coordinates for the isolated spectra of CuCl and CuBr. In the same year Koch compared all four copper(I) halides[15]. Koch has provided values of the 1931 CIE coordinates, as well as the dominant wavelength and color purity. He has concluded that copper(I) bromide provided good efficiency, even outperforming the classical copper(I) chloride. The copper(I) fluoride and the copper(I) iodide-based system were found to be inferior to the bromide and chloride. Koch briefly states that the experimental alternative blue compositions are "unsuitable for technical use". The compositions were optimized for the formation of K_2SO_4, to enable spectral measurements minimizing the interference of potassium halides.

Recently, indium has been investigated. The first results do not indicate that indium is, even from a purely technical point of view, a viable alternative emitter[17].

1.4. Blue strobes

A strobe composition burns in an oscillatory manner with a smoulder reaction occurring at all time and flash reaction occurring periodically (Fig. 3). The smoulder reaction produces relatively a low amount of heat and forms a slag at the burning front. When sufficient heat is generated, the semi-reacted slag is ignited, and a flash occurs. Then the smoulder reaction continues further to the depth of the pyrotechnic column[36].

Fig. 3. Combustion process of a 8 mm white strobe pellet. Flash frequency: 6Hz. Composition: $Ba(NO_3)_2/KClO_4/KNO_3/MgAl$ (MX51 Ecka werke)/GN/Polivinylbutyral/NC/Cu (200mesh atomized) in ratio of 56.3/4.7/4.7/26.4/2.5/1/2.5/1.9 (Courtesy of P. Alenfelt).

While colored strobes are created without significant difficulties using a nitrate oxidizer or ammonium perchlorate (AP) combined with Mg, or magnalium (MgAl) powder[37,38], a blue strobe is more difficult to make, since the high temperature flash reaction involving oxidation of Mg or MgAl can destroy the temperature sensitive $CuCl_{(g)}$ blue flame emitter.

Therefore, a blue strobe composition calls for a different chemical composition. A few of such compositions have been described by Jennings-White, who uses the AP/tetramethylammonium nitrate (TMAN)/Cu system[39] and by McCaskie who described guanidinium nitrate (GN) based blue strobe compositions[40]. Also, similar compositions as mentioned above have been analyzed in our recent work[41]. However, TMAN is difficult to obtain and possibly an expensive material. In our experience, such TMAN based compositions have difficulties of sustaining combustion, which can lead to a low wind resistance in practical applications.

2. EXPERIMENTAL

CAUTION! The mixtures described herein are potential explosives, which are sensitive to mechanical stimuli, such as impact, friction, heat, and electrostatic discharge. Although we encountered no problems in the handling of these materials, appropriate precautions and proper protective measures (safety glasses, face shields, leather coats, Kevlar gloves, and ear protectors) should be taken when preparing and manipulating them.

In previous work AGN was found to be extremely dangerous when mixed with copper bromate, $Cu(BrO_3)_2$ and copper iodate, $Cu(IO_3)_2$. The sensitivity to friction was extreme and small amounts of experimental mixtures self-ignited during storage. Also, a side product of AGN reaction with BCC (black in color, obtain under acidic conditions) had self-ignited while being wet on a filter paper.

2.1. Chemicals

For flares, Rounded Mg powder 45-100 μm (max 5% >100 μm and max 5% <45 μm, purity of 99.0-99.5%) and $Sr(NO_3)_2$ (99.5 % with <0.4 % barium nitrate, <0.05 % calcium nitrate and <0.04 % sodium nitrate) were received from Jengo S.P.A., Chlorinated rubber in the form of Pergut B10 (finer than 250 μm) from Bayer. $Sr(NO_3)_2$ was milled in a hammer mill until about 50 % of the particles were smaller than 50 μm before the experiment. 2-cyanoguanidine, Azodicarbonamide, Calcium resinate, Shellac, Strontium oxalate, Lactose, Dextrin, Phenolic resin, Lignin sulfonate, GN, and Sulfur (all very fine powders, purity 97-99%) were only passed through a 250 μm sieve to break up lumps. Melamine, 5-aminotetrazole (5-AT), Urea and Hexamine (purity 97-99%) were ground with a mortar and pestle to a fine powder and particles bigger than 150 μm were removed with a sieve. The linseed oil used was boiled type. The following formulas were applied for calculating oxygen balance (Ω_{CO2}) for variable M_r compounds: Linseed oil $C_{57}H_{92}O_6$, Calcium resinate $C_{40}H_{58}CaO_4$, Shellac $C_{16}H_{26}O_4$, Phenolic resin $C_{53}H_{45}O_7$, Lignin sulfonate $C_{20}H_{24}O_{10}CaS_2$, Chlorinated rubber $C_{10}H_{11}Cl_7$.

For blue flames and strobes AP that was employed was synthesized in Prof. Klapötke's energetic materials research group (LMU, München) by neutralizing perchloric acid with ammonia solution. A fine -50 mesh powder of the fuel TMAN was used as received. Hexamine was purchased from

SIGMA ALDRICH. Tetramethylammonium perchlorate (TMAP) was synthesized according the following protocol: perchloric acid (5.79 g, 0.0576 mol), was diluted with distilled water and tetramethylammonium hydroxide (5.25 g, 0.0576 mol) was cooled down separately in an ice bath while stirring. Merging the two solutions resulted in the flocculation of the white metathesis product. Water was evaporated at 150°C to form a crystalline product which was then placed in a drying cabinet. The fuels ethylenediammonium nitrate (EDN) and tetramethylethylenediammonium nitrate (TMEDN) were prepared as well by reacting ethylenediamine or tetramethylenediamine with an excess of nitric acid in ethanol. The precipitate products were filtered and washed with ether.

AGN was synthesized by reacting nitric acid with aminoguanidinium bicarbonate. The final product was dried in a desiccator before use and water solution of AGN had pH 7-8. Copper (II) benzoate was synthesized by reacting potassium benzoate with Cu(II) chloride dihydrate in aqueous media. Copper powder (<150 µm) was from Grüssing. Basic copper carbonate (malachite), guanidinium nitrate and PVC powder were from Sigma Aldrich. Nitrocellulose (NC) with a nitrogen content of 13.25% was from Nitrochemie Aschau GmbH. Sulfur, lactose, dextrin, phenolic resin (BLIKAS LTD., Lithuania), and red gum were used as received. All chemicals used were ground and sieved through a 50 mesh screen before conducting experiments.

2.2. Preparation of flare bodies, pellets, rods

Three main types of test units were prepared.

1. 23 mm flare bodies (red flares)
2. 13-16.8 mm dry pressed pellets (for blue illuminants and strobes)
3. 5 mm rods (blue strobes)

For flares, the compositions were hand mixed, sieved through a 30 mesh screen, cured for 4 h at 80 °C and then sieved again through 20 mesh screen to break lumps. Test compositions were pressed into metal tubes (ID = 23 mm) containing waxed paper liners (OD = 23 mm, ID = 21.6 mm). Hence, the pyrotechnic composition was compacted into a column of ID = 21.6 mm and 70-85 mm in height (Fig. 4). Flares were pressed two at a time at 2 tons with 4 increments of 11.5 g (scale accuracy 0.05 g). 2 g charge of igniter composition was pressed on top of each flare for ignition.

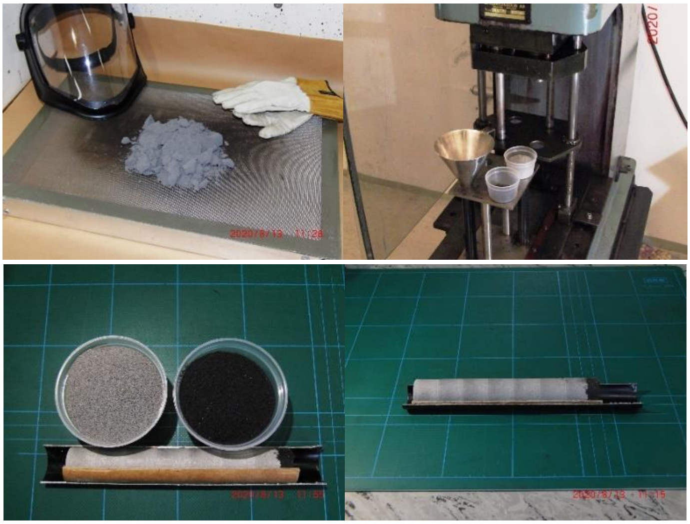


Fig. 4. Preparation of 23 mm flare bodies: Top: Sieving, pressing, bottom: composition & igniter (black), flare cut view.

The strobe compositions were mixed using a mortar and pestle (Fig. 5) Pellets of 2 g (13 mm in diameter, 5-10 mm in height, ρ ~1.6 $g{\cdot}cm^{-3}$) were pressed in one increment by a consolidation dead load of 2 tons. In some cases, for TMAN based compositions, an igniter composition was pasted on top of the pellet (~0.1 g).

Fig. 5. Preparation of 13 mm pellets: Weighing, mixing, storing, pressing.

For extruding of 5 mm diameter rods the following procedure was followed: 2-4 g of composition was moistened with either MEK or Acetone to swell or dissolve the binder material (PVC or NC). Then a 5 mm ID plastic syringe with a cut end was used as a simple pump to press 10-25 mm long rods (~0.4 g each, ρ ~1,15 g·cm^{-3}). The syringe was filled with the moist strobe composition and while facing a hard surface the plunger was pressed down by hand to eject entrapped air and to consolidate the compositions as much as possible. Finally, the compressed rod was extruded and left to dry overnight at room temperature.

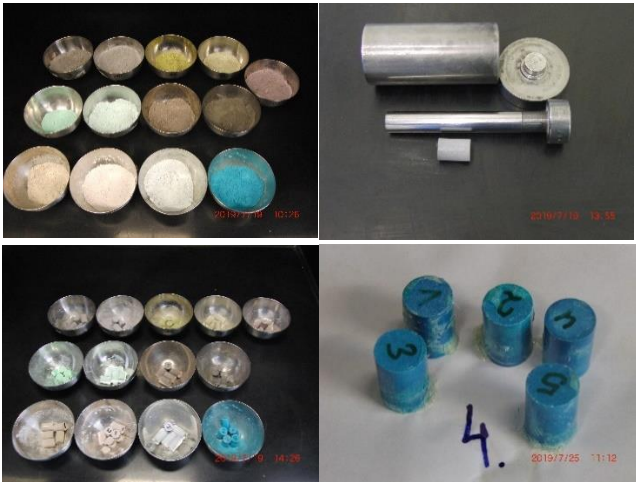


Fig. 6. Composition (50 g batches), pressing tool, pressed pellets and composition 4 from up close.

Blue flame compositions were compacted into 16.8 mm pellets, 25-30 mm height, ρ = 1.5-2.5 g·cm^{-3} using a hydraulic press (Fig. 6).

2.3. Spectrometer, lux meter, camera

For flares the experiment was performed in a wind tunnel to reduce smoke obscuration. The wind speed in the chamber, where flares were burnt, was 1 m/s. Illuminance was measured with a calibrated lux meter (LMT, I(ph)–meter 1500, data processed with DasyLab software) and emission spectra were recorded with a spectrometer (Stellar net, EPP 2000, CXR-SR; irradiance calibrated for 300–1100 nm range). The detector-sample distance was 10 m. The flares were also filmed with a video camera (Casio Exilim ex-f1) at automatic settings for the evaluation of shape, spark and slag formation.

For strobes and blue flames measurements were carried out using a HR2000+ES spectrometer with an ILX511B linear silicon CCD-array detector controlled by software from OCEAN OPTICS. The integration time for recording the emission spectra or strip charts were set according to the signal intensity. It was in the range of 5 – 500 ms. The detector-sample distance was 0.5 - 1 m. At least three samples were measured for strobes and 3-5 samples for blue flames. The performance of each composition was evaluated with respect to flame color, smoke generation and the amount of solid residue.

The combustion process was filmed with a digital video camera recorder (SONY, DCR-HC37E), Visario G2 1500 Weinberger speed camera for filming at 1000 fps and SONY RX10 III for 100 fps and 500 fps, respectively.

2.4. Characterization

The DTA curves were measured with a 552-Ex differential thermal analyzer from OZM at heating rates of 5 $°C \cdot min^{-1}$. The decomposition points for TMAN based strobe compositions were measured with a LINSEIS PT10 DSC apparatus at heating rates of 5 $°C \cdot min^{-1}$. The impact and friction sensitivities were determined using a BAM drophammer and a BAM friction tester. The ESD test was performed with Xspark 10 instrument from OZM. The sensitivities of the compounds are indicated according to the U.N. Recommendations on the Transport of Dangerous Goods (+): impact: insensitive >40 J, less sensitive >35 J, sensitive >4 J, very sensitive 4 J; friction: insensitive >360 N, less sensitive <360 N, very sensitive <80 N, extreme sensitive <10 N.

3. RESULTS AND DISCUSSION

3.1. Evaluation of the Mg-rich system for red illuminants

The first experiment was orientated to explore the effectiveness of the well-known strontium nitrate, magnesium, and chlorine donor tri-component system that contained a rather high percentage of Mg (40–60%). Typical red flare compositions described in the literature contain around 30–40% of Mg powder, 55–35% of $Sr(NO_3)_2$, 12–20% of chlorine donor and 4–10% of other additives such as additional oxidizers, binders, stabilizers, burning rate retardants etc. (Table 1). An amount of over 50 % Mg powder is more common in yellow (white) flares based on $NaNO_3$, where atomic $Na_{(g)}$ is the dominant light emitter.

Table 1. Chemical compositions typically used in red flares.

Chemical composition (wt.-%)			
$Sr(NO_3)_2$	43	55	48
$KClO_4$	9		
Mg (50-100 mesh)	29	30	
Mg (30-50 mesh)			33
PVC	12	15	15
Laminac 4116/Lupersol	7		4
Source	[2]	[1]	[22]

Having a high percentage of Mg in the composition of course requires lowering the amounts of other components which, in turn, can result in lower emitter concentration, more rapid combustion, and stronger incandescent emission. It is, however, a potential approach to gain extra candlepower from the flare composition.

A series of test compositions were prepared, see Table 2. Rounded Mg powder was chosen over “cut” Mg for its ability to burn slower. An amount of 4% of linseed oil was added to each composition as a binder. Two flares of each composition were pressed for evaluation.

Table 2. Chemical composition of 18 formulations tested in the first experiment.

Compositon #	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
$Sr(NO_3)_2$	39	35	31	42	38	34	30	41	37	33	29	40	36	32	28	39	35	31
Mg rounded (45-100 µm)	40	44	48	40	44	48	52	44	48	52	56	48	52	56	60	52	56	60
Chlorinated rubber	17	17	17	14	14	14	14	11	11	11	11	8	8	8	8	5	5	5
Linseed oil	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Density [$g\cdot cm^{-3}$]	1.56	1.53	1.49	1.60	1.56	1.53	1.49	1.61	1.56	1.52	1.49	1.59	1.55	1.51	1.48	1.59	1.56	1.51
Burning time [s]	35.0	41.0	48.8	29.0	32.6	35.0	41.0	26.8	28.7	31.0	35.6	24.9	25.6	27.6	29.6	22.4	22.8	23.0
Burning rate [$mm\cdot s^{-1}$]	2.24	1.94	1.68	2.63	2.40	2.28	2.00	2.84	2.72	2.59	2.31	3.08	3.08	2.92	2.78	3.44	3.44	3.51
Light intensity [kcd]	17.6	14.4	9.2	25.4	23.6	21.3	14.3	31.0	30.6	28.9	23.2	39.3	43.9	39.5	34.0	48.8	53.4	55.3
L(sp) [$kcd\cdot s\cdot g^{-1}$]	13.4	12.9	9.8	16.0	16.7	16.2	12.7	18.1	19.1	19.5	17.9	21.3	24.3	23.7	21.8	23.7	26.4	27.7
L(sp)/BR [$kcd\cdot s^2\cdot g^{-1}\cdot mm^{-1}$]	6.0	6.6	5.8	6.1	6.9	7.1	6.4	6.4	7.0	7.5	7.8	6.9	7.9	8.1	7.8	6.9	7.7	7.9

An important parameter that describes the performance of a pyrotechnic illuminating composition is specific luminous intensity L_{sp} (Eq. 1).

$$L_{(sp)}(kcd \cdot \mathrm{s} \cdot \mathrm{g}^{-1}) = \frac{I_v t}{m} \qquad \textit{Eq. 1}$$

Equation 1 presented in normalized units describes how much visible light in kilo candelas is produced during one second from one gram of pyrotechnic composition[16–18]. For Mg containing illuminants, this value is usually reported to be in the range of 2-7 kcd·s·g^{-1} for green colored flares with barium nitrate[42], around 15-50 kcd·s·g^{-1} for illuminating flares with sodium nitrate[16,17,20] and around 14-16 kcd·s·g^{-1} for red colored flares with strontium nitrate[21].

A drawback is that L_{sp} does not take into account burning area of the flare and the geometry of the flame. Even though the choice of the pyrotechnic composition, the ratio of its components and its density after compaction are the major factors that determines size and shape of the flame envelope, both emission and absorption take place in the envelope of the flame and absorption is a function of distance (flame width). Also, heat loss is different for flares of different diameters and, therefore, different shaped columns or pellets that contain exactly the same composition will often have different L_{sp} values. Thus, the results from this work can only be compared to other flares of similar diameter and density.

A pyrotechnic composition that possesses a high L_{sp} value is often desired, since then a lower amount of pyrotechnic composition is needed to achieve a certain effect, for example, a desired burning time of a parachute flare. And, secondly, the pyrotechnic unit can be made smaller and lighter which in turn saves space and volume for practical applications.

As a complement, the ratio of L_{sp} and burning rate (L_{sp}/BR, Table 2) was used to give guidance in determining which compositions burned both bright and slow.

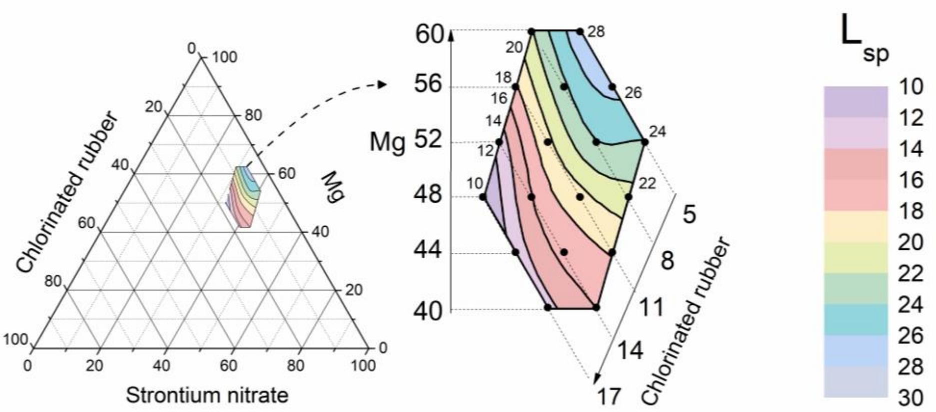


Fig. 7. L_{sp} distribution plotted in a ternary diagram of measured compositions with high Mg content. Small numbers at the end of each contour line represent L_{sp} values.

The combustion of all 18 flares was monitored with a lux meter. Since the distance between the photo diode and flare was known, a software (DasyLab) was used to calculate and plot light intensity in kilocandelas (kcd) over time. The L_{sp} values were calculated and their distribution was depicted in a ternary diagram (Fig. 7). The trend observed was that there is a significant increase of L_{sp} with decreasing amount of chlorinated rubber. The main purpose of chlorinated rubber is to serve as a chlorine donor to enhance $SrCl_{(g)}$ emitter formation, that supplements emission from $SrOH_{(g)}$. This shifts the flame color from reddish orange to red. Additionally, the use of chlorine donors is one of few possible ways to quench the $MgO_{(s/l)}$ incandescent emission via reaction with $Cl_{2(g)}$ or $HCl_{(g)}$ that yields more volatile $MgCl_{(g)}$ [25]. The color purity of chlorine-rich compositions 1-3 was measured to be 97-99% with dominant wavelength (DW) = 613-614 nm, while chlorine-low compositions, 16-18, had lower color purity of 79-87%, at DW = 605-609 nm.

Moreover, it was determined that L_{sp} values and BR are directly connected. Generally fast burning compositions result in more luminous flames with high L_{sp} values. Distribution of BR of the same system is depicted in Fig. 8 for comparison. However, from a practical perspective, high BR is only desired in tracer compositions, whereas hand flares, parachute flares etc. must contain a slow burning, yet luminous flame producing composition, which is the real challenge.

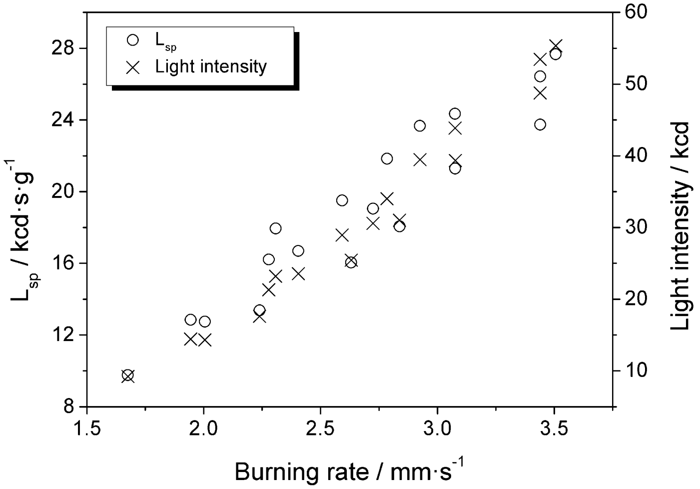


Fig. 8. L_{sp} and flare's light intensity dependence on burning rate for compositions from Table 2.

3.2. The influence of additives

After the evaluation of 18 compositions, the composition 6 was chosen as a base for further investigation, because it was slow burning, highly luminous (determined by L_{sp}/BR value) and had a decent color purity of 90%. To improve the compositions, it was considered essential to evaluate additives that at least theoretically could enhance flame size by the formation of gas or contribute positively by being an effective secondary fuel.

The use of gas generating materials has been reported back since the 1970s[44], and in recent years have been used in various illuminating pyrotechnic compositions as an energetic additive for smoother combustion, more luminous flames, and compositions emitting less smoke[19,20]. In the present work several non-exotic, gas generating materials were chosen to investigate how they affected the performance of the magnesium-rich system In addition to the gas generating materials, calcium resinate, shellac, strontium oxalate, phenolic resin, lignin sulfonate (with sodium impurities) and sulfur were also tested as additives for comparison. Additives were evaluated in “Composition 6”, which was modified by replacing 5% chlorinated rubber, by 5% additive (Table 3).

Table 3. Modified composition 6 for testing additives.

Compositions	**19-33**
$Sr(NO_3)_2$	34
Mg rounded (45-100 μm)	48
Chlorinated rubber	9
Additive	5
Linseed oil	4

Table 4. Performance parameters of compositions 19-33 with different additives.

Comp.		**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**6**
Additive		2-cyanoguanidine	Melamine	Azodicarbonamide (ADCA)	Calcium resinate	Shellac	Strontium oxalate	Lactose	Dextrin	Phenolic resin	Lignin sulfonate	5-amino tetrazole (5-AT)	Urea	Guanidinium nitrate (GN)	Hexamine	Sulfur	Chlorinated rubber
Additive chemical consistency (organic elements, %)	**C**	29	29	21	75	68	14	40	44	80	45	14	20	10	51	0	29
	H	5	5	3	9	9	0	7	6	6	5	4	7	5	9	0	2
	O	0	0	28	10	23	36	53	49	14	30	0	27	39	0	0	0
	N	67	67	48	0	0	0	0	0	0	0	82	47	46	40	0	0
O,N amount [%]		67	67	76	10	23	36	53	49	14	30	82	73	85	40	0	0
Density [$g \cdot cm^{-3}$]		1.62	1.65	1.69	1.63	1.62	1.71	1.66	1.63	1.62	1.64	1.65	1.76	1.67	1.64	1.68	1.53
Burning rate [$mm \cdot s^{-1}$]		2.39	2.51	2.23	2.27	2.17	3.11	2.26	2.31	2.15	2.63	2.56	1.99	2.39	2.40	2.92	2.28
L(sp) [$kcd \cdot s \cdot g^{-1}$]		17.4	18.3	19.7	8.8	10.7	20.3	17.6	19.2	10.9	22.5	21.0	20.1	22.7	15.3	17.9	16.2
Light intensity [kcd]		25.4	28.6	28.0	12.3	14.1	40.5	24.9	27.3	14.3	36.6	33.5	26.4	34.2	22.8	33.0	21.3
L(sp)/BR [$kcd \cdot s^2 \cdot g^{-1} \cdot mm^{-1}$]		7.3	7.3	8.8	3.9	4.9	6.5	7.8	8.3	5.1	8.6	8.2	10.1	9.5	6.4	6.2	7.1

When testing compositions 19-33, it was noted that certain compositions produced more luminous flames, while others burned very rapidly. And it was clear that not only nitrogen-rich materials were successful. For example, lactose and dextrin were almost as good as 2-cyanoguanidine and melamine when comparing light intensity values, even though they did not contain any nitrogen. Further on, experimental data was plotted in several ways to determine which factor determines an efficient composition. Finally, a trend was observed when plotting the L_{sp} values against the total amount of nitrogen and oxygen (in moles or grams) in the additive used (Fig. 9; Fig. 10) and against oxygen balance (Fig. 11).

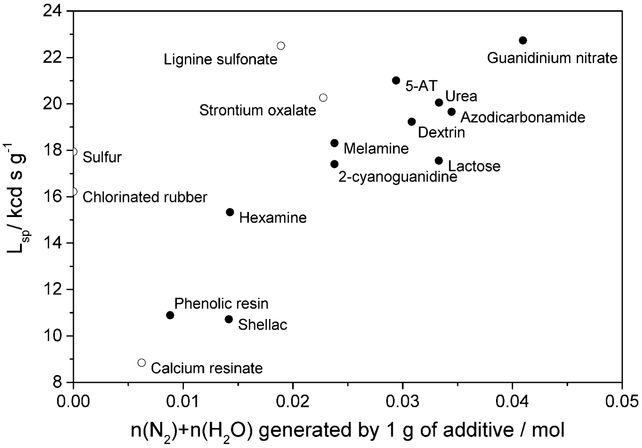


Fig. 9. L_{sp} dependence on the amount of oxygen and nitrogen (**in moles**) present in the additive.

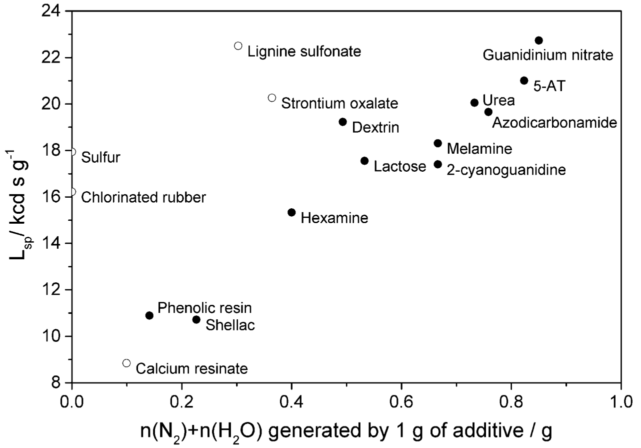


Fig. 10. L_{sp} dependence on the amount of oxygen and nitrogen (**in grams**) present in the additive.

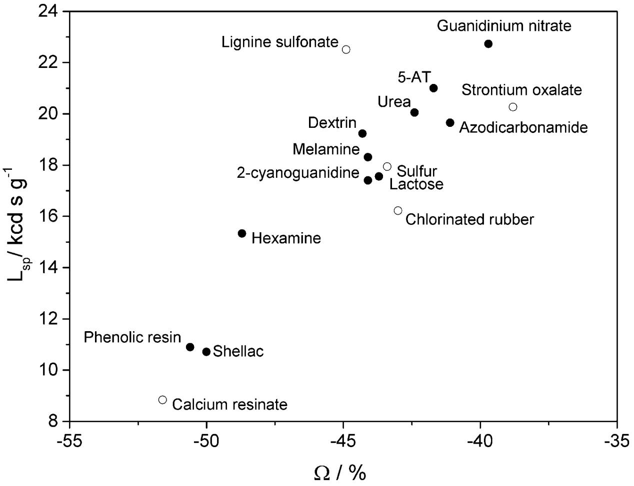


Fig. 11. L_{sp} dependence on the oxygen balance of the composition.

Several additives (calcium resinate, strontium oxalate, lignin sulfonate, sulfur and chlorinated rubber) contained other elements besides C, H, N, O; therefore, those were marked differently in the graphs. They cannot be evaluated together with fully organic additives, since some contained metal ions, i.e. Na (lignin sulfonate), Ca, Sr that are potential emitters or emitter formation enhancers. Hence, some of them, notably lignin sulfonate and strontium oxalate, show quite high L_{sp} values due to additional emitters present.

The presented trends support the fact that high nitrogen materials favor the production of more luminous flames[21], but it is evident that influence of oxygen is equally as important. Apparently, formation of $N_{2(g)}$ and $H_2O_{(g)}$ in such Mg-rich flare compositions have a similar effect on the increasing L_{sp}.

A general explanation of the observed phenomenon is that the conversion of chemical energy to light is more efficient in illuminating compositions that contains gas generating materials[2]. When gas generating materials are introduced into a composition instead of a non-gas generating material, such as chlorinated rubber, a relatively large flame envelope can result due to gas flame expansion. That, in turn, has a higher emissive area, which results in an increased light emission intensity. Other effects could be the change in the flame's absorbance and emissivity factors that directly determine the L_{sp}. When gaseous molecules replace less volatile or incandescent species, the inner absorbance in the flame envelope is decreased resulting in a more luminous flame.

According to the NASA CEA[45] code estimation of compositions (6, 31, 38) at atmospheric pressure (1 atm), $N_{2(g)}$ is in equilibrium with Mg_3N_2 at lower temperatures (1000-1500 K), however above 2000 K, $N_{2(g)}$ formation is predicted. $H_2O_{(g)}$ rapidly reacts with excess $Mg_{(g)}$ to yield $H_{2(g)}$ and $MgO_{(s/l)}$. $MgO_{(s/l)}$ is then in equilibrium reaction with soot[9] that yields $CO_{(g)}$ and $Mg_{(g)}$. Given that Mg-containing compositions reach temperatures above 2000 K[9] and all water vapor (and oxygen) reacts with excess Mg, then $N_{2(g)}$, $H_{2(g)}$, $CO_{(g)}$ molecules are formed and assist in increasing L_{sp} in such Mg-rich flare compositions.

3.3. Influence of guanidinium nitrate on flare performance

The performance of guanidinium nitrate (GN) in place of chlorinated rubber was quite impressive. Having almost the same burning and mass consumption rates, GN (comp. 31) possesses 40% higher L_{sp} value and 60% higher light intensity in comparison to comp. 6 in this system. Urea was also very efficient, and was noted for its low BR, see composition 30. However, urea is not useful in practice as it is rather hygroscopic in combination with strontium nitrate and could, therefore, be unstable together with Mg. Thus azodicarbonamide (ADCA) is a great alternative (comp. 21), which is far less hygroscopic and well performing in comparison to urea. 5-Aminotetrazole (5-AT) (and related N-rich compounds) have received much attention these days for their unique combination of high nitrogen content and high stability due to aromaticity[20]. Comp. 29 contained 5-AT and performed quite well, but with a slightly higher BR than comp. 6.

Due to excellent performance as an additive, GN was chosen for further investigation. Another advantage over other additives explored herein, is that GN by itself is an energetic material and contains an oxidizing moiety – the nitrate anion. Therefore, it can support combustion better in a strongly oxygen deficient pyrotechnic systems such as the ones of our focus. For the same reason, GN was sometimes used in the past as an oxidizer alone in illuminating compositions[46] and gas generators[2]. Therefore, the Mg-rich illuminating system could possibly tolerate even higher amounts than 5% of GN, which would be difficult for other well performing fuel-like additives from Table 4.

In fact, tests of using ADCA in the 10% range were performed, but the combustion process became uneven and pieces of burning composition were shooting out of the flare chimney as it was burning. This phenomenon is likely to occur when the gas generating material, present in the flare composition, starts to decompose in the pre-reaction zone of the composition column. In this case by "pre-reaction zone" we refer to the compacted flare composition just a short distance below the combustion surface. As a result, a piece of solid unburnt composition detaches and ejects through the flare chimney disturbing the combustion performance.

Compositions were designed with a higher amount of GN (10-25 wt.-% range). In this series of tests GN mainly replaced some of chlorinated rubber and $Sr(NO_3)_2$, while Mg amount was kept in 40-50% range (Table 5). The experiments proved that GN can be used in rather large amounts as an additive in Mg-rich compositions for low BR and higher color purity and L_{sp}.

Table 5. Formulations with 10-25% of GN and their burning characteristics.

Compositon #	**34**	**35**	**36**	**37**	**38**	**39**	**40**	**41**	**42**	**43**
$Sr(NO_3)_2$	36	31	26	36	31	26	21	31	26	21
Mg rounded (45-100 µm)	40	40	40	45	45	45	45	50	50	50
GN	15	20	25	10	15	20	25	10	15	20
Chlorinated rubber	6	6	6	6	6	6	6	6	6	6
Linseed oil	3	3	3	3	3	3	3	3	3	3
Density [$g \cdot cm^{-3}$]	1.71	1.67	1.64	1.69	1.66	1.62	1.58	1.63	1.60	1.57
Burning time [s]	39.0	47.8	54.4	32.7	41.0	50.4	57.0	33.0	43.5	54.9
Burning rate [$mm \cdot s^{-1}$]	1.83	1.53	1.37	2.22	1.80	1.50	1.36	2.27	1.75	1.42
Light intensity [kcd]	17.9	14.5	11.8	25.5	21.0	16.1	13.5	30.9	22.1	15.4
L(sp) [$kcd \cdot s \cdot g^{-1}$]	15.1	15.0	14.0	18.1	18.7	17.6	16.7	22.1	20.9	18.3
L(sp)/BR [$kcd \cdot s^2 \cdot g^{-1} \cdot mm^{-1}$]	8.3	9.8	10.2	8.2	10.4	11.8	12.3	9.7	11.9	12.9
Flame color purity [%]	85	92	94	83	91	97	99	89	95	97
Spark formation*	0	1	1	0	0	1	2	0	1	2

* defines the relative amount of sparks generated outside the flame envelope. 0 – no sparks; 1 – some sparks; 2 - lots of sparks.

Sparks or glowing slag were observed to form during combustion only in certain compositions. In the first experiments, compositions with the highest Mg content had high burning rates of >3 $mm \cdot s^{-1}$. These compositions produced fine sparks that were ejected upwards and were not observed falling down.

Some GN modified compositions from Table 5 were rather slow burning (<1.8 $mm \cdot s^{-1}$). These tended to produce larger sparks or glowing slag pieces that fell down. None the less, certain slow burning compositions possessed high color saturation (39, 40, 43), and some others (37, 38, 41) burned efficiently and clean (Table 5, Fig. 12)

When compositions from Table 5 were tested, an interesting phenomenon was observed when evaluating the emission spectra. In Fig. 13 emission spectra of compositions 37-40 are compared. The incandescence emission seemed to have decreased with decreasing burning rate and increasing GN wt.-%. The lower burning rate can affect the proportion of how much solid particles remain deposited on the flare's metal chimney and how much that enters the flame. Also, lower burning rate can affect the kinetic parameters, which determine how big spark particles are formed. Perhaps the explanation behind comp. 40 performance (lots of sparks, yet a high purity red flame) is that spark particles that formed were relatively big and not as hot to give strong incandescence. Fine solid particles that easily can be dispersed and heated up possibly emit stronger incandescence emission, which could explain composition 37 performance (higher burning rate and lower color purity). Additionally, low burning rate can cause more solid particles to be deposited on the walls of the chimney, because reaction products travel slower from the burning surface, which provides more time for solids to settle. That can also cause the flame color purity to increase.

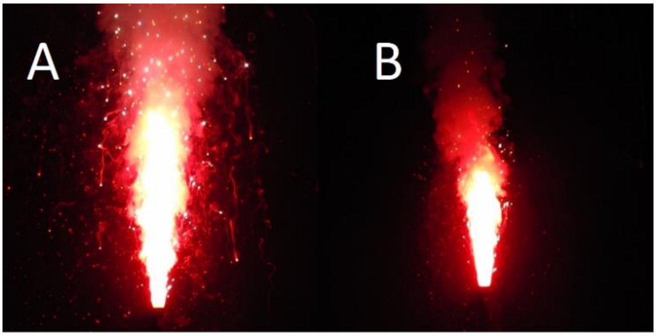
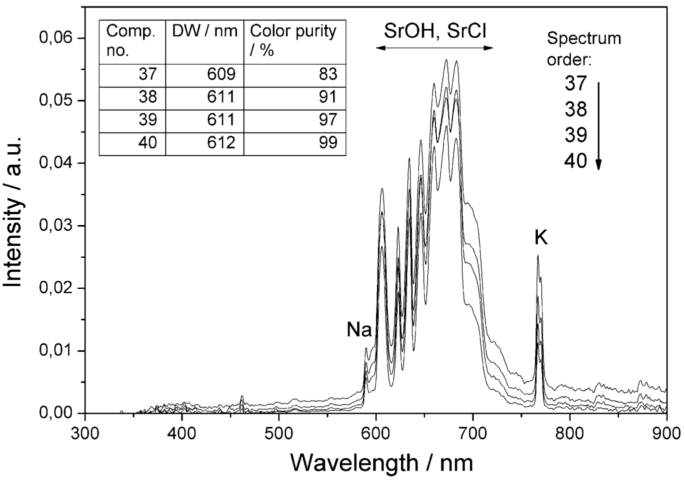


Fig. 12. Combustion of flares with composition 11 (A) producing some sparks and glowing slag, and 38 (B) producing very few sparks.

Additionally, not a single composition from Table 4 shot out burning pieces of solid composition, which was a rare, but possible case for compositions 1-33. The uniform and slow burning is likely achieved due to GN property to melt prior to decomposition, which seals the pores in the composition, before generating gases and combusting.



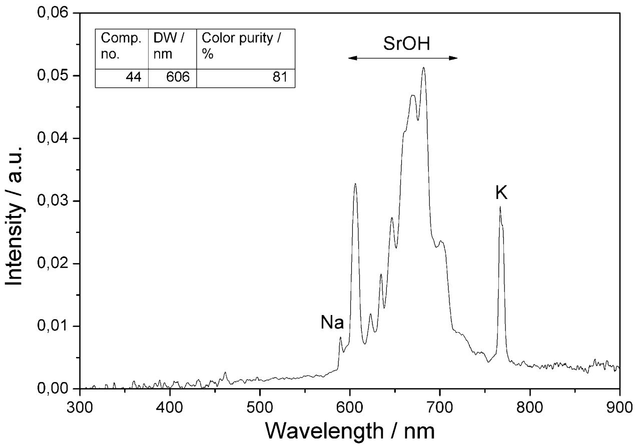
Comp. no.	DW / nm	Color purity / %
37	609	83
38	611	91
39	611	97
40	612	99

Fig. 13. Flame emission spectra of compositions 37-40. A decrease of incandescence emission results in increasing color purity and a dominant wavelength (DW) shift.

3.4. Properties of chlorine-free composition

By further tuning compositions with GN and 6% of chlorinated rubber, and an inspiration from recent papers[14,22], a chlorine-free, Mg-rich composition was evaluated. Even though it was similar to compositions 34-43, it possessed slightly different spectral characteristics. Since $SrCl_{(g)}$ emission was absent, the emission spectrum was solely composed of strong $SrOH_{(g)}$ emission together with atomic $Na_{(g)}$, $K_{(g)}$ emissions (Fig. 14). Chlorine is known to quench incandescence emission of solid particles such as $MgO_{(s/l)}$, $SrO_{(s/l)}$, by reacting with them, and forming more volatile chlorides $MgCl_{(g)}$, $SrCl_{(g)}$. Therefore, with absence of Cl, incandescence emission of the chlorine-free composition was stronger and resulted in a decreased color purity of around 79-82%.

The final comparison of compositions that possess similar BR (in groups) is presented in Table 6, together with the chlorine-free composition 44.



Comp. no.	DW / nm	Color purity / %
44	606	81

Fig. 14. Flame emission spectrum of chlorine-free, Mg-rich composition 44. $Na_{(g)}$, $K_{(g)}$ peaks are present due to impurities.

Table 6. Comparison of two groups of compositions from this work, that possessed similar burning/mass consumption rates and Cl free composition 44.

Group	**A**			**B**		**CCl - free**
Comp. No.	**6**	**21**	**31**	**3**	**39**	**44**
$Sr(NO_3)_2$	34	34	34	31	26	34
Mg rounded (45-100)	48	48	48	48	45	48
Chlorinated rubber	14	9	9	17	6	
Linseed oil	4	4	4	4	3	4
ADCA		5				
GN			5		20	13
Magnesium stearate						1
Burning rate [$mm \cdot s^{-1}$]	2.24	2.23	2.39	1.68	1.50	1.71
L_{sp} [$kcd \cdot s \cdot g^{-1}$]	16.7	19.7	22.7	9.8	17.6	16.2
Light intensity [kcd]	21.5	28.0	34.2	9.2	16.1	17.4
L_{sp} /BR [$kcd \cdot s^2 \cdot g^{-1} \cdot mm^{-1}$]	7.4	8.8	9.5	5.8	11.8	9.5
Flame color purity [%]	89	88	87	92	97	80

3.5. Blue illuminants

Pyrotechnic blue illuminant formulations were gathered from different sources. Ten of them having the highest color saturation (purity) based on the information in the literature were selected for this experiment. All the selected blue flame compositions contain four main components: an oxidizer, a fuel, a copper source and a chlorine source. The variety of chemical components was another criterion for the compositions being as different one from another as possible. This can provide more information about the best compositions and the best chemical components for generating blue flames with a high color saturation. The selected compositions are presented in Table 7 and their combustion characteristics are given in Table 8.

Table 7. Experimental compositions: chemicals, ratios, sources.

No.	Source	Composition & ratio	Ratio	Comments
1	Hahma	AP/Cu/CR/Hexamine/CP	62/14/4/10/10	Optimized for maximum [HCl+Cu]/[CuO] formation
2	McGriffen[47]	AP/Cu/Stearic acid/Paraffin	74/11/11/4	Ashless blue flare
3	Naud[48]	AP/5-AT/BCC	47.5/47.5/5	N-rich blue
4	Dumont[49,50]*	AP/Copper benzoate/Dex	79/17.5/3.5	Classic AP/Cu benzoate blue
5	Hardt[6]	$KClO_3$/Paris green/Stearic acid/HCB/Dex	62/21/8/4/5	Copper acetoarsenite-containing
6	Ofca[51]	$KClO_3$/CuOCl/Lactose/CP/Dex	65/13/13/5/4	Chlorate-lactose blue
7	Veline[52]	$KClO_4$/CuO/Red Gum/CR/MgAl/Dex	53/14/9/14/6/4	Firework star with MgAl
8	Stanbridge[53]	$KClO_4$/CuO/HCB/S/Dex	39/37/6.5/15/2.5	Chinese blue for small pellets
9	Naud[54]	$KClO_4$/CuO/PVC/Hex/Red Gum/Dex	61/17/10/6/3/3	Naud Ref. blue
10	Pihko**	$KClO_4$/CuO/Hexamine/CR	62/13/10/15	Perchlorate-Hexamine blue

Private communication: *Modification by Arno Hahma (2012), ** Petri Pihko (1988)

50 g of each composition (except 25g of No. 5) were prepared. Five 10 g pellets (16.80 mm diameter) were pressed out of each composition. The values presented in Table 7 are an average over 5 parallel measurements. It must be

noted that even though pellets were ignited from the top, not all of them burned evenly (cigarette burning). For compositions 5-10, that were based on potassium chlorate and perchlorate, the surface flame propagation was more pronounced than that to the depth of the pellet. For that reason, the recorded burn rate data presented in Table 7 is not as precise as it was expected.

The first composition burned with a uniform tall flame, especially during the first seconds. It was one of the very few compositions passing the 50% p_e threshold and had DW of 445 nm, which is the lowest of all 10 compositions. This composition also possesses the highest I_v and L_{sp} values among AP based compositions in this study.

The second composition was different from the first one due to wax and stearic acid as fuels. Occasionally, large yellow spots appeared in the blue flame envelope due to soot formation. This can be addressed to the largest oxygen deficit resulting in a reduced p_e. The burn rate was also the lowest among the 10 compositions studied.

The third composition was unique because of its high nitrogen content, which was achieved by using 5-AT as the main fuel. The poor fuel properties of this compound resulted in a composition, which could not sustain combustion on its own. However, the composition could be burned by holding a glowing sparkler wire on the burning surface. It should be noted that this composition is a derivative from the original presented by Naud at al[48].

The composition 4 was comprised of AP, which was an oxidizer and chlorine source and copper benzoate, a fuel and a copper source. This well-balanced composition ($\Omega = -5.4$) passed the 50% p_e threshold while its I_v and L_{sp} values remained on the average level.

The composition 5 was unique due to the use of copper acetoarsenite. An interesting note is stated by Shimizu[10,25]: “copper acetoarsenite was used in Japan in almost all blue compositions in 1980’s as it produces a very pretty blue”. Nowadays, such compositions are used less due to toxicity and environmental concerns. This composition produces more smoke compared to AP compositions (1-4) due to the presence of potassium, which creates solid particles.

The composition 6 had the highest oxygen balance of $\Omega = +3.7$. The ingredient CP was difficult to distribute evenly throughout the composition, which in addition to the positive Ω may have contributed to the lower performance of the composition. Also, a decrease in color saturation was observed during the combustion of each pellet.

The composition 7 is a popular one in fireworks. The metallic fuel MgAl increases the flame temperature and light output accordingly but results to a reduced color saturation. With p_e of 30%, the composition 6 had the highest I_v and L_{sp} of the tested compositions.

The composition 8 had the highest p_e of 55.7%. This composition is unique for its high copper oxide content (37%), low potassium perchlorate content of 39% and for the absence of an energetic fuel such as wax, hexamine, etc. Sulfur is used as the main fuel instead. Sulfur helps to scavenge potassium in the flame resulting in an increased chlorine concentration promoting $CuCl_{(g)}$ emitter formation[15,25]. HCB acts as a chlorine donor.

The composition 9 was chosen as a reference from Naud[54]. It was similar to composition 10 with a similar p_e of 41% It had only a slightly lower L_{sp} and I_v values.

The composition 10 was an efficient blue flame composition yielding p_e of 39% with L_{sp} of 414 $cd \cdot s \cdot g^{-1}$. It also produced the largest amounts of glowing slag on the test plate, where pellet was fixed.

Table 8. Experimental results: Oxygen balance (Ω), Burn time, average pellet length, burn rate, TMD - theoretical maximum density TMD % (indicates the fraction of measured density divided by TMD), I_v, L_{sp}, and color coordinates are presented. The mass of all pellets was in the range 9.5-11.7 g, except composition 5, which was limited to 4.8-5 g for each pellet. The white point was set at x = 1/3, y = 1/3.

No.	**Ω [%]**	**t [s]**	**l [mm]**	**BR [$mm \cdot s^{-1}$]**	**TMD [$g \cdot cm^{-3}$]**	**TMD [%]**	**I [cd]**	**±**	**L_{sp} [$cd \cdot s \cdot g^{-1}$]**	**±**	**p_e [%]**	**±**	**DW [nm]**	**CIE x**	**CIE y**
1	-20.2	17.5	23.2	1.3	1.98	96%	91	6.6	162	12.1	51.6	±1.2	453.7	0.240	0.173
2	-26.3	42.5	26.0	0.6	2.01	85%	22	2.5	94	4.1	30.4	±4.1	556.2	0.328	0.251
3	-15.1	27.5	32.7	1.2	1.75	83%	10	2.3	26	3.2	38.1	±1	432.8	0.269	0.210
4	-5.4	12.5	26.0	2.1	1.75	95%	79	18.3	98	2.5	52	±1.6	463.2	0.233	0.179
5	-12.7	9.0	11.3	1.3	2.17	90%	58	0.8	107	4.3	45.3	±1.9	469.6	0.240	0.208
6	3.7	8.0	23.5	3.0	2.18	86%	46	3.2	37	1.8	28.6	±3.4	462.8	0.278	0.250
7	-12.8	11.6	24.7	2.1	2.16	83%	388	27.6	454	22.9	29.8	±2	464.1	0.276	0.246
8	-3.2	6.9	19.8	2.9	3.02	73%	108	21.7	75	8	55.7	±2.6	467.9	0.221	0.175
9	-5.5	8.0	22.9	2.9	2.31	82%	267	19.7	218	15.9	40.8	±1.6	477.3	0.242	0.240
10	-5.8	11.1	23.1	2.1	2.30	82%	365	48.4	414	35.8	38.6	±0.2	481.1	0.242	0.261

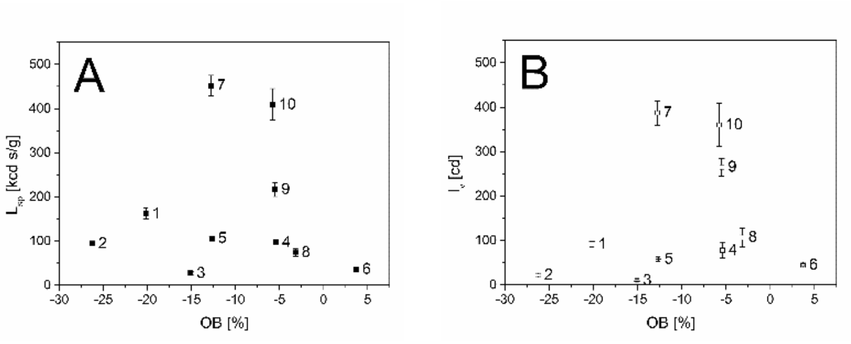


Fig. 15. L_{sp} (A) and I_v (B) dependence on the oxygen balance.

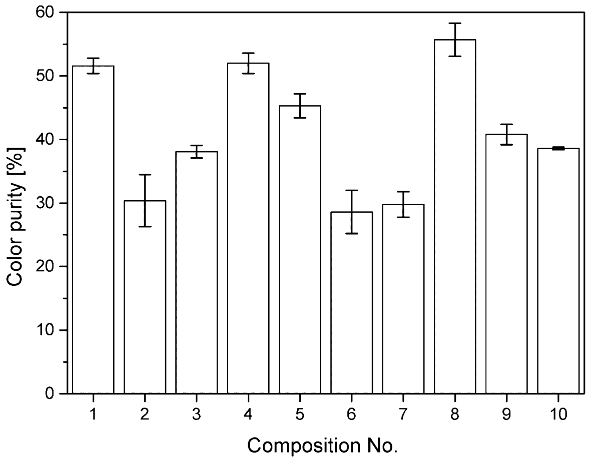


Fig. 16. The distribution of p_e.

The Ω of all compositions lies in the range of -26 to +4%. The compositions at the extreme ends (6 and 2) had low L_{sp} and I_v values, which may be related to the unbalanced system. Too low Ω results in soot formation, while too high Ω may cause the emitter species to be oxidized. The L_{sp} and I_v dependence on Ω are depicted in Figure 15.

The measured p_e lies in the range of 28 – 56% (Fig. 16). The lowest p_e of ~30% was measured for compositions 2,6,7 and the highest exceeding 50% for compositions 1,4,8. Deep blue flame compositions with high p_e are usually observed to burn with a relatively dim flame compared to the bright ones having a low p_e. In this work, composition 8 flame was indeed the least luminous of the $KClO_4$ compositions (107 cd, 74 cd·s·g^{-1}). However, p_e reached 56% on average from 5 pellets, with one pellet reaching 57.7%. By observing the p_e vs time graphs some pellets of the composition 8 peaked at

65% p_e during the first seconds of combustion, before the p_e dropped to 50-57%. Possibly the reduction of the color purity is associated with slag formation on the burning surface. The composition 8 is designed to be used as small stars in fireworks. Therefore, it possibly did not deliver the best performance when burned as a 16 mm diameter, 10 g pellet.

The emission spectra were recorded for each of 10 compositions. The main focus of interest was to observe how the $CuCl_{(g)}$ emissions compare to the CuOH, CuO, Na and black body emissions (K atomic emission at 767 nm is outside the visible spectrum). In figure 17A $KClO_3$ compositions 5,6 are compared. Composition 5 has a less pronounced grey body radiation and strong $CuCl_{(g)}$ emissions at 400-470 nm; hence, it possesses a higher color purity than composition 6. In Figure 17B, the spectra of compositions 8 and 10 are compared. The CuOH emission from composition 10 appears much more pronounced compared to composition 8. This emission decreases the color purity of the composition 10; however, the latter is much brighter burning. In Figure 18, the raw spectra of composition 6 are depicted at selected times. The intensity decreased as a function of time. This phenomenon was not observed with other compositions, at least not to such a strong extent. This effect may have resulted from both (i) the CP being unevenly distributed in the composition and (ii) also the slag formation.

Finally, the CIE x/y coordinates plotted in the CIE 1931 color diagram (Fig. 19) are located in the blue and blueish-white region of the chromaticity diagram. The compositions 1,4,8 show a noticeable shift towards the blue region of the chromaticity diagram.

Video captures of the burning pellets are collected in Figure 20. From these photos the flame size, shape, smoke and slag formation can be estimated. The AP based compositions 1,2,3,4, tend to burn with little smoke and no slag formation. The flame, especially in the beginning of the combustion, is tall and narrow. Later on, it evolves to a shape seen in Figure 20 (1,2,3,4). The $KClO_3$ and $KClO_4$ compositions (5-10) produce some slag and a significant amount of smoke. Some of them had higher I_v, L_{sp} and p_e values than AP compositions, which are often considered superior blue flame compositions. The reason for the higher light output can be associated with smoke reflection during the measurements. If the smoke in the measurement chamber reflects some of the emitted light from the flame towards the spectrometer, the reflected light adds to the recorded data. This effect could not be completely avoided, because it is not possible to extract the smoke at the edge of the flame completely. On the other hand, the eye will also perceive this, and the pyrotechnic composition will appear brighter than it actually is. In that sense, no error is produced, when the back reflection is ignored.

NASA CEA2 code was used to estimate the transient species present in the flames of tested compositions (supplements). Only composition 5 was omitted, as there was no data on arsenic species. The adiabatic flame temperatures range from 1840 K for composition 8, to 2690 K for composition 10. Besides the high concentration of typical combustion products i.e. H_2O, CO_2, CO, H_2, N_2, a substantial amount of HCl (0.15 mol-%) was produced for AP compositions 1 – 4. Moreover, both KCl, HCl were present in $KClO_3$ and $KClO_4$ based compositions 6 - 10. The target species for this experiment was CuCl. While most compositions had around 0.03-0.05 mole-% of CuCl produced, compositions 8 had 0.07 mole-% of CuCl, which is in relation to the high performance of this composition described earlier. This can be associated with very high concentration (37 wt.-%) of CuO used in the compositions, that shifts the equilibrium towards CuCl formation.

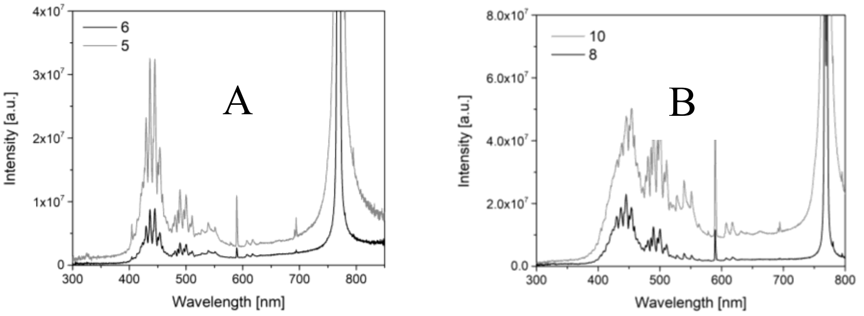


Fig. 17. Emission spectra of compositions 5,6 (A), 8,10 (B).

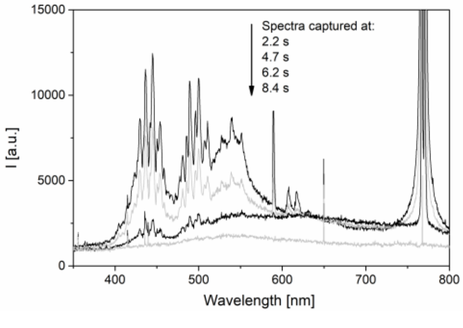


Fig. 18. The composition 6 pellet flame’s raw emission spectra recorded at 2.2, 4.7, 6.2, 8.4 s after ignition. A decrease in the intensity is observed. The strongest emission in the blue region is observed after the ignition and the least intense emission is observed in the last seconds of combustion process.

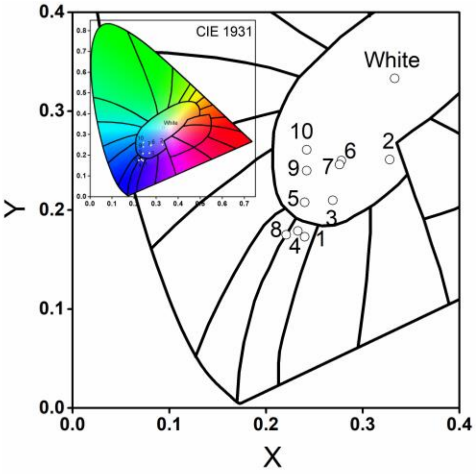


Fig. 19. Zoomed in chromaticity diagram including the evaluated compositions with the full diagram in the upper left corner.

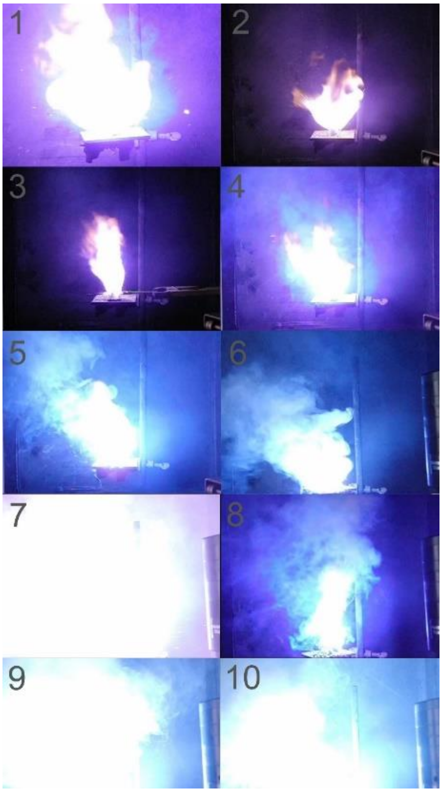


Fig. 20. Video captures of each burning composition (3 s after ignition).

3.6. Blue strobes

The idea of using a AP/GN base for blue strobes has been already investigated by McCaskie[40]. The high percentage of GN requires a lot of energy to melt it and, even with catalytic help of copper compounds, it decomposes slowly. Therefore, GN based strobe compositions are possible; however, their performance does not surpass TMAN based compositions. Some TMAN based compositions have been tested containing 55% AP, 30% TMAN, 15% of copper sources, that include Cu, CuO, Cu(II) benzoate, BCC, and up to additional 2% of additives that are NC or sulfur. Such compositions possessed medium sensitivity to friction (120-360 N) and shock (4-15 J). Such compositions burn fiercely with a strobing behavior and a re-erupting blue flame. However, when burnt as 13 mm pellets the flashes were overlapping and some compositions did not sustain combustion. In addition to that, TMAN is a rather expensive material for the use in pyrotechnics and fireworks; therefore, AGN was suggested as a possible replacement that could surpass GN in its reactivity and have an advantage over TMAN being more easily available and cheaper option. A series of strobe compositions containing AP, GN, AGN, different copper sources (Cu, CuO, Cu_2O, BCC) were tested.

BCC was chosen over copper and copper oxides as it could produce a blue flame flash of higher color purity and a better flash separation. However, CuO can also work. PVC was also employed as recommended by E. McCaskie. PVC seems to serve well as a low-energetic fuel that possibly assists the smolder reaction[55]. After several experiments of testing different additives and varying the oxygen balance of such compositions led to a narrow area of a working blue strobe compositions. Such working compositions possessed a distinct strobing behavior, sustainable combustion and a seemingly good blue color of the strobe flashes. In Table 9 three different blue strobe compositions (GN, AGN, TMAN based) are compared. In Fig. 21 and 22 their strobing patterns are presented, that were obtained by monitoring the light intensity at 450 nm in time. Two types of samples were tested: 5 mm rods (0.4 g sample) and 13 mm pellets (2 g). The 5 mm rod samples were made with an intention of having a minimal energetic feedback, which could help lowering the strobe frequency.

Table 9. Blue strobe chemical compositions of a GN base (A), AGN base (B), TMAN base (reference). Strobe frequency, linear burn rate, chemical stability and sensitivity parameters are present.

Compositions		A	B	Ref.
AP		30	25	55
GN		50		
AGN			55	
TMAN				30
PVC		5	5	
$CuCO_3 \cdot Cu(OH)_2$ (BCC)		15	15	
Cu powder (40-100 mesh)				15
NC powder				+1%
Frequency, Hz	13 mm	3.5±2	8±2	>10
	5 mm rods	const.	3.8±2	>10
Linear burning rate (5 mm rod), mm/s		1.4	1.1	5.2*
CIE coordinates**	X	0.262	0.249	0.236
	Y	0.296	0.275	0.289
Color purity,** %		27	32	35
Chemical stability (DTA), ^{o}C		247	179	245
Sensitivity tests	Impact (J)	15	10	6
	Friction (N)	>360	>360	240
	ESD (mJ)	42	33	51

*unusually high combustion rate resulted from the enhanced surface flame propagation of this particular composition. The linear burning rate is expected to be lower.

**light produced by the flash reaction

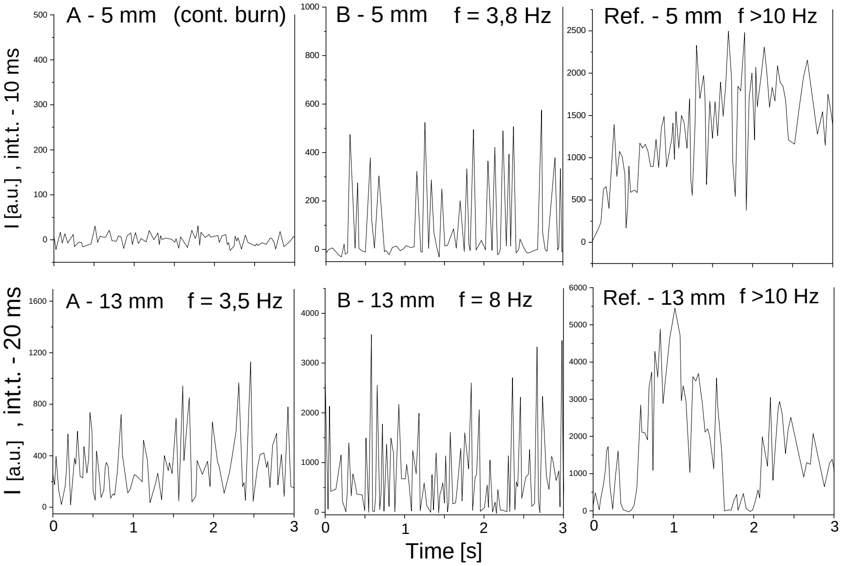


Fig. 21. Light intensity at 450 nm vs time.

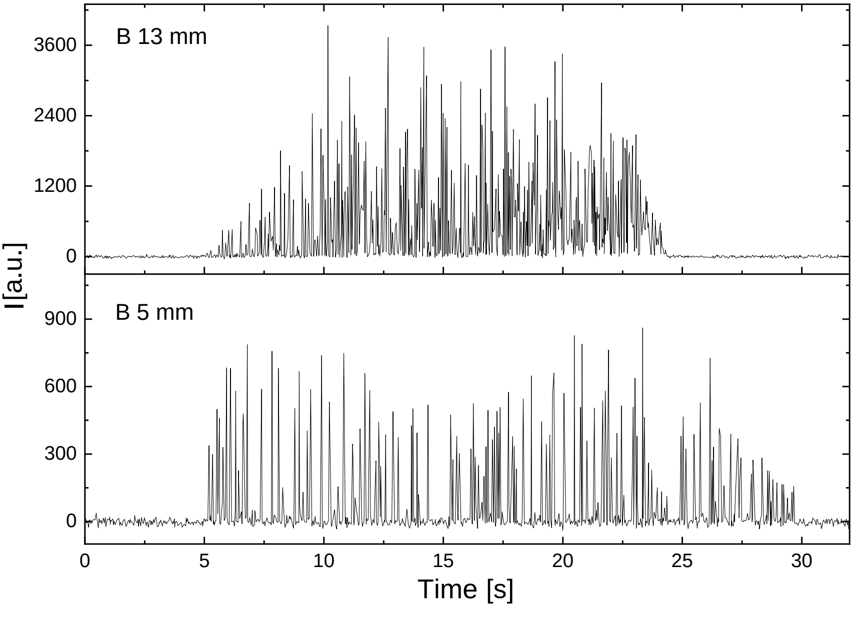


Fig. 22. Consistent over time strobing pattern of composition B tested as a 5 mm rod and 13 mm pellet. From the ignition point the rod was consumed in 25 s at a linear burn rate of 1,1 mm/s. Light intensity was registered at 450 nm.

The composition A with GN produced the strobing effect (13 mm pellet), even though the light intensity of the flashes was rather weak. The 5 mm rod of A burned constantly with a very weak re-appearing blue flame that was not registered by spectrometer.

The reference composition with TMAN burned with overlapping blue flashes as seen in Fig. 21.

The B composition performed quite well producing stable and distinct (Fig. 22) blue flashes when tested as both 5 rods and 13 mm pellets. Due to good performance as a blue strobe the composition B was analyzed further to evaluate its chemical stability and strobe mechanism.

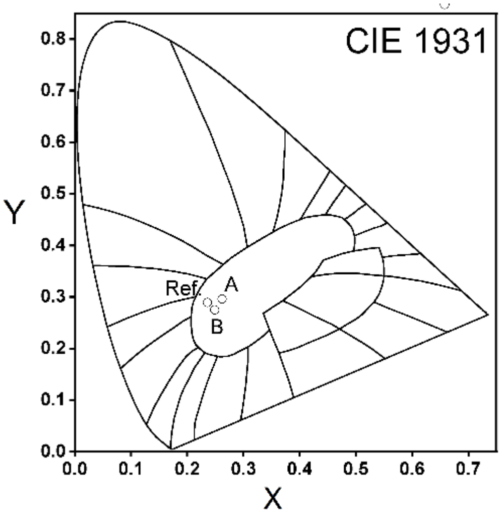


Fig. 23 Chromaticity diagram indicating color points of the flash reactions of A, B and reference compositions.

The chromaticity diagram (Fig. 23) shows that the blue strobe light has a color purity in the range of 27% to 35%, when the Illuminant C point is set as a reference.

3.7 Humidity test

Blue strobes are generally known to degrade over time due to possible ageing reactions that can occur. For example, AP can react with metallic copper, salts can undergo double exchange reactions, acid-base as well as complex formation reactions are also possible.

Therefore, a humidity test was performed in order to estimate how moisture sensitive is the composition B at room temperature (Table 10). Each test was performed in a desiccator with a saturated salt solution over a 3-day period. Three samples of ~0.6 g were weighed with an analytical scale before and after exposure to enhanced relative humidity.

Table 10. Exposure of composition B to different relative humidity generated by saturated salt solutions at room temperature.

Salt		K_2CO_3	NaBr	NaCl	KNO_3
Relative humidity at 25 °C, %		43	57.6	75.3	93.6
Pellets	Weight change	0	0.0004	-0.0005	-0.0246
	Color change/cracks	no	no	no	yes*
Powder	Weight change	0.001	-0.002	-0.0115	-0.0375
	Color change	no	Greyish violet (lite)	Greyish violet	deep purple**

*In 6 h purple spots appear
**In 3 h turns grey-violet, in 6h purple, after three days - deep purple

After exposure to RH 75%, the first significant change in sample's weight was registered. Moisture induces a reaction that releases gases, which causes the weight loss and the color change.

The color change was also registered in several sample compositions that were stored before pressing pellets. However, well dried compositions did not cause such reaction for up to 2 months of storage at room temperature.

It must be noted that dry and acid-free AGN was used in our experiments (water solution shows pH of 7-8 on universal indicator paper). In our experience, compositions with non-acidic AGN have significantly greater shelf life.

When 3 g of acid-free AGN is dissolved in water and 1 g of finely ground BCC is added to the solution, the color of undissolved BCC changed first to light violet and then to purple. Bubbling is observed. After stirring the suspension and letting react overnight, 2.8 g of purple precipitate is formed, which is likely to be a Cu aminoguanidinium complex. When dried and ignited as loose powder, the complex material burns fiercely producing a green flame that comes from $CuOH_{(g)}$ emissions. The chemical stability this complex species is quite unclear, and as mentioned before, AGN and BCC reaction's side product had self-ignited one time during drying. Therefore, long term stability tests at elevated temperatures are suggested before using in practice.

3.8 Differential thermal analysis (DTA)

DTA measurement was performed for composition B and certain compositions with AGN. It was found that BCC catalyses the decomposition of AGN and significantly changes the DTA curve of AGN (Fig. 24). The B curve is very similar to AGN/BCC with the same decomposition point at 179 °C, meaning that AP and PVC do not participate in this process.

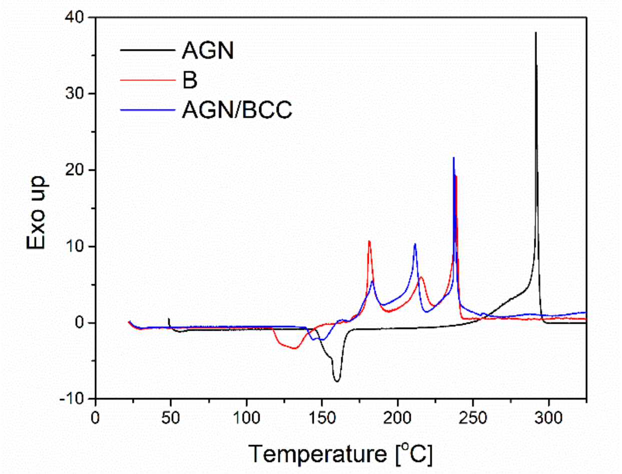


Fig. 24. DTA curves of pure AGN, AGN/BCC (55/15 wt.-%. ratio) and composition B.

Sometimes during the incremental heating of the DTA sample, the test composition B (and very similar ones) showed a high-order deflagration (likely at 238 °C) that were powerful enough to rupture the mini glass test tube of the DTA instrument. The sample weight was ~40 mg.

Generally, the AP/TMAN based strobe compositions were thermally stable up to 245 °C.

3.9 Origin of the bright blue flash

The high-speed camera videos give interesting information on the strobe reactions observed in this work. There have been a few curious phenomena registered that are described; however, it is somewhat difficult to draw a clear conclusion from the latter that would help to explain the strobe reactions that occur in AGN/AP/BCC system. However, they give some clues.

During the smolder phase gases are generated from the reaction surface (Fig. 25). Around 50% of the smolder reaction time small blue-glowing lines of gases appear at the reaction surface as well as micro blue flashes (Fig. 26A).

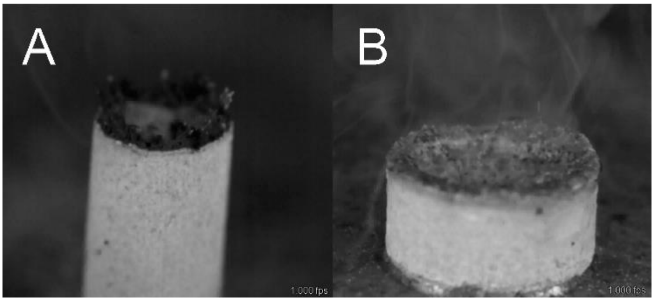


Fig. 25. Smoldering surface of composition B 5 mm rod (A); 13 mm pellet (B) (capture from the high-speed camera footage at 1000 fps). Heavy boiling and gas generation is observed on the molten reaction surface. Whitish boiling reactants can be observed in the center of both samples.

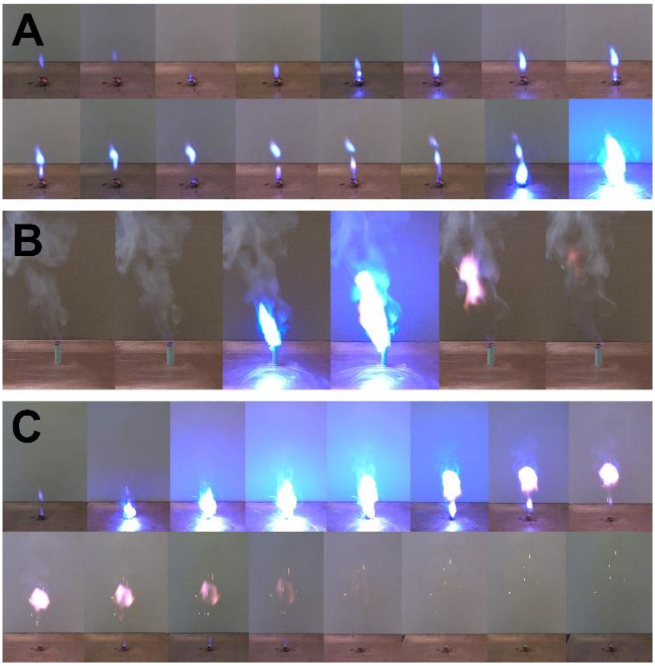


Fig. 26. High speed camera footage of the oscillatory burning B composition. A) Glowing gases appear at the reaction surface at all time (500 fps); bright flame spot appearing prior to the flash reaction can be seen in the fifth frame; in the last frame flash reaction starts. B) and C) capture series of the occurring blue flash at 100 fps and 500 fps respectively. The blue color is associated to the emission of $CuCl_{(g)}$ and reddish tip to CuO.

As the glowing gases eject from the burning surface, sometimes, especially few milliseconds before the flash reaction, a significantly brighter flame spot appears (Fig. 26A, the fifth frame) that travels upwards with the flow of gases. Perhaps this is a region of higher temperature or a piece of molten reactive composition being ejected from the pellet‘s surface, that has a delayed ignition and burns to produce a significantly bright blue flash/spot, that is associated to the same brightness and color of the flash reaction (Fig. 26A).

The flash reaction seems to be a result of (i) rapid exothermic reaction that causes the ejection of flammable gases from the boiling surface or (ii) an ignition of gases that have already been formed above the pellet (Fig. 26B). Possibly it can be a combination of the two as well.

The first assumption is made from our previous work with TMAN strobes and the evidence from the current DTA measurement, as the exothermic decomposition at ~240 °C tends to be quite energetic often breaking the mini test tube of the sample.

The second assumption followed observing the ash scaffold formation (Fig. 27) and analyzing the high-speed camera footage. Most test samples burned rather clean without significant ash formation, however, few samples of a 5 mm rods burned leaving a thin scaffold of ash that was almost as tall as the 20 mm long test sample (Fig. 27). Also, the ash scaffold was observed to be glowing red during combustion, indicating the surface temperature of 600-900 °C.

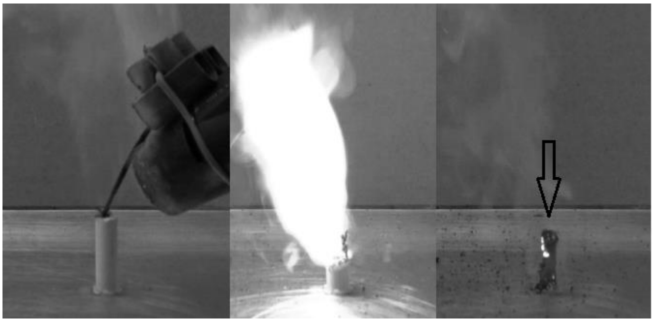


Fig. 27. The ash scaffold is formed due to a strong heat loss to the surrounding atmosphere during the combustion of 5 mm rod (comp. B). Partially red glowing ash scaffold in the last frame is observed.

Interestingly, being thin and fragile as the scaffold is, it did not fall apart due the strobe reaction that would make one expect to have a certain pressure fluctuation at the surface that is accompanied by the popping sound observed every time when testing compressed and uncompressed B composition. For example, a classical white strobe composition based on AP/MgAl/$BaSO_4$ [10] burns to produce flashes that are more similar to a small portions of flash powder deflagrating. This produces pressure fluctuations, that can be seen when such composition is compact into a cardboard casing, that eventually burns off and the remaining's of the paper casing are blown away by the pressure waves of the flashes. However, in the case of rod, the ash scaffold remained still, indicating that there are no significant pressure fluctuations at the burning surface, what supports the second assumption.

Moreover, in Fig. 26B it can be seen, the erupted blue flash did not create pressure that would blow away the smoke cloud that had been formed from the beginning. This would indicate that the flame had spread through the flammable semi-reacted smoke above the pellet, consuming it, however not creating any significant pressure in the flame envelope. This also supports our personal observations during measurements. Visually, the combustion of the B comp. rod produced a rather steady flow of gases from the rod's surface that only flashed rapidly, and the flashes did not disturb the uniform flow of the gases. Also, the popping sound was very distinct and observed all time for tests of comp. B.

CONCLUSIONS

1) Oxygen and nitrogen-rich additives were noted for their ability to increase the specific luminosity (L_{sp}) of a Mg-rich flare composition. The resulting flares can exceed the 22 kcd s/g efficiency, with a burning rate of 2.1 mm/s. This way, pyrotechnic flares can be made brighter, with more saturated color flames.

2) Guanidinium nitrate showed the best performance as an additive in the tested system. While maintaining low BR, it produced 40% higher L_{sp} and 60% higher light intensity in comparison with a similar GN-free composition. The preferred amount was in the range of 0-15 wt.-%. Changes in flame's emissivity and absorbance factors, as well as the total emissive area, have probably had the greatest influence on the increase of flare's illuminating performance. Different from conventional compositions, a rather small amount of chlorine donor (4-6 wt.-%) was found to be sufficient to achieve a deep red flame when used in combination with gas generating additives and high amount of Mg. Mg-rich and Cl-free composition can also be obtained using GN as an energetic additive. The resulting flame's color purity is in the 80% range.

3) Even though highly regarded in older literature, Paris green-containing composition did not surpass the other top compositions in color purity nor in light intensity. While it contains both Cu and As, only copper seemingly contributed to the emission spectrum and no As emission was registered. While Paris green-containing composition 5 had purity p_e = 45.3% and produced light of I_v = 58 cd and L_{sp} = 107 cd·s·g^{-1}, a well-balanced, As-free composition 10 produced much stronger emission of I_v = 365 cd, L_{sp} 414 cd·s·g^{-1} and had a similar, perhaps only slightly lower p_e of 38.6%. The highest average purity (p_e) of 55.7% (and up to 58% for a single pellet) was observed from the composition 8 with 108 cd, 75 cd·s·g^{-1}. The peak p_e = 65% was registered during the first 3 seconds of combustion. The dominant wavelength of this composition was 468 nm. $KClO_4$/S system used in the composition 8 was found useful for producing a blue flame with high purity. It also proves that KOH continuum and $K_{(g)}$ do not interfere significantly with desired $CuCl_{(g)}$ emissions.

4) AGN and TMAN were proved to be a suitable strobe moderator in combination with AP and BCC for producing a blue strobe pyrotechnic pellet. The strobe pellets were observed to be very sensitive to any deviations of the composition stoichiometry and geometrical parameters of the pellet. The amount of additive (NC, sulfur) was only tolerated in 1-2% range. Blue strobe composition in powder form showed sensitivity to moisture at RH = 58-75%, and better resistance with RH = 75-94% when the pellet was bound with PVC/MEK.

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SUPPLEMENTS

1. Chemical equilibrium calculations

The chemical equilibrium calculations were performed for compositions from table 7 with NASA CEA code using „hp“ problem at p = 1.013 bar, t = 2000 K.

Note: Composition 5 was impossible to model as the program lacks As species in the database. Also ΔH_f of Paris Green was not found.

Heat of formation (ΔH_f) values and formulae used for calculations:

Ingredient	Formula	ΔH_f (kJ/mol)
5-aminotetrazole	CN_5H_3	324
Ammonium perchlorate	NH_4ClO_4	-295.8
Chlorinated paraffin (64% Cl)	$C_{15.5}H_{12.25}Cl_{8.75}$	-765*
Chlorinated rubber	$C_{10}H_{11}Cl_7$	-395*
Copper	Cu	0
Copper benzoate	$CuC_{14}H_{10}O_4$	-682
Copper carbonate, basic (malachite)	$Cu_2CH_2O_5$	-1067
Copper oxychloride	$Cu_4Cl_2H_6O_6$	-1657
Copper(II) oxide	CuO	-156
Dextrin	$C_6H_{10}O_5$	-948.4†
Hexachlorobenzene	C_6Cl_6	-131
Hexamine	$C_6H_{12}N_4$	124.1
Lactose monohydrate	$C_{12}H_{24}O_{12}$	-2519
Magnalium	$Al_{12}Mg_{17}$	-3.7± 0.1
Paraffin	$C_{20}H_{42}$	-682.5
Polyvinyl chloride	C_2H_3Cl	-94.6
Potassium chlorate	$KClO_3$	-398
Potassium perchlorate	$KClO_4$	-433
Red gum	$C_{30}H_{30}O_{13}$	-550**
Stearic acid	$C_{18}H_{36}O_2$	-947.7
Sulfur	S	0

† values for starch

* estimated by Barry T. Sturman.

** estimated by DJ.

Compositions:

No.	Composition	Ratio
1	AP/Cu/CR/Hexamine/CP	62/14/4/10/10
2	AP/Cu/Stearic acid/Paraffin	74/11/11/4
3	AP/5-AT/BCC	47.5/47.5/5
4	AP/Copper benzoate/Dex	79/17.5/3.5
6	$KClO_3$/CuOCl/Lactose/CP/Dex	65/13/13/5/4
7	$KClO_4$/CuO/Red Gum/CR/MgAl/Dex	53/14/9/14/6/4
8	$KClO_4$/CuO/HCB/S/Dex	39/37/6.5/15/2.5
9	$KClO_4$/CuO/PVC/Hex/Red Gum/Dex	61/17/10/6/3/3
10	$KClO_4$/CuO/Hexamine/CR	62/13/10/15

Calculations:

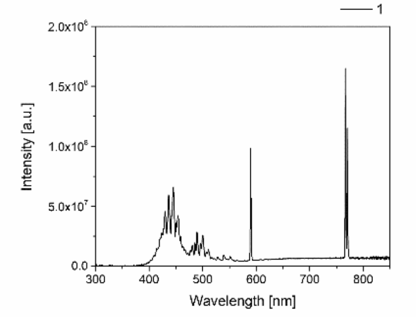
1		2		3	
T, K	2320	T, K	2230	T, K	2690
	MOLE FRACTIONS		MOLE FRACTIONS		MOLE FRACTIONS
*CO	0.15548	*CO	0.17812	*CO	0.10709
*CO_2	0.07437	*CO_2	0.06787	*CO_2	0.03205
*Cl	0.00392	*Cl	0.00148	*Cl	0.00925
*Cu	0.01353	*Cu	0.01086	*Cu	0.00681
CuCl	0.04957	CuCl	0.03253	CuCl	0.00398
CuO	0.00001	CuOH	0.00003	CuO	0.00001
CuOH	0.00004	Cu_2	0.00003	CuOH	0.00002
Cu_2	0.00003	*H	0.00272	*H	0.01831
*H	0.00355	HCl	0.12421	HCl	0.08358
HCl	0.17086	*H_2	0.16456	*H_2	0.11442
*H_2	0.11057	H_2O	0.33752	H_2O	0.22921
H_2O	0.29951	*NO	0.00003	*NO	0.00131
*NO	0.00009	*N_2	0.0791	*N_2	0.38207
*N_2	0.11662	*O	0.00001	*O	0.00094
*O	0.00003	*OH	0.00091	*OH	0.01015
*OH	0.00177	*O_2	0.00001	*O_2	0.00076
*O_2	0.00004				

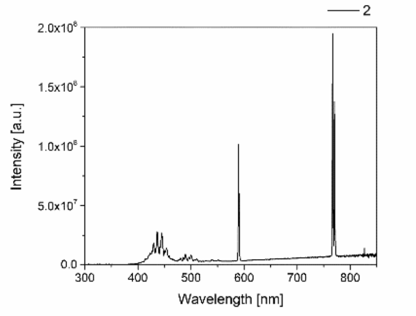
4		**6**		**7**	
T, K	**2630**	**T, K**	**2060**	**T, K**	**2690**
	MOLE FRACTIONS		MOLE FRACTIONS		MOLE FRACTIONS
*CO	0.09624	*CO	0.0033	AlCl	0.00001
*CO_2	0.1661	*CO_2	0.31845	AlOCl	0.00001
*Cl	0.02549	*Cl	0.00126	AlOH	0.00002
ClO	0.00003	*Cu	0.0035	*CO	0.25047
Cl_2	0.00003	CuCl	0.05081	*CO_2	0.16319
*Cu	0.00481	CuO	0.00007	*Cl	0.01077
CuCl	0.01125	CuOH	0.00012	ClO	0.00001
CuO	0.00004	Cu_2	0.00001	*Cu	0.04349
CuOH	0.00003	Cu_3Cl_3	0.0001	CuCl	0.03124
*H	0.00778	*H	0.00006	CuO	0.00017
HCl	0.15268	HCL	0.01925	CuOH	0.00013
HOCl	0.00001	*H_2	0.0007	Cu_2	0.00009
HO_2	0.00001	H_2O	0.32143	*H	0.01001
*H_2	0.03239	*K	0.0002	HCl	0.05631
H_2O	0.36597	KCl	0.23203	*H_2	0.03624
*NO	0.00262	KO	0.00001	H_2O	0.15792
*N_2	0.09345	KOH	0.00342	*K	0.00566
*O	0.00323	K_2Cl_2	0.00155	KCl	0.15482
*OH	0.02301	*O	0.0002	KH	0.00001
*O_2	0.01482	*OH	0.00356	KO	0.00008
		*O_2	0.03995	KOH	0.00275
				K_2Cl_2	0.00007
				*Mg	0.00449
				MgCl	0.00235
				$MgCl_2$	0.00908
				*MgO	0.00127
				MgOH	0.00059
				$Mg(OH)_2$	0.00069
				*O	0.00194
				*OH	0.01206
				*O_2	0.00341
				$MgAl_2O_{4(l)}$	0.02085
				$MgO_{(cr)}$	0.01981

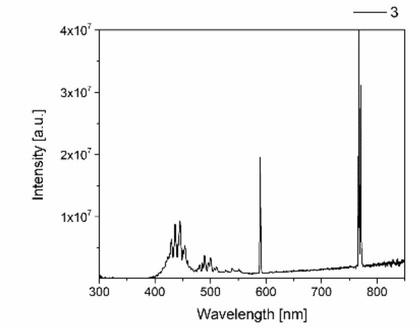
8		9		10	
T, K	**1840**	**T, K**	**2430**	**T, K**	**2510**
	MOLE FRACTIONS		MOLE FRACTIONS		MOLE FRACTIONS
*CO	0.00044	*CO	0.08588	*CO	0.11412
*CO_2	0.17012	*CO_2	0.27812	*CO_2	0.23538
*Cl	0.00067	*Cl	0.00303	*Cl	0.00959
*Cu	0.00055	*Cu	0.04291	ClO	0.00001
CuCl	0.06493	CuCl	0.0489	Cl_2	0.00001
CuO	0.00001	CuO	0.00026	*Cu	0.0232
CuOH	0.00001	CuOH	0.0003	CuCl	0.04582
Cu_3Cl_3	0.00848	Cu_2	0.00021	CuO	0.00013
HCl	0.01108	*H	0.00211	CuOH	0.00013
*H_2	0.00003	HCl	0.0265	Cu_2	0.00005
H_2O	0.0514	*H_2	0.01306	*H	0.00344
*K	0.00001	H_2O	0.25389	HCl	0.06661
KCl	0.19999	*K	0.00325	*H_2	0.01678
KOH	0.00031	KCl	0.18185	H_2O	0.21576
K_2Cl_2	0.00445	KO	0.00007	*K	0.00208
K_2SO_4	0.00001	KOH	0.00564	KCl	0.18507
*O	0.00002	K_2Cl_2	0.0002	KO	0.00004
*OH	0.00034	*NO	0.00079	KOH	0.00244
*O_2	0.01204	*N_2	0.03678	K_2Cl_2	0.00015
SO	0.00009	*O	0.00084	*NO	0.00115
SO_2	0.34724	*OH	0.00867	*N_2	0.05998
SO_3	0.00038	*O_2	0.00674	*O	0.00125
$Cu_2O_{(L)}$	0.1274			*OH	0.01025
				*O_2	0.00656

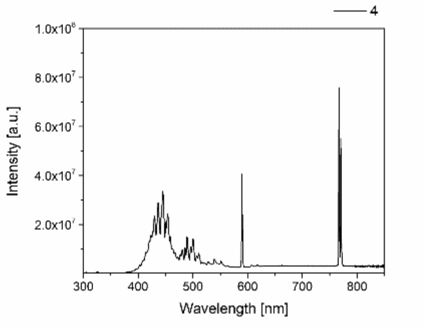
2. Emission spectra

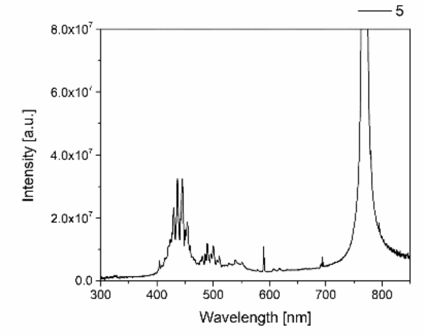
These spectra are the sum of all spectra recorded for one pellet (out of five) during combustion. The background is subtracted.

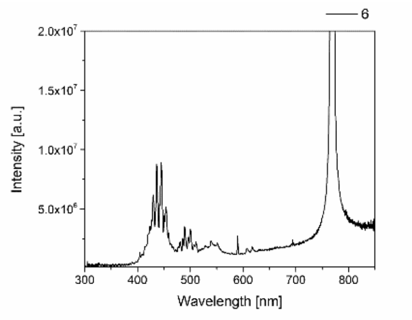


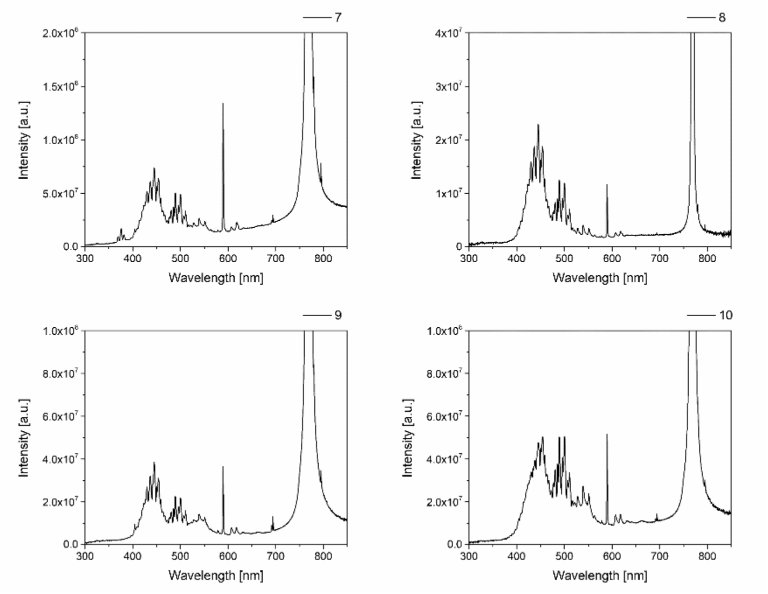











7
2.0x10⁸
1.5x10⁸
1.0x10⁸
5.0x10⁷
0.0
Intensity [a.u.]
300
400
500
600
700
800
Wavelength [nm]
8
4x10⁷
3x10⁷
2x10⁷
1x10⁷
0
Intensity [a.u.]
300
400
500
600
700
800
Wavelength [nm]
9
1.0x10⁸
8.0x10⁷
6.0x10⁷
4.0x10⁷
2.0x10⁷
0.0
Intensity [a.u.]
300
400
500
600
700
800
Wavelength [nm]
10
1.0x10⁸
8.0x10⁷
6.0x10⁷
4.0x10⁷
2.0x10⁷
0.0
Intensity [a.u.]
300
400
500
600
700
800
Wavelength [nm]

SANTRAUKA

Įžanga ir naujumas

Pirotechniniu mišiniu yra apibūdinamas bent dvikomponentis kietafazis heterogeninis mišinys, kuris geba reaguoti save palaikančia egzotermine reakcija. Reakcijos metu išsiskiria sąlyginai didelis kiekis šilumos, taip pat šviesos (liepsna, kibirkštys), garso, dūmų.

Pirotechninių mišinių sudėtingumas yra susijęs su jų chaotiškumu. Faktiškai kiekvienos pirotechninės reakcijos metu išsiskiriant dideliam kiekiui šilumos, yra stebimos visos trys agregatinės reagentų ir reaktantų būsenos, kartais netgi plazma. Prieš užsidegant pirotechniniam mišiniui, dalis jo paviršiuje esančių komponentų išsilydo. Tada, vykstant cheminei degimo reakcijai, susidaro produktai: dujos, kietosios dalelės, skysčio lašeliai. Įvertinant tai, kad temperatūra gali svyruoti drastiškai nuo maždaug 300 °C iki 3500 °C, tampa sudėtinga modeliuoti ir matuoti tokio tipo mišinius. Svarbiausi registruojami tokių eksperimentų parametrai yra:

- Linijinis degimo greitis (mm/s)
- Liepsnos emisijos spektras (UV, VIS, IR)
- Šviesos stipris (cd)
- Specifinis šviesos stipris (cd·s/g)
- Parametrai registruojami filmuojant:
  - Šlako susidarymas
  - Kibirkštys
  - Liepsnos forma, atmosferinio deguonies difuzija
  - Degimo paviršius
  - Degimo profilis (intensyvumo, šviesumo pokyčiai)
  - Garsas

20-ojo amžiaus autoriai G.W. Weingart[3], B.E. Douda[4], A.A. Shidlovski[1], J.H. McLain[5], A. Hardt[6], R. Lancaster[7], T. Shimizu[8–10], J.A. Conkling[11] reikšmingai prisidėjo savo knygomis prie pirotechnikos suvokimo iš mokslinės, techninės ir meninės perspektyvos.

Paskutiniais metais labiausiai buvo nagrinėjamos specifinės pirotechnikos sritys t. y.: apšviečiamieji mišiniai, spalvotos liepsnos, pul-suojančio degimo pirotechniniai mišiniai, IR spinduoliai, molekulės su dideliu azoto kiekiu, termitiniai mišiniai.

Šiame darbe buvo tiriami apšviečiamieji mišiniai, spalvotos liepsnos ir pulsuojančio degimo pirotechniniai mišiniai.

Apšviečiamoji pirotechnika

Tokio tipo pirotechniniai mišiniai pasižymi specifine savybe: degdami išskiria išskirtinai didelį kiekį spinduliuotės regimojoje arba UV, IR spektrų dalyse. Tai pritaikoma kariniams tikslams, pvz., apšviesti karo lauką arba IR liepsnoms, kurios naudojamos priešraketinėje gynyboje.

Dažniausiai, bet ne visada, intensyvi spinduliuotė pirotechniniuose užtaisuose yra susijusi su aukšta liepsnos temperatūra, kuri padeda sužadinti kuo didesnį kiekį atomų arba molekulių.

Tokio tipo mišinių pagrindinės sudedamosios medžiagos yra šarminių arba šarminių žemių metalų nitratai, pvz., $Sr(NO_3)_2$, $NaNO_3$, kurie veikia kaip oksidatoriai ir spinduolių šaltiniai. Taip pat įeina metalinis kuras (dažniausiai Mg, Al, Zr) bei mažesni kiekiai chlorintų organinių junginių (pvz., chlorintos gumos) SrCl, BaCl spinduolių emisijai sužadinti, rišiklių (epoksidai), degimo greičio modifikatorių (stearino rūgštis), stabilizatorių (virtas linų aliejus).

Nors ir turintis gana prastą atsparumą drėgmei, magnis yra nepakeičiamas kuras tokio tipo užtaisuose. Jis degdamas su oksidatoriumi sukuria labai aukštą liepsnos temperatūrą, dėl ko pasiekiama maksimali spinduolių šviesos emisija.

Svarbiausi kriterijai geram UV-VIS liepsnos mišiniui yra: a) degti maksimaliai ryškiai, b) turėti sodrią liepsnos spalvą, kurios sodrumas būtų >80 % (pvz., raudonasis pavojaus signalas jūrai), c) degant išskirti kuo mažiau šlako, d) būti chemiškai stabiliam ir mažai kenksmingam.

Spalvotos liepsnos mišiniai

Tokio tipo mišiniai yra labai panašūs į apšviečiamuosius, tačiau, jiems svarbesnis faktorius už liepsnos ryškumą yra spalvos sodrumas. Tokio tipo mišiniai yra taikomi fejerverkuose. Prie jų priskirtini ir mėlynos liepsnos mišiniai, kurių liepsnos sodrumas, deja, nėra didelis (100-500 cd; 30-65 % p_e).

Pulsuojančio degimo mišiniai

Pulsuojantis degimas pirotechnikoje yra apibrėžiamas kaip pirotechninio mišinio degimas, kurio metu šviesa išsiskiria ne pastoviai, o cikliškai ir dažniausiai pastoviu periodu viso degimo metu. Taip degimo metu stebimas liepsnos mirksėjimas, kurio metu organoleptiškai galima išskirti atskirus blyksnius ir tarp jų esančią „tamsiąją“ fazę.

Šie mišiniai turi panašumo į apšviečiamuosius, nes jų degimo metu stebimi blyksniai yra ne ką mažiau ryškūs už apšviečiamojo mišinio liepsną.

Galima išskirti kelis tipus literatūroje aprašytų pulsuojančio degimo mišinių. a) NH_4ClO_4 / Mg pagrindu, b) $Ba(NO_3)_2$ / MgAl pagrindu, c) NH_4ClO_4 / guanidinio nitrato / vario katalizatoriaus pagrindu.

Iš „a“ tipo mišinių nesudėtinga išgauti spalvotus blyksnius, kurie yra vieni patraukliausių efektų fejerverkuose. Tačiau mėlynos spalvos pulsuojantis mišinys yra labai sudėtingas, ir šiuo metu nerasta tokia sudėtis, kuri būtų gerai veikianti ir chemiškai stabili. „c“ tipo mišinys yra iš esmės skirtas mėlynai pulsuojančiai liepsnai išgauti.

Tikslas

Pagerinti apšviečiamųjų pirotechninių mišinių specifinį šviesos stiprį, neprarandant liepsnos spalvos sodrumo bei mišinio cheminio stabilumo.

Uždaviniai

Šiai daktaro disertacijai buvo suformuluoti uždaviniai:

a) Ištirti ir nustatyti, kokį Mg kiekį gali toleruoti apšviečiamieji pirotechniniai mišiniai, išlaikydami mažą (<2,1 mm/s) degimo greitį ir neprarasdami liepsnos spalvos sodrumo bei šviesos intensyvumo. Ištirti $Sr(NO_3)_2$/Mg/CR trikomponentę sistemą stebint šviesos intensyvumą, efektyvumą, sordrumą. Ištirti priedus, kurie galėtų pagerinti mišinio savybes.

b) Rasti tinkamiausią priedą ir jį ištirti, bandant didesnius jo kiekius. Įvertinti, kokius priedo kiekius mišinys gali toleruoti, degdamas stabiliai.

c) Optimizuoti mėlynos liepsnos mišinius. Apžvelgti geriausius mėlynų liepsnų mišinius, jų įvairovę, specifines savybes ir medžiagas, kurios padeda išgauti sodriausią liepsnos spalvą. Palyginti geriausius mišinius matuojant jų liepsnų šviesos intensyvumą, efektyvumą, spektrą, CIE 1931 koordinates, sodrumą ir dominuojantį bangos ilgį.

d) Rasti chemiškai stabilų pulsuojančios mėlynos liepsnos mišinį. Atkartoti jau paskelbtus tokio tipo mišinius. Išbandyti kitus pulsavimo moderatorius. Išbandyti kitus vario katalizatorius.

Ginamieji teiginiai

1. Naudojant apavalių grūdelių magnio miltelius ir kombinuojant mišinį kartu su dujas generuojančiu komponentu, galima sukurti itin efektyvų (>22 kcd·s/g) pirotechninį mišinį, kuris dega <2,1 mm/s greičiu.
2. Guanidinio nitratas yra tinkamas priedas apšviečiamiesiems mišiniams (naudojant 0-15 %), padedantis padidinti efektyvumą (L_{sp}) net iki 60 %.
3. Pulsuojančios mėlynos liepsnos mišiniui gali būti naudojamas aminoguanidinio nitratas.
4. Mėlynos liepsnos mišiniai su santykinai dideliu spalvos sodrumu (p_e >50 %) gali būti sukurti nenaudojant tokių arseno darinių kaip „Paryžiaus žaluma“.

Eksperimentinė dalis

Šiems tyrimams naudoti reagentai buvo laboratorinio grynumo, išskyrus kai kurias sunkiau prieinamas medžiagas, kurios buvo susintetintos arba gautas techninio grynumo mėginys.

Mišinių ruošimui reagentai buvo sumalti iki tokio smulkumo, kad nesunkiai būtų prasijojami per 0,6 mm sietelį. Kai kuriais atvejais buvo aktyvuojamos rišamosios medžiagos tam, kad mišinys neišsisluoksniuotų jį beriant arba presuojant. Kai kuriais atvejais buvo užtepamas dengiamasis mišinys tam, kad mėginiai lengviau užsidegtų. Jo sudėtis buvo a) 75 % $KClO_4$, 20 % beržo anglies ir 5 % šelako b) 65 % CuO ir 35 % Mg c) 80 % KNO_3, 15 % anglies ir 5 % chlorintos gumos.

Buvo naudojami trijų tipų mėginiai:

1. 40 g mišinio, ir 2 g dengiamojo mišinio, supresuoti į 21,6 mm metalinę tūtą (aukštis ~70 mm);

2. 13-16,8 mm sausos tabletės (mėlynoms liepsnoms ir pulsuojančiam degimui), supresuotos iš 2-10,5 g mišinio (aukštis 5-30 mm);

3. 5 mm strypeliai (0,5 g mišinio, 25 mm aukščio).

40 g užtaisai buvo tiriami reguliuojamo greičio vėjo tunelyje, o mažesnieji – traukos spintoje. Mėginiai buvo uždegami dujiniu degikliu arba dagtimi. 40 g užtaisai buvo padegami nuotoliniu būdu, naudojant trintimi aktyvuojamą degiklį.

Šviesos intensyvumas buvo matuojamas šviesos stiprio matuokliu LMT, I(ph)–meter 1500, arba kalibruotu OceanOptics spektrometru JAZ ULM, kuris kartu registravo ir emisijos spektrus. Atstumas nuo mėginio iki detektoriaus buvo nuo 0,3 m mažiems mėginiams (2-5 g) iki 10 m 40 g užtaisams. Integravimo laikas buvo parenkamas pagal signalo stiprumą.

Degimo proceso analizei mišinys buvo filmuojamas su SONY DCR-HC37E kamera. 1000 kadrų per sekundę greičio filmavimui buvo panaudota Visario G2 1500 Weinberger „speed camera”, o SONY RX10 III buvo naudojama filmuoti 100 ir 500 kadrų per sekundę greičiu.

Be degimo proceso registravimo, geriausiai veikiantys mišiniai arba jų svarbūs komponentai buvo papildomai tiriami. DTA analizė buvo atlikama 552-Ex diferenciniu terminiu analizatoriumi iš OZM, kaitinimo sparta 5 °C min^{-1}. Jautrumas smūgiui ir trinčiai buvo matuojamas BAM krentančiu kūju ir BAM trinties testeriu. Atsparumas elektrostatinei iškrovai buvo matuojamas su Xspark 10 instrumentu iš OZM. Jautrumai buvo vertinami pagal „Jungtinių tautų rekomendacijas pavojingų medžiagų transportavimui“:

smūgiui:

- nejautrus >40 J,
- mažai jautrus >35 J,
- jautrus >4 J,
- labai jautrus <4 J;

trinčiai:

- nejautrus >360 N,
- mažai jautrus <360 N,
- labai jautrus <80 N,
- itin jautrus <10 N.

Raudonų liepsnų mišiniai modifikuoti panaudojant dujas generuojančius priedus su dideliu Mg kiekiu

Pirmojo eksperimento tikslas buvo ištirti gerai šių tyrimų srityje pažįstamos $Sr(NO_3)_2$/Mg/PVC sistemos efektyvumą, kuri turėtų ypač didelį kiekį Mg (40-60 %). Literatūroje aprašomus mišinius sudaro 30–40 % Mg, 55–35 % $Sr(NO_3)_2$, 12–20 % chlorintų organinių darinių, 4–10 % kitų priedų kaip oksidatoriai, rišikliai, stabilizatoriai, degimo greičio modifikatoriai.

Mg kiekio mišinyje didinimas gali turėti ir neigiamą įtaką kitiems liepsnos parametrams, tokiems, kaip: a) sumažėjusi spinduolių koncentracija, b) padidėjęs degimo greitis, c) padidėjęs foninis švytėjimas, kuris sumažina liepsnos spalvos grynumą.

Eksperimento metu buvo ištirta 18 skirtingų mišinių, kurių sudėtis yra: 40-60 % Mg, 28-42 % $Sr(NO_3)_2$, 5–17 % chlorintos gumos, 4 % virinto linų aliejaus. Atsižvelgiant į degimo greitį ir specifinį šviesos stiprį, optimalus mišinys buvo pasirinktas tolimesniam tyrimui.

Priedų įtaka

Bandant išgauti geresnes degimo savybes, buvo panaudoti priedai. Naujo mišinio sudėtis buvo 48 % Mg, 34 % $Sr(NO_3)_2$, 9 % chlorintos gumos, 4 % virinto linų aliejaus ir 5 % priedo.

Dujas generuojantys priedai pirotechnikoje jau yra žinomi nuo 1970 metų, tačiau dar iki šių laikų jie yra bandomi taikyti apšviečiamojoje pirotechnikoje, mažesnio dūmingumo užtaisuose ir dujų generatoriuose. Išbandytos medžiagos buvo 2-cianoguanidinas, melaminas, azodikarbonamidas, kalcio rezinatas, šelakas, stroncio oksalatas, laktozė, dekstrinas, fenolinė derva, lignino sulfonatas, 5-aminotetrazolas, urėja, guanidinio nitratas, heksaminas, siera.

Guanidinio nitratas

Išbandžius priedus paaiškėjo, kad guanidinio nitratas pasižymi puikiomis savybėmis kaip priedas tokio tipo mišiniuose, todėl sėkmingai gali būti dedamas vietoje chlorintos gumos. Su guanidinio nitratu pagamintas užtaisas turėjo panašų degimo greitį kaip ir mišinys su chlorinta guma, tačiau jo šviesos stipris buvo 60 % didesnis, o specifinis šviesos stipris – 40 % didesnis.

Vėliau buvo nustatytas guanidinio nitrato kiekis mišinyje, kuris yra tinkamas su dideliu magnio kiekiu. Toleruojama riba siekė 25 %.

Mišinys be chloro

Degant chlorintiems organiniams junginiams, ypač žemesnėje temperatūroje, padidėja polichlorintų bifenilų susidarymo tikimybė. Tokie junginiai yra kancerogeniniai, dėl šios priežasties buvo tiriamas mišinys, kuris pasižymėtų dideliu specifiniu šviesos stipriu bei neturėtų chloro. Buvo surastas mišinys, sudarytas iš 48 % Mg, 34 % $Sr(NO_3)_2$, 13 % guanidinio nitrato, 4 % virinto linų aliejaus ir 1 % magnio stearato.

Tokio tipo mišinys duoda liepsną, kurios pagrindinis spinduolis aukštoje temperatūroje yra SrOH. Nors liepsnos spalovos sodrumas yra 15% mažesnis, tačiau specifinis šviesos stipris vis tik lieka panašus į mišinio su chloru.

Mėlynos liepsnos

Pirotechnikoje vienas didžiausių iššūkių yra didelio sodrumo spalvotos, ypač mėlynos, liepsnos gavimas. Šio eksperimento tikslas buvo palyginti geriausius žinomus mėlynos liepsnos mišinius spektrofotometru ir nustatyti kurio mišinio liepsnos spalva yra sodriausia. Tam tikslui buvo surinktos populiariausios mėlynų liepsnų mišinių formulės. Pagrindiniai oksidatoriai buvo NH_4ClO_4, $KClO_3$ ir $KClO_4$. Mišiniai gana smarkiai skyrėsi deguonies balansu, įnešamu vario ir chloro kiekiu, kurais.

Išmatavus šių mišinių liepsnas spektrofotometru, buvo nustatyta, kad liepsnų sodrumo vertės yra 28-58 % intervale. Mišinys, sudarytas iš $KClO_4$, CuO, heksachlorbenzeno, sieros, dekstrino santykiu 39/37/6,5/15/2,5, davė sodriausią mėlyną liepsną – 52 % (5 tablečių vidurkis). Maksimalus sodrumas (65 %) buvo stebimas pirmąsias 3 degimo sekundes. Liepsnos šviesos stipris buvo 108 cd, o specifinis šviesos stipris – 75 $cd \cdot s \cdot g^{-1}$. Dominuojantis bangos ilgis - 468 nm.

Mėlynos liepsnos pulsuojančio degimo mišiniai

Pulsuojančio degimo pirotechniniai mišiniai yra naudojami fejerverkų gamyboje. Tokio tipo baltos spalvos mišiniai yra žinomi jau ilgą laiką. Raudonos, žalios ir geltonos spalvos pulsuojančio degimo mišiniai gana nesunkiai gaunami, kombinuojant stroncio arba bario nitratą su MgAl milteliais, tačiau mėlynos splvos pirotechninis pulsuojantis mišinys yra kur kas sudėtingesnis. Šio tyrimo tikslas buvo ištirti mišinius, kurie naudoja a) guanidinio nitratą (GN), b) aminoguanidinio nitratą (AGN), c) tetrametilamonio nitratą (TMAN) kaip degimo moderatorius.

Visi tokio tipo mišiniai naudoja amonio perchloratą kaip oksidatorių (25-55 %), degimo moderatorių arba energentinį kurą (30-55 %), vario druską arba vario oksidą (6-20 %). Optimizuojant mišinius buvo gauta stabiliai pulsuojanti mėlyna liepsna su aminoguanidinio nitratu. Jos pulsavimo dažnis buvo 4-8 Hz. Šiuo atveju dažnis priklausė nuo degančio paviršiaus ploto. Su TMAN irgi gaunama pulsuojanti liepsna, tačiau dėl skirtingo deguonies balanso mišinys sunkiau dega ir dažniau užgęsta savaime. Tai nutinka, kai smilkimo reakcija užtrunka per ilgai ir nepakanka šilumos įvykti blyksnio reakcijai. GN yra mažiau reaktingas negu pastarieji, todėl jo mišiniai dega vibruojančia liepsna, o ne pulsuoja.

Išvados

Medžiagos, turinčios didelį deguonies ir azoto kiekį, padėjo gauti didesnį liepsnos šviesį apšviečiamuosiuose mišiniuose su dideliu magnio kiekiu.

Guanidinio nitratu modifikuojant mišinį, buvo gautas didžiausias, 60 % didesnis už palyginamąjį bandinį specifinis šviesos stipris (efektyvumas) naudojant 4-6 % chloro donoro mišinyje. Mišinys be chloro buvo sukurtas naudojant guanidino nitratą, tačiau jo liepsnos sodrumas neviršijo 80 %.

Nors ir vertinamas senoje literatūroje, Paryžiaus žaluma (vario acetoarsenitas) nepralenkė kitų vario junginių be arseno savo liepsnos sodrumu (45 % p_e lyginant su 50-55 % p_e naudojant CuO ir Cu atitinkamai). Naudojant $KClO_4$/S bazinį mišinį, pavyko gauti labai didelio sodrumo mėlyną liepsną, kuri degimo metu siekė iki 65 %. Tai taip pat parodo, kad KOH švytėjimas liepsnoje yra nereikšmingas ir netrukdo $CuCl_{(g)}$ molekulių sužadinimui, kurios lemia mėlyną spinduliuotę. Ryškiausią mėlyną liepsną pavyko gauti kaip papildomą kurą naudojant MgAl. Toks mišinys degė 388 cd šviesos stipriu ir 454 $cd \cdot s \cdot g^{-1}$ efektyvumu. Tačiau šiuos parametrus pavyko gauti prarandant liepsnos sodrumą, kuris buvo tik apie 30%.

Mėlynos liepsnos pulsuojančio degimo mišinys buvo sėkmingai sukurtas degimo moderatoriumi naudojant AGN. Mišiniai su AGN ir su TMAN yra labai jautrūs bet kokioms mišinio modifikacijoms. Kitų priedų kiekis mišinyje negali viršyti 1-2 %.

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WORK EXPERIENCE:

1. 2018 (7 months) Junior researcher at Vilnius University.
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3. 2010 – 2014 (part time) Pyrotechnitian at UAB Blikas.

PROFESSIONAL TRAINING

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ORIGINAL PAPERS

Paper 1

An experimental comparison of selected blue flame pyrotechnics

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An experimental comparison of selected blue flame pyrotechnics

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Dedication: In memory to Dr. Bernard E. Douda

Abstract: In this research 10 different pyrotechnic blue flame compositions were designed and compared. Chromaticity and luminosity parameters of the flame were measured using Ocean Optics JAZ-ULM VIS-Spectrometer equipped with a cosine corrector. Color saturation, luminous intensity, specific luminous intensity, oxygen balance, burn rate, actual and theoretical maximum density, color coordinates (X,Y) are presented and discussed.

Key words: Blue flare pyrotechnic; Copper chloride; Fireworks; Pyrotechnics; Illuminating flame.

Abbreviations

AP – ammonium perchlorate
5-AT – 5-aminotetrazole
BCC - basic copper carbonate (malachite)
Dex – dextrin
HCB – hexachlorobenzene
CuOCl – copper oxychloride
CR – chlorinated rubber
CP - chlorinated paraffin
MgAl – powdered magnesium-aluminium 50/50 alloy
PVC – polyvinyl chloride
Ω – oxygen balance
I_v – light intensity (cd)
p_e – color saturation or purity
L_{sp} – specific luminous intensity (cd s / g)

Introduction

A blue pyrotechnic flame color with high saturation or color purity (p_e), is one of the biggest challenges in pyrotechnics. While several suitable pyrotechnic compositions can be formulated with a reasonable effort for red, green and yellow at high color purity and high luminous intensity (I_v), there are much fewer examples for blue illuminants available.

An excellent historic perspective on colored flame development is given in the thesis by *Sturman*[1]. He discusses the evolution of colored flames throughout the years, even from the period before the introduction of potassium chlorate into pyrotechnic compositions.

One of the first spectroscopic investigations that reported an analysis of blue flames was carried out by *Barrow & Caldin*[2]. They identified the emitting species as CuCl. Interestingly, mercury(I) chloride was used in these compositions as chlorine source.

Blue flames have been studied by several researchers and academics over the past decades. *Douda* has contributed significantly to the understanding of colored flames[3].

A systematic study of compositions, which are generating blue flames, was performed by *Shimizu*[4]. He utilized a self-made spectrograph containing a sample holder, a 0.04 mm slit, water prisms, lenses and a photographic plate.

The proliferation of relatively low-cost spectrometers has been helpful for studying pyrotechnic flames. Pyrotechnic compositions are assessed in a "static" way, whereby the sample is burned, and the smoke is removed well enough to ensure a free line of sight to the sample. In 2003, Brian Ingram investigated the spectra of red, green and blue pyrotechnic flames[5]. *Meyerriecks* and *Kosanke* studied the principal emitters in colored flames[6]. They utilized solutions of various chemicals in combination with a nebulizer and an oxygen/propane/acetylene flame.

Several papers have been published about the desired emitter in pyrotechnic flames comprising a copper and a chlorine source[7]. *Dolata* speculated about the formation of a trimer of CuCl[8]. This was quickly followed by *Sturman*, who provided disproof of this hypothesis[9].

While static measurements are a sound and reproducible method for characterizing compositions, such measurements are not representative of the true environment in the most of applications. In actual use, pyrotechnic compositions have to burn at various airspeeds. Consequently, mixing of ambient air will alter the flame stoichiometry and temperature. Furthermore, pyrotechnic stars may extinguish in flight.[10,11].

Few publications are available about "Round Robin trials" of spectral color measurements. *Douda* has reviewed 81mm mortar flares as test objects[12].

Recent efforts have been made to identify alternatives to the well-known copper-chlorine based systems. Some of us have published work on copper(I)bromide, and compared it to copper(I)chloride[13]. The work includes the 1931 CIE coordinates for the isolated spectra of CuCl and CuBr. In the same year *Koch* compared all four copper(I)halides[14]. He provided values of the 1931 CIE coordinates, as well as the dominant wavelength and color purity. He has concluded that copper(I)bromide provided good efficiency, even outperforming the classical copper(I)chloride. The copper(I) fluoride and the copper(I) iodide based system were found to be inferior to the bromide and chloride. The formulations tested by *Koch* were optimized for the formation of K_2SO_4, to enable spectral measurements minimizing the interference of potassium.

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Recently, the flame color of pyrotechnics containing metallic indium has been investigated. These results do not indicate that indium is, even from a purely technical point of view, a viable alternative emitter[15].

The goal of the present study was to compare the p_e and dominant wavelength of the best-known blue flame (star) compositions. An overview of pyrotechnic blue illuminants helps to select the best compounds for achieving the highest color saturation in a practical application.

Results and Discussion

Pyrotechnic blue illuminant formulations were gathered from different sources. Ten of them having the highest color saturation based on the information in the literature were selected for this experiment. All the selected blue flame compositions contain four main components: an oxidizer, a fuel, a copper source and a chlorine source. The variety of chemical components was another criterion for the compositions being as different one from another as possible. This can provide more information about the best compositions and the best chemical components for generating blue flames with a high color saturation. The selected compositions are presented in Table 1 and their combustion characteristics are given in Table 2.

Table 1. Experimental compositions: chemicals, ratios, sources.

No.	Source	Composition & ratio	Ratio	Comments
1	Hahma	AP/Cu/CR/Hexamine/CP	62/14/4/10/10	Optimized for maximum ([HCl+Cu]/[CuO]) formation
2	McGriffen[16]	AP/Cu/Stearic acid/Paraffin	74/11/11/4	Ashless blue flare
3	Naud[17]	AP/5-AT/BCC	47,5/47,5/5	N-rich blue
4	Dumont[18,19]*	AP/Copper benzoate/Dex	79/17,5/3,5	Classic AP/Cu benzoate blue
5	Hardt[20]	KC/Paris green/Stearic acid/HCB/Dex	62/21/8/4/5	Copper acetoarsenite containing
6	Ofca[21]	KC/CuOCl/Lactose/CP/Dex	65/13/13/5/4	Chlorate-lactose blue
7	Veline[19,22]	KP/CuO/Red Gum/CR/MgAl/Dex	53/14/9/14/6/4	Firework star with MgAl
8	Stanbridge[23]	KP/CuO/HCB/S/Dex	39/37/6,5/15/2,5	Chinese blue for small pellets
9	Naud[24]	KP/CuO/PVC/Hex/Red Gum/Dex	61/17/10/6/3/3	Naud Ref. blue
10	Pihko**	KP/CuO/Hexamine/CR	62/13/10/15	Perchlorate-Hexamine blue

Private communication: *Modification by Hahma (2012), ** Petri Pihko (1988)

50 g of each composition (except 25g of No. 5) were prepared. Five 10 g pellets (16.80 mm diameter) were pressed out of each composition. The values presented in Table 2 are an average over 5 parallel measurements. It must be noted that even though pellets were ignited from the top, not all of them burned evenly (cigarette burning). For compositions 5-10, that were based on potassium chlorate and perchlorate, the surface flame propagation was more pronounced than that to the depth of the pellet. For that reason, the recorded burn rate data presented in Table 2 is not as precise as it was expected.

The first composition #1 burned with a uniform tall flame, especially during the first seconds. It was one of the very few compositions passing the 50% p_e threshold and had dominant wavelength (DW) of λ = 445 nm, which is the lowest of all 10 compositions. This composition also possesses the highest I_v and L_{sp} values among all ammonium perchlorate (AP) based compositions tested in this study.

Composition #2 was different from #1 due to wax and stearic acid as fuels. Occasionally, large yellow spots appeared in the blue flame envelope due to soot formation. This can be addressed to the largest oxygen deficit resulting in a reduced p_e. The burn rate was also the lowest among the ten compositions studied.

Composition #3 was unique because of its high nitrogen content, which was achieved by using 5-aminotetrazole (5-AT) as the main fuel. The poor fuel properties of this compound resulted in a composition, which could not sustain combustion on its own. The heat feedback from the flame wasn't sufficient enough to sustain combustion. However, the composition could be burned by holding a glowing sparkler wire on the burning surface. It should be noted that this composition is a derivative from the original presented by Naud[17].

Composition #4 has the fewest number of components with AP as an oxidizer and chlorine source, copper(II) benzoate serves as a fuel and a copper source. This nearly oxygen-balanced composition (Ω = -5.4) passed the 50% p_e threshold while its I_v and L_{sp} values remained on the average level.

The composition #5 was unique due to the use of copper acetoarsenite. An interesting note is stated by Shimizu[10,25] : "copper acetoarsenite was used in Japan in almost all blue compositions in 1980's as it produces a very pretty blue". Nowadays, such compositions are nearly obsolete due to toxicity and environmental concerns. This composition produces more smoke compared to AP compositions (1-4) due to the presence of potassium, which creates solid particles.

Composition #6 had the highest oxygen balance of Ω = +3.7. Chlorinated paraffin (CP) was difficult to mix evenly with other components the composition, which in addition to the positive Ω may have contributed to the lower performance of the composition. Also, a decrease in color saturation was observed during the combustion of each pellet.

Composition #7 is a popular one in fireworks. The metallic fuel MgAl increases the flame temperature and light output accordingly but results to a reduced color saturation. With p_e of 30%, composition #7 had the highest I_v and L_{sp} of the tested compositions.

Composition #8 had the highest p_e of 55.7 wt.-%. This composition is unique for it's high copper oxide content (37%), low potassium perchlorate content of 39 wt.-% and for the absence of an energetic fuel such as wax, hexamine etc. Sulfur is used as the main fuel instead. Sulfur helps to scavenge potassium in the flame resulting in an increased chlorine concentration promoting CuCl emitter formation[10,14]. HCB acts as a chlorine donor.

Composition #9 was chosen as a reference from Naud[24]. It was similar to composition #10 with a similar p_e of 41% It had only a slightly lower L_{sp} and I_v values.

Composition #10 was an efficient blue flame composition yielding p_e of 39% with L_{sp} of 414 cd·s·g^{-1}. It also produced the largest amounts of glowing slag on the test plate, where pellet was fixed.

Table 2. Experimental results: Oxygen balance (Ω), Burn time, average pellet length, burn rate, TMD - theoretical maximum density TMD % (indicates the fraction of measured density divided by TMD), I_v, L_{sp}, and color coordinates are presented. The mass of all pellets was in the range 9.5-11.7 g, except composition #5, which was limited to 4.8-5 g for each pellet. The white point was set at x = 1/3, y = 1/3.

No.	Ω [%]	t [s]	l [mm]	BR [mm·s^{-1}]	TMD [g·cm^{-3}]	TMD [%]	I [cd]	±	L_{sp} [cd·s·g^{-1}]	±	p_e [%]	±	DW [nm]	CIE x	CIE y
1	-20.2	17.5	23.2	1.3	1.98	96%	91	6.6	162	12.1	51.6	1.2	453.7	0.240	0.173
2	-26.3	42.5	26.0	0.6	2.01	85%	22	2.5	94	4.1	30.4	4.1	556.2	0.328	0.251
3	-15.1	27.5	32.7	1.2	1.75	83%	10	2.3	26	3.2	38.1	1	432.8	0.269	0.210
4	-5.4	12.5	26.0	2.1	1.75	95%	79	18.3	98	2.5	52.0	1.6	463.2	0.233	0.179
5	-12.7	9.0	11.3	1.3	2.17	90%	58	0.8	107	4.3	45.3	1.9	469.6	0.240	0.208
6	3.7	8.0	23.5	3.0	2.18	86%	46	3.2	37	1.8	28.6	3.4	462.8	0.278	0.250
7	-12.8	11.6	24.7	2.1	2.16	83%	388	27.6	454	22.9	29.8	2	464.1	0.276	0.246
8	-3.2	6.9	19.8	2.9	3.02	73%	108	21.7	75	8.0	55.7	2.6	467.9	0.221	0.175
9	-5.5	8.0	22.9	2.9	2.31	82%	267	19.7	218	15.9	40.8	1.6	477.3	0.242	0.240
10	-5.8	11.1	23.1	2.1	2.30	82%	365	48.4	414	35.8	38.6	0.2	481.1	0.242	0.261

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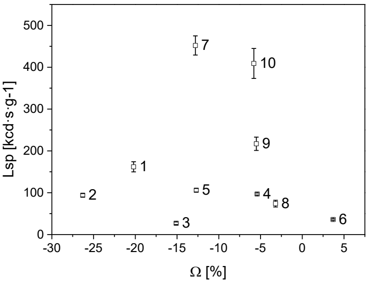

Fig. 1. L_{sp} dependence on the oxygen balance

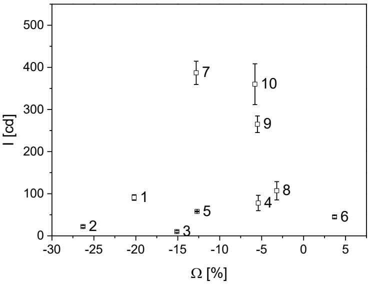

Fig. 2. I_v dependence on the oxygen balance.

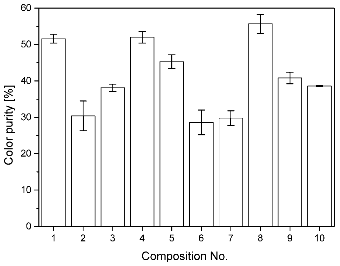

Fig. 3. The distribution of p_e.

The Ω of all compositions lies in the range of -26 to +4%. The compositions at the extreme ends (#6 and #2) had low L_{sp} and I_v values, which may be related to the unbalanced system. Too low Ω results in soot formation, while too high Ω may cause the emitter species to be oxidized. The L_{sp} and I dependence on Ω are depicted in Figures 1 and 2.

The measured p_e lies in the range of 28 – 56% (Fig. 3). The lowest p_e of ~30% was measured for compositions #2,6,7 and the highest exceeding 50% for compositions #1,4,8. Deep blue flame compositions with high p_e are usually observed to burn with a reletvely dim flame compared to the bright ones having a low p_e. In this work, composition #8 flame was indeed the least luminous of the $KClO_4$ compositions (107 cd, 74 cd·s·g^{-1}). However, p_e reached 56% on average from 5 pellets, with one pellet reaching 57.7%. By observing the p_e vs time graphs some pellets of the composition #8 peaked at 65% p_e during the first seconds of combustion, before the p_e dropped to 50-57%. Possibly the reduction of the color purity is associated with slag formation on the burning surface. The composition #8 is designed to be used as small stars in fireworks. Therefore, it possibly did not deliver the best performance when burned as a 16 mm diameter, 10 g pellet.

The emission spectra were recorded for each of 10 compositions. The main focus of interest was to observe how the CuCl emissions compare to the CuOH, CuO, Na and black body emissions. In figure 4 $KClO_3$ compositions 5,6 are compared. Composition #5 has a less pronounced grey body radiation and strong CuCl emissions at 400-470 nm, hence it possesses a higher color purity than composition #6. In Figure 5, the spectra of compositions #8 and #10 are compared. The CuOH emission from composition #10 appears much more pronounced compared to composition #8. This emission decreases the color purity of the composition #10, however the latter is much brighter burning. In Figure 6, the raw spectra of composition #6 are depicted at selected times. The intensity decreased as a function of time. This phenomenon was not observed with other compositions, at least not to such a strong extent. This effect may have resulted from both (i) the CP being unevenly distributed in the composition and (ii) also the slag formation.

Finally, the CIE x/y coordinates plotted in the CIE 1931 color diagram (Fig. 7) are located in the blue and blueish-white region of the chromaticity diagram. The compositions #1,4,8 show a noticeble shift towards the blue region of the chromaticity diagram.

Video captures of the burning pellets are collected in Figure 8. From these photos the flame size, shape, smoke and slag formation can be estimated. The AP based compositions #1, 2, 3, 4, tend to burn with little smoke and no slag formation.

The flame, especially in the beginning of the combustion, is tall and narrow. Later on, it evolves to a shape seen in Figure 8. The $KClO_3$ and $KClO_4$ compositions (#5 - #10) produce some slag and a significant amount of smoke. Some of them had higher I_v, L_{sp} and p_e values than AP compositions, which are often considered superior blue flame compositions. The reason for the higher light output can be associated with smoke reflection during the measurements. If the smoke in the measurement chamber reflects some of the emitted light from the flame towards the spectrometer, the reflected light adds to the recorded data. This effect could not be completely avoided, because it is not possible to extract the smoke at the edge of the flame completely. On the other hand, the eye will also perceive this and the pyrotechnic composition will appear brighter than it actually is. In that sense, no error is produced, when the back reflection is ignored.

NASA CEA2 code was used to estimate the transient species present in the flames of tested compositions (supporting information). Only composition #5 was omitted, as there was no data on arsenic species. The adiabatic flame temperatures range from 1840K for composition #8, to 2690K for composition #10. Besides the high concentration of typical combustion products i.e. H_2O, CO_2, CO, H_2, N_2 substantial amount of HCl (0.15 mol-%) was produced for AP compositions #1 – #4. Moreover, both KCl, HCl were present in KC and KP based compositions #6 - #10. The target species for this experiment is CuCl. While most compositions had around 0.03-0.05 mole-% of CuCl produced, compositions #8 had 0.07 mole-% of CuCl, which is in relation to the high performance of this composition described earlier. This can be associated with very high concentration (37 wt.-%) of CuO used in the compositions, that shifts the equilibrium towards CuCl formation.

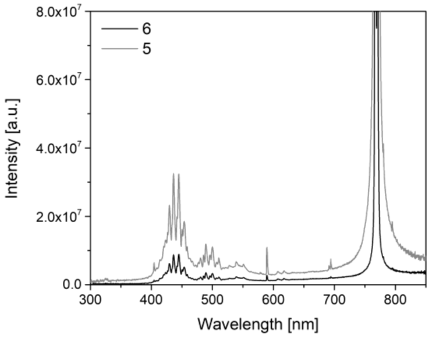

Fig. 4. Emission spectra of compositions #5 and #6.

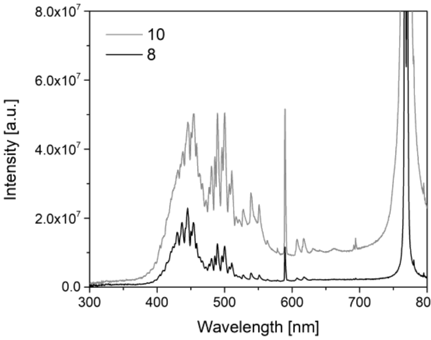

Fig. 5. Emission spectra of the compositions #8 and #10.

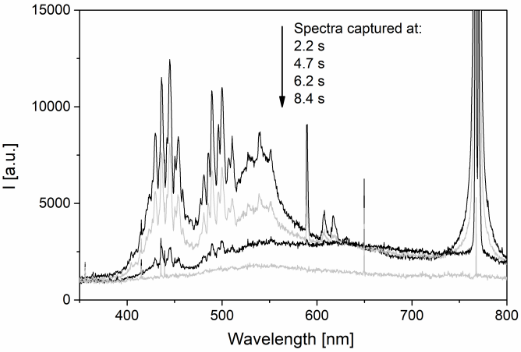

Fig. 6. The composition #6 pellet flame's raw emission spectra recorded at 2.2, 4.7, 6.2, 8.4 s after ignition. A decrease in the intensity is observed. The strongest emission in the blue region is observed after the ignition and the least intense emission is observed in the last seconds of combustion process.

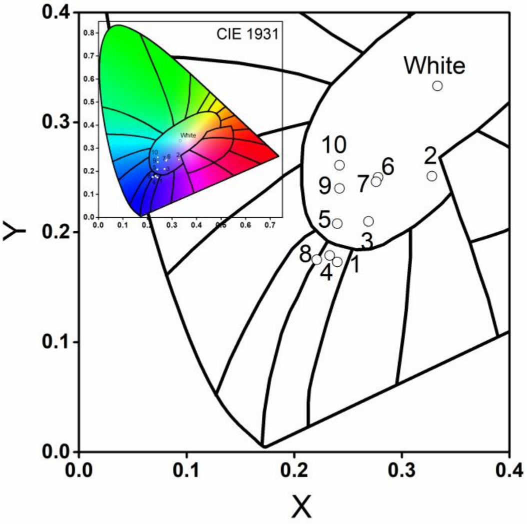

Fig. 7. Zoomed in chromaticity diagram including the evaluated compositions with the full diagram in the upper left corner.

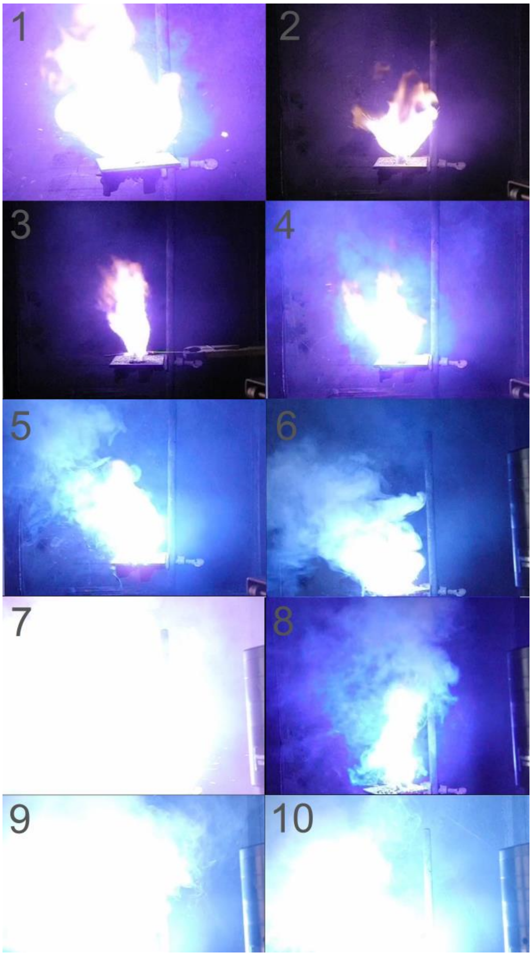

Fig. 8. Video captures of each burning composition.

Conclusions

Ten different blue pyrotechnic flame compositions were compared with the focus at the color saturation p_e. The measured values lie in the range of 28 – 58%. The highest average p_e of 55.7% (and up to 58% for a single pellet) was observed from the composition #8 with 108 cd, 75 cd·s·g^{-1}. The peak p_e = 65% was registered during the first 1 to 3 seconds of combustion. The dominant wavelength of this composition was 468 nm.

$KClO_4$/S system used in the composition #8 was found useful for producing a blue flame with high purity. It also proves that KOH continuum and $K_{(g)}$ do not interfere significantly with desired CuCl emissions when sulfur is used as fuel.

Similar to composition #8, but brighter and more efficient was the AP based composition #1 with 91 cd and 162 cd·s·g^{-1}. The p_e was just slightly under 52% with a very low dominant wavelength of 453 nm.

Composition #7 lies at the other extreme with 388 cd, 454 cd·s·g^{-1} This was the brightest composition, but had a mere 29.8% saturation.

The composition #10 appeared to be well balanced, simple and practical. Yielding a 365 cd bright flame and L_{sp} of 414 cd·s·g^{-1} it is almost as bright as the composition #7. With a p_e of 38.6%, it has one of the best brightness to p_e ratios.

Hexamine was found to be a useful fuel in blue flame compositions. It has a high energy density of 30 MJ/kg being a good, energetic, non-metallic fuel burning with a non-sooty flame. Moreover, it is a synthetic compound that can be obtained in a high purity.

5-AT containing composition #3 burned with significant difficulties. Most probably a fuel mixture of hexamine and 5-AT would have been more useful for this composition.

Even though highly regarded in older literature, Paris green composition did not surpass the other top compositions in color purity nor in luminous intensity. Hence, Paris green and HCB (which can be easily replaced by a non-toxic chlorine source for composition #8) are discouraged from being used in practise.

This kind of experimental examination has not been done to date, wherein a rather diverse range of blue flame pyrotechnic compositions are examined quantitatively with a spectrometer. Very few researchers in general have reported CIE coordinates with p_e, I_v, L_{sp} values for blue flames. In addition, some old-fashioned ingredients were tested to demonstrate that arsenic-containing ingredients (Paris Green) offer no benefit in the color purity, and other, more novel, compositions show better performance.

Experimental Section

The following chemicals were used: Ammonium perchlorate, potassium perchorate (d50 10 µm), potassium chlorate (20 µm) were all reagent grade, 5-AT from Sigma 02312TE, Hexamine B. Kraft 16932.5600, Stearic acid Merck 673, Paraffin wax ($C_{31}H_{64}$) Te-ce-wax H994 powder, Dextrin Roth 6777.1, Lactose monohydrate Roth 8921.1, Red gum ($C_6H_6O_{2.6}$) Ilotulitus Oy, Hyrylä, Finland, MgAl MX 077 Eckart Werke in Fürth, Sulfur JT Baker 0335 USP, PVDC Solvin 910 Solvay, Belgium, ground to 20 µm, CP ($C_{10}H_{15}Cl_7$) Leuna-tenside GmbH CP135, Chlorinated rubber ($C_{10}H_{11}Cl_7$) S10 Covestro 00549421, HCB old sample, PVC Solvin 374MB, Cu powder electrolytic Ecka 71, Eckart Werke, basic copper carbonate ($Cu_2(CO_3)(OH)_2$ malachite) Sigma 20.789-6, Copper benzoate was synthesized from potassium benzoate and a soluble copper salt, Paris green ($Cu_4As_6C_4H_6O_8$ was synthesized from arsenic trioxide and copper acetate, CuOCl (synthesized), CuO Omikron GmbH 10-0334.

The compositions were prepared by mixing the dry ingredients and passing through a 40-mesh sieve. The homogeneous powder mixture was moistened with a solvent to activate the particular binder. The compositions #1, #6 were moistened with dichloromethane to dissolve the CP. The composition #2 was moistened with n-Hexane to dissolve the paraffin and all the others, except the composition #3, were moistened with water to dissolve dextrin. The composition #3 was used without any binder.

The compositions were pressed to nominally 10 g pellets having a nominal diameter of 16,80 mm at 1,15 kbar pressure. Five pellets were pressed for each composition and measured with a digital caliper at ±0.01 mm precision. The dimensions were used for calculating the densities and percentage of the TMD as well as the burn rates of each pellet.

The spectra were recorded with Ocean Optics JAZ-ULM VIS-Spectrometer equipped with a cosinus corrector. The spectrometer was run in its high-speed absolute calibration mode and placed 0.5 meters apart from the pellet. The cosinus corrector has an angle view of ±60 degrees and could record the entire flame despite of the short distance needed because of the low light output of blue illuminants. The resulting spectra were recorded already calibrated. The calibration was verified against a NIST traceable calibration lamp. The verification confirmed the factory calibration is correct and precise. Hence, no correction of the raw data was necessary.

The combustion times were recorded using a Casio Exilim EX-FH20 camera at 210 Hz frame rate and VGA-resolution. This camera has a considerably higher time resolution and precision than the spectrometer, which often had to be run at 500 ms integration. In addition, the video recordings remain as a reference for each pellet. The video recordings were automatically edited to include one second before and after the combustion. The combustion times were defined as the beginning and the end of the sum curve exceeding a threshold level set at 10 % of the maximum intensity of the pellet.

All pellets were measured in a free state without wind. The pellets were lacquered with 30% solution of Synthesia E37 nitrocellulose in ethanol:diethyl ether 1:2 to make them burn only at the end face (cigarette burning). This way, the burn time reflects the true burn rate, when divided by the pellet length. We did, however, encounter some problems with the lacquer film peeling off due to poor adhesion. This may have caused some loss of the composition, however the losses were less than 0.2 g for each pellet and were ignored.

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Contributions

D.J.: Conceptualization, investigation, data analysis, writing - original draft.
A.H.: Conceptualization, methodology, investigation, writing - review & editing, validation.
R.W.: Writing - original draft (introduction part), writing - review & editing, validation.
T.K.: Conceptualization, supervision, revision, funding acquisition.
A.R.: Supervision, writing - review & editing, funding acquisition, submission.

Keywords: blue • flare • pyrotechnics • illuminating • flame • copper chloride • fireworks

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Paper 2

The Performance of Red Flare Pyrotechnic Compositions modified with Gas Generating Additives

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Full Paper

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The Performance of Red Flare Pyrotechnic Compositions Modified with Gas Generating Additives

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To Rev. *Ronald Lancaster* a.k.a. "Master blaster pastor"

Abstract: In this work, an effective, but still not well-explored area of red flare pyrotechnic formulations was investigated. High magnesium content (40–60% w.t.) and the presence of conventional gas generating materials were the specific features of formulations explored herein. Such illuminant compositions possessed a low burning rate and high specific luminous intensity. The investigated system was based on strontium nitrate, rounded magnesium powder, chlorinated rubber, binder and gas generating additives. Emission spectra, light intensity and burning time have been measured during the experiment and recalculated to the specific luminous intensity and color purity. Additives in the form of 2-cyanoguanidine, Melamine, Azodicarbonamide, Calcium resinate, Shellac, Strontium oxalate, Lactose, Dextrin, Phenolic resin, Lignin sulfonate, 5-aminotetrazole, Urea, Guanidinium nitrate (GN), Hexamine and Sulfur were evaluated in Mg-rich flare compositions. The use of GN was studied more carefully as an exceptionally efficient additive that increased the flares light intensity by 60%, in comparison to the standard GN-free composition, while maintaining high color purity of 90–97%.

Keywords: Magnesium · Red Flare · Guanidinium nitrate · Fireworks · Pyrotechnics

1 Introduction

Magnesium containing pyrotechnic compositions have been used since the late 19th century, but it was not until the period between the World Wars that price and availability enabled a more extended production and development of high temperature, magnesium fueled, illuminating pyrotechnic products [1].

Before and during the Second world war products like hand-flares, signal ammunition and parachute-flares were improved to a similar level of efficiency as we see today. A lot of work was done to deepen the understanding of the underlying phenomena during the 1950s to 1960s [2], though without affecting much of the products already in use. The main driving force in development in recent years has been focused on eliminating certain unwanted ingredients and to a certain degree improving flame color depth [3–12].

Although having problems with corrosion induced by moisture [13] and being a relatively expensive ingredient, Mg is absolutely indispensable for the production of illuminating flares and the emission of high intensity colored light in both military and civil applications. The reason for this is a couple of unique chemical properties of Mg that distinguishes it from all other possible fuels for high temperature colored light production in pyrotechnics. First of all, the oxidation of magnesium produces large amounts of heat, which directly relates to a high number of excited molecules in the flame [14]. As a result, the flame is very luminous and spectral emitters like $SrCl_{(g)}$, $SrOH_{(g)}$, $BaCl_{(g)}$, $BaOH_{(g)}$ can produce flames that have high color saturation. Secondly, Mg has a low vaporization temperature, 1107 °C, which is much lower than its oxide's decomposition temperature of ~3200 °C. This satisfies the Glassman criteria for metal vapor phase combustion [15], which results in an extended vapor phase diffusion combustion zone, that allows for a large radiative area.

Generally, fundamental demands for a good UV-VIS pyrotechnic flare composition are: a) burning with luminous flame with maximum candlepower; b) having a distinct flame color of purity higher than 80% (e.g. red distress signal); c) preferably creating a minimum of slag, d) being chemically stable and containing chemicals of minimum toxicity. Slag formation is unwanted since long-lived burning sparks and glowing slag is always a fire hazard and could make a handheld flare dangerously to use and burn

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off the vanes to the canopy in a parachute suspended flare. Even more important is that a flare producing lots of slags is probably not delivering its best pyrotechnic performance (maximum light output in the case of illuminants).

In this work, a novel area of flare formulations was investigated. First, a series of high Mg content compositions were evaluated. Then nitrogen and oxygen generating materials were added in an unusually Mg-rich area of the formulation. Finally, guanidinium nitrate (GN) was successfully added to the pyrotechnic illuminant that induced an unusual low burning rate together with a high specific luminous intensity.

2 Experimental Section

Rounded Mg powder 45–100 μm (max 5% $>$100 μm and max 5% $<$45 μm, purity of 99.0-99.5%) and $Sr(NO_3)_2$ (99.5% with $<$0.4% barium nitrate, $<$0.05% calcium nitrate and $<$0.04% sodium nitrate) were received from Jengo S.P.A., Chlorinated rubber in the form of Pergut B10 (finer than 250 μm) from Bayer. $Sr(NO_3)_2$ was milled in a hammer mill until about 50% of the particles were smaller than 50 μm before the experiment. 2-cyanoguanidine, Azodicarbonamide, Calcium resinate, Shellac, Strontium oxalate, Lactose, Dextrin, Phenolic resin, Lignin sulfonate, GN, and Sulfur (all very fine powders, purity 97–99%) were only passed through a 250 μm sieve to break up lumps. Melamine, 5-aminotetrazole (5-AT), Urea and Hexamine (purity 97–99%) were ground with a mortar and pestle to a fine powder and particles bigger than 150 μm were removed with a sieve. The linseed oil used was boiled type. The following formulas were applied for calculating oxygen balance (Ω_{CO2}) for variable M_r compounds: Linseed oil $C_{57}H_{92}O_6$, Calcium resinate $C_{40}H_{58}CaO_4$, Shellac $C_{16}H_{26}O_4$, Phenolic resin $C_{53}H_{45}O_7$, Lignin sulfonate $C_{20}H_{24}O_{10}CaS_2$, Chlorinated rubber $C_{10}H_{11}Cl_7$.

The compositions were hand mixed, sieved through a 30 mesh screen, cured for 4 h at 80°C and then sieved again through 20 mesh screen to break lumps.

Test flares were pressed into metal tubes (ID = 23 mm) containing waxed paper liners (OD = 23 mm, ID = 21.6 mm). Hence, the pyrotechnic composition was compacted into a column of ID = 21.6 mm and 70–85 mm in length. Flares were pressed two at a time at 2 tons with 4 increments of 11.5 g (scale accuracy 0.05 g). 2 g charge of igniter composition was pressed on top of each flare for ignition.

The experiment was performed in a wind tunnel to reduce smoke obscuration. The wind speed in the chamber, where flares were burnt, was 1 m·s^{-1}. Illuminance was measured with a calibrated lux meter (LMT, I(ph)–meter 1500, data processed with DasyLab software) and emission spectra were recorded with a spectrometer (Stellar net, EPP 2000, CXR-SR; irradiance calibrated for 300–1100 nm range). The flares were also filmed with a video camera (Casio Exilim ex-f1) at automatic settings for the evaluation of shape, spark and slag formation.

3 Results and Discussion

3.1 Evaluation of the Mg-Rich System

The first experiment was orientated to explore the effectiveness of the well-known strontium nitrate, magnesium, and chlorine donor tri-component system that contained a rather high percentage of Mg (40–60%). Typical red flare compositions described in the literature contain around 30–40% of Mg powder, 55–35% of $Sr(NO_3)_2$, 12–20% of chlorine donor and 4–10% of other additives such as additional oxidizers, binders, stabilizers, burning rate retardants, etc. (Table 1). An amount of over 50% Mg powder is more common in yellow (white) flares based on $NaNO_3$, where atomic $Na_{(g)}$ is the dominant light emitter.

Having a high percentage of Mg in the composition, of course, requires lowering the amounts of other components which in turn can result in lower emitter concentration, more rapid combustion, and stronger incandescent emission. It is, however, a potential approach to gain extra candlepower from the flare composition.

A series of test compositions were prepared, see Table 2. Rounded Mg powder was chosen over "cut" Mg for its ability to burn slower. An amount of 4% of linseed oil was added to each composition as a binder. Two flares of each composition were pressed for evaluation.

An important parameter that describes the performance of a pyrotechnic illuminating composition is specific luminous intensity L_{sp} (Eq. 1).

$$L_{(sp)}(kcd \cdot s \cdot g^{-1}) = \frac{I_v t}{m} \tag{1}$$

Equation 1 presented in normalized units describes how much visible light in kilo candelas is produced during one second from one gram of pyrotechnic composition [16–18]. For Mg containing illuminants, this value is usually reported to be in the range of 2–7 kcd·s·g^{-1} for green colored flares with barium nitrate [19], around 15–50 kcd·s·g^{-1} for illuminating flares with sodium nitrate [16,17,20] and around 14–

Table 1. Chemical compositions typically used in red flares.

Chemical composition (w.t.%)			
$Sr(NO_3)_2$	43	55	48
$KClO_4$	9		
Mg (50-100 mesh)	29	30	
Mg (30-50 mesh)			33
PVC	12	15	15
Laminac 4116/Lupersol	7		4
Source	[16]	[17]	[4]

Table 2. Chemical composition of 18 formulations tested in first experiment.

Compositon #	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
$Sr(NO_3)_2$	39	35	31	42	38	34	30	41	37	33	29	40	36	32	28	39	35	31
Mg rounded (45–100 μm)	40	44	48	40	44	48	52	44	48	52	56	48	52	56	60	52	56	60
Chlorinated rubber	17	17	17	14	14	14	14	11	11	11	11	8	8	8	8	5	5	5
Linseed oil	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Density [$g\,cm^{-3}$]	1,56	1,53	1,49	1,60	1,56	1,53	1,49	1,61	1,56	1,52	1,49	1,59	1,55	1,51	1,48	1,59	1,56	1,51
Burning time [s]	35,0	41,0	48,8	29,0	32,6	35,0	41,0	26,8	28,7	31,0	35,6	24,9	25,6	27,6	29,6	22,4	22,8	23,0
Burning rate [$mm\,s^{-1}$]	2,24	1,94	1,68	2,63	2,40	2,28	2,00	2,84	2,72	2,59	2,31	3,08	3,08	2,92	2,78	3,44	3,44	3,51
Light intensity [kcd]	17,6	14,4	9,2	25,4	23,6	21,3	14,3	31,0	30,6	28,9	23,2	39,3	43,9	39,5	34,0	48,8	53,4	55,3
L(sp) [$kcd\,s\,g^{-1}$]	13,4	12,9	9,8	16,0	16,7	16,2	12,7	18,1	19,1	19,5	17,9	21,3	24,3	23,7	21,8	23,7	26,4	27,7
L(sp)/BR [$kcd\,s^2\,g^{-1}\,mm^{-1}$]	6,0	6,6	5,8	6,1	6,9	7,1	6,4	6,4	7,0	7,5	7,8	6,9	7,9	8,1	7,8	6,9	7,7	7,9

16 $kcd \cdot s \cdot g^{-1}$ for red-colored flares with strontium nitrate [18].

A drawback is that L_{sp} does not take into account the burning area of the flare and the geometry of the flame. Even though the choice of the pyrotechnic composition, the ratio of its components and its density after compaction are the major factors that determine size and shape of the flame envelope, both emission and absorption take place in the envelope of the flame and absorption is a function of distance (flame width). Also, heat loss is different for flares of different diameters and therefore, different shaped columns or pellets that contain exactly the same composition will often have different L_{sp} values. Therefore, the results from this work can only be compared to other flares of similar diameter and density.

A pyrotechnic composition that possesses a high L_{sp} value is often desired, since then a lower amount of pyrotechnic composition is needed to achieve a certain effect, for example, the desired burning time of a parachute flare. And, secondly, the pyrotechnic unit can be made smaller and lighter which in turn saves space and volume for practical applications.

As a complement, the ratio of L_{sp} and burning rate (L_{sp}/BR, Table 2) was used to give guidance in determining which compositions burned both bright and slow.

The combustion of all 18 flares was monitored with a lux meter. Since the distance between the photodiode and flare was known, a software (DasyLab) was used to calculate and plot light intensity in kilo candelas (kcd) over time. The L_{sp} values were calculated and their distribution was depicted in a ternary diagram (Figure 1). The trend observed was that there is a significant increase of L_{sp} with a decreasing amount of chlorinated rubber. The main purpose of chlorinated rubber is to serve as a chlorine donor to enhance $SrCl_{(g)}$ emitter formation, which supplements emission from $SrOH_{(g)}$. This shifts the flame color from reddish-orange to red. Additionally, the use of chlorine donors is one of few possible ways to quench the $MgO_{(s/l)}$ incandescent emission via reaction with $Cl_{2(g)}$ or $HCl_{(g)}$ that yields more volatile $MgCl_{(g)}$ [14]. The color purity of chlorine-rich compositions 1–3 was measured to be 97–99%

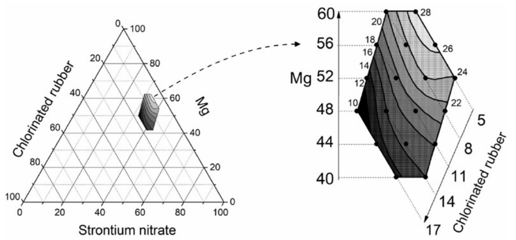

Figure 1. L_{sp} distribution plotted in a ternary diagram of measured compositions with high Mg content. Small numbers at the end of each contour line represent L_{sp} values.

with a dominant wavelength of (DW) = 613–614 nm, while chlorine-low compositions, 16–18, had lower color purity of 79–87 %, at DW = 605–609 nm.

Moreover, it was determined that L_{sp} values and BR are directly connected. Generally, fast-burning compositions result in more luminous flames with high L_{sp} values. The distribution of BR of the same system is depicted in Figure 2 for comparison. However, from a practical perspective, high BR is only desired in tracer compositions, whereas hand flares, parachute flares etc. must contain a slow-burning, yet luminous flame producing composition, which is the real challenge.

3.2 The Influence of Additives

After the evaluation of 18 compositions, the composition 6 was chosen as a base for further investigation, because it was slow-burning, highly luminous (determined by L_{sp}/BR value) and had a decent color purity of 90 %. To improve the compositions, it was considered essential to evaluate additives that at least theoretically could enhance the flame size by the formation of gas or contribute positively by being an effective secondary fuel.

The use of gas generating materials has been reported back since the 1970s [21], and in recent years have been used in various illuminating pyrotechnic compositions as an energetic additive for smoother combustion, more luminous flames, and compositions emitting less smoke [5,11,22,23]. In the present work several non-exotic, gas generating materials were chosen to investigate how they affected the performance of the magnesium-rich system In addition to the gas generating materials, calcium resinate, shellac, strontium oxalate, phenolic resin, lignin sulfonate (with sodium impurities) and sulfur were also tested as additives for comparison. Additives were evaluated in “Composition 6”, which was modified by replacing 5 % chlorinated rubber, by 5 % additive (Table 3).

When testing compositions 19–33, it was noted that certain compositions produced more luminous flames, while others burned very rapidly. And it was clear that not only nitrogen-rich materials were successful. For example, lactose and dextrin were almost as good as 2-cyanoguanidine and melamine when comparing light intensity values, even though they did not contain any nitrogen. Further on, experimental data was plotted in several ways to determine which factor determines an efficient composition. Finally, a trend was observed when plotting the L_{sp} values against the total amount of nitrogen and oxygen (in moles or grams) in the additive used (Figure 3; Figure 4) and against oxygen balance (Figure 5).

Several additives (calcium resinate, strontium oxalate, lignin sulfonate, sulfur, and chlorinated rubber) contained other elements besides C, H, N, O therefore, those were marked differently in the graphs. They cannot be evaluated together with fully organic additives, since some contained metal ions, i. e. Na (lignin sulfonate), Ca, Sr that are potential emitters or emitter formation enhancers. Hence, some of them, notably lignin sulfonate and strontium oxalate, show quite high L_{sp} values due to additional emitters present.

The presented trends support the fact that high nitrogen materials favor the production of more luminous flames [18], but it is evident that the influence of oxygen is equally as important. Apparently, the formation of $N_{2(g)}$ and

Table 3. Modified composition 6 for testing additives.

Compositons	19–33
$Sr(NO_3)_2$	34
Mg rounded (45–100 μm)	48
Chlorinated rubber	9
Additive	5
Linseed oil	4

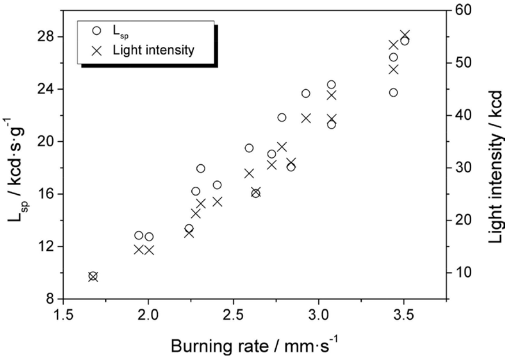

Figure 2. L_{sp} and flare’s light intensity dependence on composition's burning rate for compositions from Table 2.

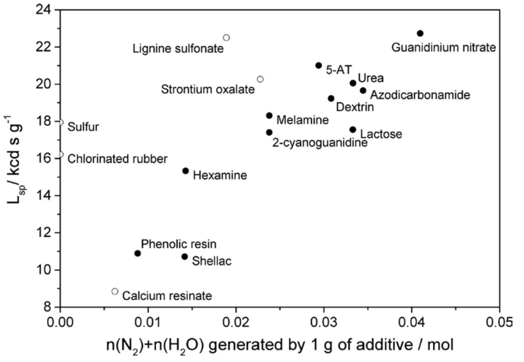

Figure 3. L_{sp} dependence on the amount of oxygen and nitrogen (in moles) present in the additive.

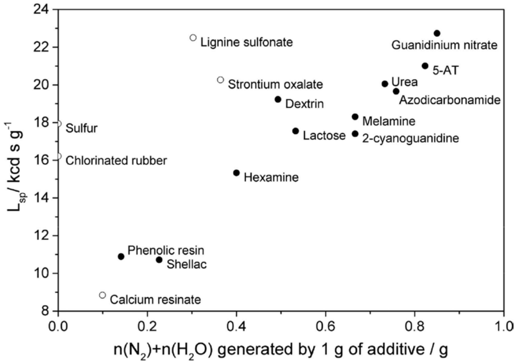

Figure 4. L_{sp} dependence on the amount of oxygen and nitrogen (in grams) present in the additive.

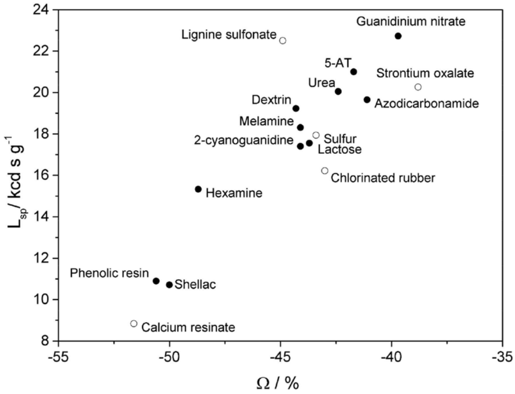

Figure 5. L_{sp} dependence on the oxygen balance of the composition.

$H_2O_{(g)}$ in such Mg-rich flare compositions, have a similar effect on the increasing L_{sp}.

A general explanation of the observed phenomenon is that the conversion of chemical energy to light is more efficient in illuminating compositions that contain gas generating materials [16]. When gas generating materials are introduced into a composition instead of a non-gas generating material, such as chlorinated rubber, a relatively large flame envelope can result due to gas flame expansion. That, in turn, has a higher emissive area, which results in an increased light emission intensity. Other effects could be the change in the flames absorbance and emissivity factors that directly determine the L_{sp}. When gaseous molecules replace less volatile or incandescent species, the inner absorbance in the flame envelope is decreased resulting in a more luminous flame.

According to the NASA CEA [24] code estimation of compositions (6, 31, 38) at atmospheric pressure (1 atm), $N_{2\,(g)}$ is in equilibrium with Mg_2N_3 at lower temperatures (1000-1500 K), however above 2000 K, $N_{2(g)}$ formation is predicted. $H_2O_{(g)}$ rapidly reacts with excess $Mg_{(g)}$ to yield $H_{2(g)}$ and $MgO_{(s/l)}$. $MgO_{(s/l)}$ is then in equilibrium reaction with soot [25] that yields $CO_{(g)}$ and $Mg_{(g)}$. Given that Mg containing compositions reach temperatures above 2000 K [25] and all water vapor (and oxygen) reacts with excess Mg, then $N_{2(g)}$, $H_{2(g)}$, $CO_{(g)}$ molecules are formed and assist in increasing L_{sp} in such Mg-rich flare compositions.

3.3 Influence of Guanidinium Nitrate on Flare Performance

The performance of guanidinium nitrate (GN) in place of chlorinated rubber was quite impressive. Having almost the same burning and mass consumption rates, GN (comp. 31) possesses 40% higher L_{sp} value and 60% higher light intensity in comparison to comp. 6 in this system. Urea was also very efficient and was noted for its low BR, see composition 30. However, urea is not useful in practice as it is rather hygroscopic in combination with strontium nitrate and could, therefore, be unstable together with Mg. Thus azodicarbonamide (ADCA) is a great alternative (comp. 21), which is far less hygroscopic and well-performing in comparison to urea. 5-Aminotetrazole (5-AT), (and related N-rich compounds) have received much attention these days for their unique combination of high nitrogen content and high stability due to aromaticity [5,18]. Comp. 29 contained 5-AT and performed quite well, but with a slightly higher BR than comp. 6.

Due to excellent performance as an additive, GN was chosen for further investigation. Another advantage over other additives explored herein is that GN by itself is an energetic material and contains an oxidizing moiety – the nitrate anion. Therefore, it can support combustion better in a strongly oxygen-deficient pyrotechnic system such as the ones of our focus. For the same reason, GN was sometimes used in the past as an oxidizer alone in illuminating compositions [26,27] and gas generators [16]. Therefore, the Mg-rich illuminating system could possibly tolerate even higher amounts than 5% of GN, which would be difficult for other well-performing fuel-like additives from Table 4.

In fact, tests of using ADCA in the 10% range were performed, but the combustion process became uneven and pieces of burning composition were shooting out of the flaring chimney as it was burning. This phenomenon is likely to occur when the gas generating material, present in the flare composition, starts to decompose in the pre-reaction zone of the composition column. In this case by "pre-reaction zone," we refer to the compacted flare composition just a short distance below the combustion surface. As a result, a piece of solid unburnt composition detaches and

Table 4. Performance parameters of compositions 19–33 with different additives.

Comp.		19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	6
Additive		2-cyanoguanidine	Melamine	Azodicarbonamide (ADCA)	Calcium resinate	Shellac	Strontium oxalate	Lactose	Dextrin	Phenolic resin	Lignin sulfonate	5-amino tetrazole (5-AT)	Urea	Guanidinium nitrate (GN)	Hexamine	Sulfur	Chlorinated rubber
Additive chemical consistency (organic elements, %)	C	29	29	21	75	68	14	40	44	80	45	14	20	10	51	0	29
	H	5	5	3	9	9	0	7	6	6	5	4	7	5	9	0	2
	O	0	0	28	10	23	36	53	49	14	30	0	27	39	0	0	0
	N	67	67	48	0	0	0	0	0	0	0	82	47	46	40	0	0
O,N amount [%]		67	67	76	10	23	36	53	49	14	30	82	73	85	40	0	0
Density [$g\,cm^{-3}$]		1,62	1,65	1,69	1,63	1,62	1,71	1,66	1,63	1,62	1,64	1,65	1,76	1,67	1,64	1,68	1,53
Burning rate [$mm\,s^{-1}$]		2,39	2,51	2,23	2,27	2,17	3,11	2,26	2,31	2,15	2,63	2,56	1,99	2,39	2,40	2,92	2,28
L(sp) [$kcd\,s\,g^{-1}$]		17,4	18,3	19,7	8,8	10,7	20,3	17,6	19,2	10,9	22,5	21,0	20,1	22,7	15,3	17,9	16,2
Light intensity [kcd]		25,4	28,6	28,0	12,3	14,1	40,5	24,9	27,3	14,3	36,6	33,5	26,4	34,2	22,8	33,0	21,3
L(sp)/BR [$kcd\,s^2 g^{-1} mm^{-1}$]		7,3	7,3	8,8	3,9	4,9	6,5	7,8	8,3	5,1	8,6	8,2	10,1	9,5	6,4	6,2	7,1

ejects through the flaring chimney disturbing the combustion performance.

Compositions were designed with a higher amount of GN (10–25% w.t. range). In this series of tests, GN mainly replaced some of the chlorinated rubber and $Sr(NO_3)_2$, while the Mg amount was kept in 40–50% range (Table 5). The experiments proved that GN can be used in rather large amounts as an additive in Mg-rich compositions for low BR and higher color purity and L_{sp}.

Sparks or glowing slag were observed to form during combustion only in certain compositions. In the first experiments, compositions with the highest Mg content had high burning rates of >3 mm·s^{-1}. These compositions produced fine sparks that were ejected upwards and were not observed falling down.

Some GN modified compositions from Table 5 were rather a slow-burning (<1.8 mm s^{-1}). These had a tendency to produce larger sparks or glowing slag pieces that fell down. None the less, certain slow-burning compositions possessed high color saturation (39, 40, 43), and some others (37, 38, 41) burned efficiently and clean (Table 5, Figure 6)

When compositions from Table 5 were tested, an interesting phenomenon was observed when evaluating the emission spectra. In Figure 7 emission spectra of compositions 37–40 are compared. The incandescence emission seemed to have decreased with decreasing burning rate and increasing GN w.t.%. The lower burning rate can affect the proportion of how much solid particles remain deposited on the flare's metal chimney and how much that enters the flame. Also, the lower burning rate can affect the kinetic parameters, which determine how big spark particles are formed. Perhaps the explanation behind comp 40 performance (lots of sparks, yet a high purity red flame) is that spark particles that formed were relatively big and not as hot to give strong incandescence. Fine solid particles that easily can be dispersed and heated up possibly emit stronger incandescence emission, which could explain composition 37 performance (higher burning rate and lower color purity). Additionally, a low burning rate can cause

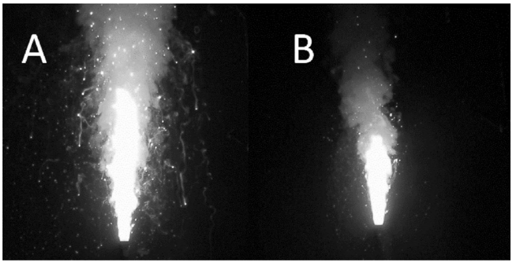

Figure 6. Combustion of flares with composition 11 (A) producing some sparks and glowing slag, and 38 (B) producing very few sparks.

Table 5. Formulations with 10–25 % of GN and their burning characteristics.

Compositon #	34	35	36	37	38	39	40	41	42	43
$Sr(NO_3)_2$	36	31	26	36	31	26	21	31	26	21
Mg rounded (45–100 μm)	40	40	40	45	45	45	45	50	50	50
GN	15	20	25	10	15	20	25	10	15	20
Chlorinated rubber	6	6	6	6	6	6	6	6	6	6
Linseed oil	3	3	3	3	3	3	3	3	3	3
Density $[g\,cm^{-3}]$	1,71	1,67	1,64	1,69	1,66	1,62	1,58	1,63	1,60	1,57
Burning time [s]	39,0	47,8	54,4	32,7	41,0	50,4	57,0	33,0	43,5	54,9
Burning rate $[mm\,s^{-1}]$	1,83	1,53	1,37	2,22	1,80	1,50	1,36	2,27	1,75	1,42
Light intensity [kcd]	17,9	14,5	11,8	25,5	21,0	16,1	13,5	30,9	22,1	15,4
L(sp) $[kcd\,s\,g^{-1}]$	15,1	15,0	14,0	18,1	18,7	17,6	16,7	22,1	20,9	18,3
L(sp)/BR $[kcd\,s^2\,g^{-1}\cdot mm^{-1}]$	8,3	9,8	10,2	8,2	10,4	11,8	12,3	9,7	11,9	12,9
Flame color purity [%]	85	92	94	83	91	97	99	89	95	97
Spark formation*	0	1	1	0	0	1	2	0	1	2

* defines the relative amount of sparks generated outside the flame envelope. 0 – no sparks; 1 – some sparks; 2 lots of sparks.

more solid particles to be deposited on the walls of the chimney because reaction products travel slower from the burning surface, which provides more time for solids to settle. That can also cause an increase in flame color purity.

Additionally, not a single composition from Table 4 shot out burning pieces of solid composition, which was a rare, but possible case for compositions 1–33. The uniform and slow-burning is likely achieved due to GN property to melt prior to decomposition, which seals the pores in the composition, before generating gases and combusting.

A final comparison of compositions that possess similar BR (in groups) is presented in Table 6, together with the final chlorine-free composition 44.

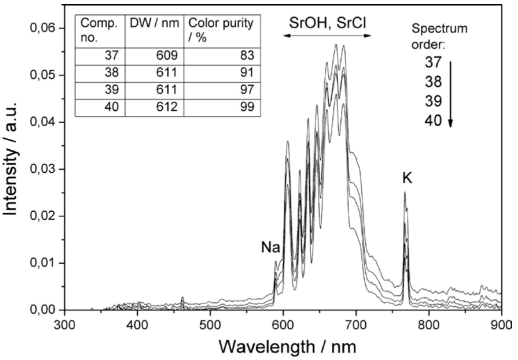

Figure 7. Flame emission spectra of compositions 37–40. A decrease of incandescence emission results in increasing color purity and a dominant wavelength (DW) shift.

3.4 Properties of Chlorine-Free Composition

By further tuning compositions with GN and 6 % of chlorinated rubber, and inspiration from recent papers [4,11], a chlorine-free, Mg-rich composition was evaluated. Even

Table 6. Comparison of two groups of compositions from this work, that possessed similar burning/mass consumption rates and Cl free composition 44.

Group	A			B		C (Cl-free)
Comp. No.	6	21	31	3	39	44
$Sr(NO_3)_2$	34	34	34	31	26	34
Mg rounded (45–100)	48	48	48	48	45	48
Chlorinated rubber	14	9	9	17	6	
Linseed oil	4	4	4	4	3	4
ADCA		5				
GN			5		20	13
Magnesium stearate						1
Burning rate $[mm\,s^{-1}]$	2,24	2,23	2,39	1,68	1,50	1,71
L_{sp} $[kcd\,s\,g^{-1}]$	16,7	19,7	22,7	9,8	17,6	16,2
Light intensity [kcd]	21,5	28,0	34,2	9,2	16,1	17,4
L_{sp} /BR $[kcd\,s^2\,g^{-1}\cdot mm^{-1}]$	7,4	8,8	9,5	5,8	11,8	9,5
Flame color purity [%]	89	88	87	92	97	80

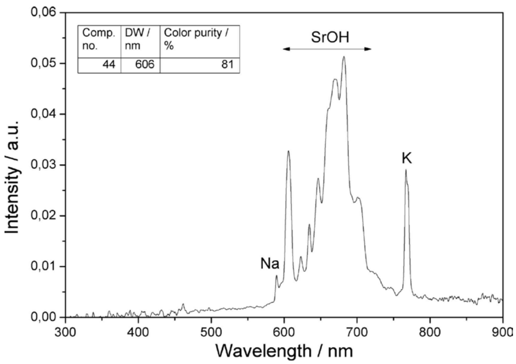

Figure 8. Flame emission spectrum of chlorine-free, Mg-rich composition 44. $Na_{(g)}$, $K_{(g)}$ peaks are present due to impurities.

though it was similar to compositions 34–43, it possessed slightly different spectral characteristics. Since $SrCl_{(g)}$ emission was absent, the emission spectrum was solely composed of strong $SrOH_{(g)}$ emission together with atomic $Na_{(g)}$, $K_{(g)}$ emissions (Figure 8). Chlorine is known to quench incandescence emission of solid particles such as $MgO_{(s/l)}$, $SrO_{(s/l)}$, by reacting with them, and forming more volatile chlorides $MgCl_{(g)}$, $SrCl_{(g)}$. Therefore, with the absence of Cl, the incandescence emission of the chlorine-free composition was stronger and resulted in a decreased color purity of around 79–82 %.

4 Conclusions

In this work, an effective area of red flare formulations specific for their high Mg content (40–60 % w.t.), low burning rate (BR), and presence of non-exotic gas generating materials was investigated.

A series of additives were tested in order to increase the performance of an illuminating flare composition. Certain oxygen and nitrogen-rich additives were noted for their ability to increase the specific luminosity (L_{sp}). Finally, a trend was found indicating that L_{sp} value is proportional to the total amount of oxygen and nitrogen present in the gas generating additive. Guanidinium nitrate showed the best performance as an additive in the tested system. While maintaining low BR, it produced 40 % higher L_{sp} and 60 % higher light intensity in comparison with a similar GN-free composition. Changes in flame's emissivity and absorbance factors, as well as the total emissive area, have probably had the greatest influence on the increase of flare's illuminating performance.

Different from conventional compositions, a rather small amount of chlorine donor (4–6 % w.t.) was found to be sufficient to achieve a deep red flame when used in combination with gas-generating additives and high amount of Mg. Finally, Mg-rich and Cl-free composition were investigated using GN, which burned with a similar light intensity and efficiency as chlorine-containing composition, but with decreased flame color purity in the 80 % range.

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Paper 3

Blue Strobe Pyrotechnic composition based on Aminoguanidinium Nitrate

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Blue Strobe Pyrotechnic Composition Based on Aminoguanidinium Nitrate

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Abstract: A new blue strobe pyrotechnic composition based on aminoguanidinium nitrate (AGN) is described. Alternative compositions from the literature that contain either tetramethylammonium nitrate or guanidinium nitrate are compared to the new AGN composition. Pyrotechnic compositions were processed into 13 mm pellets and 5 mm rods. Strobe frequency, linear burning rate, chromaticity coordinates and color purity (of the flash reaction), sensitivity to mechanical stimulii, DTA curves, humidity tests, high speed camera footage are reported and discussed. Finally a discussion of the strobe reaction mechanism has been included.

Keywords: Blue strobe · Copper chloride emitter · Aminoguanidinium nitrate · Fireworks · Pyrotechnics

1 Introduction

A strobe composition burns in an oscillatory manner with a smolder reaction occurring at all time and flash reaction occurring periodically. The smolder reaction produces relatively a low amount of heat and forms a slag at the burning front. When sufficient heat is generated, the semi-reacted slag is ignited, and a flash occurs. Then the smolder reaction continues further to the depth of the pyrotechnic column [1].

While colored strobes are created without significant difficulties using a nitrate oxidizer or ammonium perchlorate (AP) combined with Mg, or magnalium (MgAl) powder [2,3], a blue strobe is more difficult to make, since the high temperature flash reaction involving oxidation of Mg or MgAl can destroy the temperature sensitive CuCl blue flame emitter.

Therefore, a blue strobe composition calls for a somewhat different chemical composition. A few of such compositions have been described by Jennings-White, that uses the AP/tetramethylammonium nitrate (TMAN)/Cu system [4] and by McCaskie who described guanidinium nitrate (GN) based blue strobe compositions [5]. Also, similar compositions as mentioned above have been analyzed in our recent work [6]. However, TMAN is somewhat difficult to obtain and possibly an expensive material. In our experience, such TMAN based compositions have difficulties of sustaining combustion, which can lead to a low wind resistance in practical applications.

In this work GN and aminoguanidinium nitrate (AGN) were employed as replacements for TMAN in blue strobe compositions containing AP, polyvinyl chloride (PVC) and basic copper carbonate, $CuCO_3 \cdot Cu(OH)_2$ (BCC). Due to better performance, AGN composition was studied in more detail.

2 Experimental Section

CAUTION! The mixtures described herein are potential explosives, which are sensitive to mechanical stimuli, such as impact, friction, heat, and electrostatic discharge. Although we encountered no problems in the handling of these materials, appropriate precautions and proper protective measures (safety glasses, face shields, leather coats, Kevlar gloves, and ear protectors) should be taken when preparing and manipulating them.

N.B., in previous work AGN was found to be extremely dangerous when mixed with copper bromate, $Cu(BrO_3)_2$ and copper iodate, $Cu(IO_3)_2$. The sensitivity to friction was extreme and small amounts of experimental mixtures self-ignited during storage. Also a side product of AGN reaction with BCC (black in color, obtain under acidic conditions) had self-ignited while being wet on a filter paper.

AP and AGN were synthesized in Prof. Klapötke's energetic materials research group (LMU, München). AP by neutralizing perchloric acid with ammonia solution. AGN by reacting nitric acid with aminoguanidinium bicarbonate. The final product was dried in a desiccator before use and water solution of AGN had pH 7–8. Copper powder ($<$ 150 μm) was from Grüssing. Basic copper carbonate, guanidinium nitrate and PVC powder were from Sigma Aldrich.

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Nitrocellulose (NC) with a nitrogen content of 13.25 % was from Nitrochemie Aschau GMBH. All chemicals used were ground with a mortar and pestle and passed through 30 mesh screen before conducting experiments.

The strobe compositions were mixed using a mortar and pestle. Pellets of 2 g (13 mm in diameter, ~10 mm in height, $\rho \sim 1.57\ g\,cm^{-3}$) were pressed in one increment by a consolidation dead load of 2 tons. For extruding of 5 mm diameter rods the following procedure was followed: 2–4 g of composition was moistened with either MEK or Acetone to swell or dissolve the binder material (PVC or NC). Then a 5 mm ID plastic syringe with a cut end was used as a simple pump to press 10–25 mm long rods (~0.4 g each, $\rho \sim 1{,}15\ g\,cm^{-3}$). The syringe was filled with the moist strobe composition and while facing a hard surface the plunger was pressed down by hand to eject entrapped air and to consolidate the compositions as much as possible. Finally the compressed rod was extruded and left to dry overnight at room temperature.

Spectrometric measurements were carried out using a HR2000+ES spectrometer with an ILX511B linear silicon CCD-array detector controlled by software from OCEAN OPTICS. The integration time for recording the emission spectra was set to 20 ms whereas it was set to 5–10 ms for frequency measurements. The detector-sample distance was 1 m for 13 mm pellets and 0.5 m for 5 mm pellets. The DTA curves were measured with a 552-Ex differential thermal analyzer from OZM at heating rates of $5\,^{\circ}C\,min^{-1}$. Visario G2 1500 Weinberger speed camera was used for filming at 1000fps and SONY RX10 III for 100 fps and 500 fps respectively. The impact and friction sensitivities were determined using a BAM drophammer and a BAM friction tester. The ESD test was performed with Xspark 10 instrument from OZM. The sensitivities of the compounds are indicated according to the U.N. Recommendations on the Transport of Dangerous Goods (+): impact: insensitive >40 J, less sensitive >35 J, sensitive >4 J, very sensitive 4 J; friction: insensitive >360 N, less sensitive $=360$ N, sensitive <360 N >80 N, very sensitive <80 N, extreme sensitive <10 N.

3 Results and Discussion

3.1 Aminoguanidinium Nitrate Blue Strobe

The idea of using a AP/GN base for blue strobes has been already investigated by McCaskie [5]. The high percentage of GN requires a lot of energy to melt it and even with catalytic help of copper compounds, it's decomposes slowly. Therefore, GN based strobe compositions are possible, however their performance does not surpass TMAN based compositions.

Hence AGN was suggested as a possible replacement that could surpass GN in its reactivity and have an advantage over TMAN being more easily available and cheaper option. A series of strobe compositions containing AP, GN, AGN, different copper sources (Cu, CuO, Cu_2O, BCC) were tested.

BCC was chosen over copper and copper oxides as it was capable of producing a blue flame flash of higher color purity and a better flash separation. However, CuO can also work. PVC was also employed as recommended by E. McCaskie. PVC seems to serve well as a low-energetic fuel that possibly assists the smolder reaction [7]. After several experiments of testing different additives and varying the oxygen balance of such compositions led to a narrow area of a working blue strobe compositions. Such working compositions possessed a distinct strobing behavior, sustainable combustion and a seemingly good blue color of the strobe flashes. In Table 1 three different blue strobe compositions (GN, AGN, TMAN based) are compared. In Figure 1 their strobing patterns are presented, that were obtained by monitoring the light intensity at 450 nm in time. Two types of samples were tested: 5 mm rods (0.4 g sample) and 13 mm pellets (2 g). The 5 mm rod samples were made with an intention of having a minimal energetic feedback, that could help lowering the strobe frequency.

The composition A with GN produced the strobing effect (13 mm pellet), even though the light intensity of the flashes was rather weak. The 5 mm rod of A burned constantly with a very weak re-appearing blue flame that was not registered by spectrometer.

The reference composition with TMAN burned with an overlapping blue flashes as seen in Figure 1.

The B composition performed quite well producing stable and distinct (Figure 2) blue flashes when tested as both 5 rods and 13 mm pellets. Due to good performance as a blue strobe the composition B was analyzed further to evaluate its chemical stability and strobe mechanism. The chromaticity diagram (Figure 3) shows the color purities of the flash reactions of A, B and reference composition.

3.2 Humidity Test

Blue strobes are generally known to degrade over time due to possible ageing reactions that can occur. For example, AP can react with metallic copper, salts can undergo double exchange reactions, acid-base as well as complex formation reactions are also possible.

Therefore, a humidity test was performed in order to estimate how moisture sensitive is the composition B at room temperature (Table 2). Each test was performed in a desiccator with a saturated salt solution over a 3-day period. Three samples of ~0.6 g were weight with an analytical scale before and after exposure to enhanced relative humidity.

After exposure to RH 75 % the first significant change in sample's weight was registered. Moisture induces a reaction that releases gases, which causes the weight loss and the color change.

Table 1. Blue strobe chemical compositions of a GN base (A), AGN base (B), TMAN base (reference). Strobe frequency, linear burn rate, chemical stability and sensitivity parameters are present.

Compositions		A	B	Ref.
NH_4ClO_4		30	25	55
GN		50		
AGN			55	
TMAN				30
PVC		5	5	
$CuCO_3 \cdot Cu(OH)_2$ (BCC)		15	15	
Cu powder (40–100 mesh)				15
NC powder				+1 %
Frequency, Hz	13 mm	3,5 ± 2	8 ± 2	> 10
	5 mm rods	const.	3,8 ± 2	> 10
Linear burning rate (5 mm rod), mm/s		1,4	1,1	5,2*
CIE coordinates**	X	0,262	0,249	0,236
	Y	0,296	0,275	0,289
Color purity,**%		27	32	35
Chemical stability (DTA), °C		247	179	245
Sensitivity tests	Impact (J)	15	10	6
	Friction (N)	> 360	> 360	240
	ESD (mJ)	42	33	51

* unusually high combustion rate resulted from the enhanced surface flame propagation of this particular composition. The linear burning rate is expected to be lower. ** Light produced by the flash reaction.

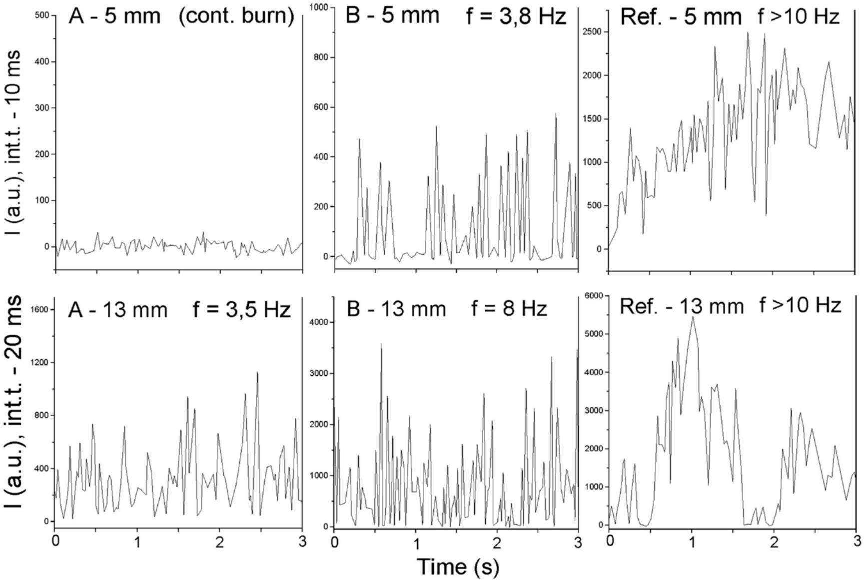

Figure 1. Light intensity at 450 nm vs time.

The color change was also registered in several sample compositions that were stored before pressing pellets. However, well dried compositions did not cause such reaction for up to 2 months of storage at room temperature.

It must be noted that dry and acid-free AGN was used in our experiments (water solution shows pH of 7–8 on universal indicator paper). In our experience, compositions with non-acidic AGN have significantly greater shelf life.

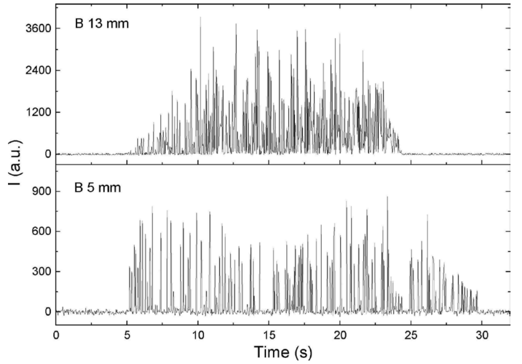

Figure 2. Consistent over time strobing pattern of composition B tested as a 5 mm rod and 13 mm pellet. From the ignition point the rod was consumed in 25 s at a linear burn rate of 1,1 mm/s. Light intensity was registered at 450 nm.

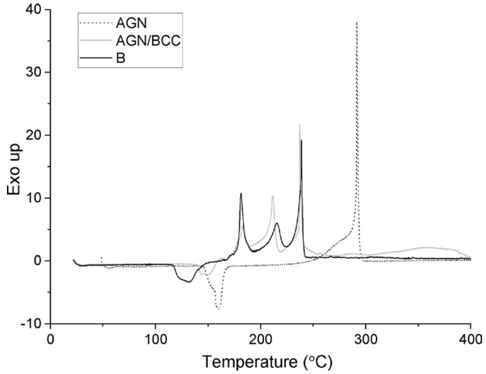

Figure 4. DTA curves of pure AGN, AGN/BCC (55/15 w.t. ratio) and composition B.

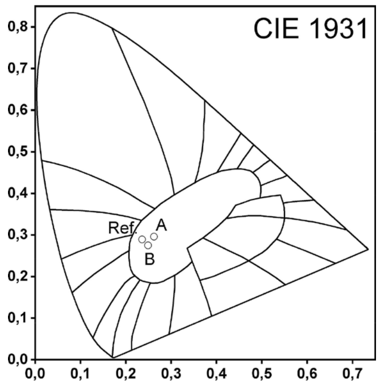

Figure 3. Chromaticity diagram indicating color points of the flash reactions of A, B and reference compositions.

When 3 g of acid-free AGN is dissolved in water and 1 g of finely ground BCC is added to the solution, the color of undissolved BCC changed first to light violet and then to purple. Bubbling is observed. After stirring the suspension and letting react overnight, 2,8 g of purple precipitate is formed, which is likely to be a Cu aminoguanidinium complex. When dried and ignited as loose powder, the complex material burns fiercely producing a green flame that comes from $CuOH_{(g)}$ emissions. The chemical stability this complex species is quite unclear, and as mentioned before, AGN and BCC reaction's side product had self-ignited one time during drying. Therefore, long term stability tests at elevated temperatures are suggested before using in practice.

3.3 Differential Thermal Analysis (DTA)

DTA measurement was performed for composition B and certain compositions with AGN. It was found that BCC catalyzes the decomposition of AGN and significantly changes the DTA curve of AGN (Figure 4). The B curve is very similar to AGN/BCC with the same decomposition point at 179 °C, meaning that AP and PVC do not participate in this process.

Sometimes during the incremental heating of the DTA sample, the test composition B (and very similar ones) showed a high-order deflagration (likely at 238 °C) that were powerful enough to rupture the mini glass test tube of the DTA instrument. The sample weight was ~40 mg.

Table 2. Exposure of composition B to different relative humidity generated by saturated salt solutions at room temperature.

Salt		K_2CO_3	NaBr	NaCl	KNO_3
Relative humidity at 25 °C, %		43	57,6	75,3	93,6
Pellets	Weight change	0	0,0004	-0,0005	−0,0246
	Color change/cracks	no	no	no	yes*
Powder	Weight change	0,001	−0,002	−0,0115	−0,0375
	Color change	no	greyish violet (lite)	greyish violet	deep purple**

* In 6 h purple spots appear. ** In 3 h turns grey-violet, in 6 h purple, after three days – deep purple.

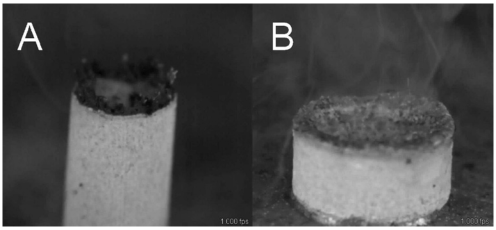

Figure 5. Smoldering surface of composition B 5 mm rod (A); 13 mm pellet (B) (capture from the high-speed camera footage at 1000 fps). Heavy boiling and gas generation is observed on the molten reaction surface. Whitish boiling reactants can be observed in the center of both samples.

3.4 Origin of the Bright Blue Flash

The high-speed camera videos give interesting information on the strobe reactions observed in this work. There have been a few curious phenomena registered that are described, however it is somewhat difficult to draw a clear conclusion from the latter that would help to explain the strobe reactions that occur in AGN/AP/BCC system. However, they give some clues.

During the smolder phase gases are generated from the reaction surface (Figure 5). Around 50 % of the smolder reaction time small blue-glowing lines of gases appear at the reaction surface as well as micro blue flashes (Figure 6A).

As the glowing gases eject from the burning surface, sometimes, especially few miliseconds before the flash reaction, a significantly brighter flame spot appear (Figure 6A, fifth frame) that travels upwards with the flow of gases. Perhaps this is a region of higher temperature or a piece of molten reactive composition being ejected from the pellet's surface, that has a delayed ignition and burns to produce a significantly bright blue flash/spot, that is associated to the same brightness and color of the flash reaction (Figure 6A).

The flash reaction seems to be a result of (i) rapid exothermic reaction that causes the ejection of flammable gases from the boiling surface or (ii) an ignition of gases that have already been formed above the pellet (Figure 6B). Possibly it can be a combination of the two as well.

The first assumption is made from our previous work with TMAN strobes and the evidence from the current DTA measurement, as the exothermic decomposition at ~240 °C tends to be quite energetic often breaking the mini test tube of the sample.

The second assumption followed observing the ash scaffold formation (Figure 7) and analyzing the high-speed camera footage. Most test samples burned rather clean without significant ash formation, however, few samples of a 5 mm rods burned leaving a thin scaffold of ash that was almost as tall as the 20 mm long test sample (Figure 7). Also the ash scaffold was observed to be glowing red during combustion, indicating the surface temperature of 600–900 °C.

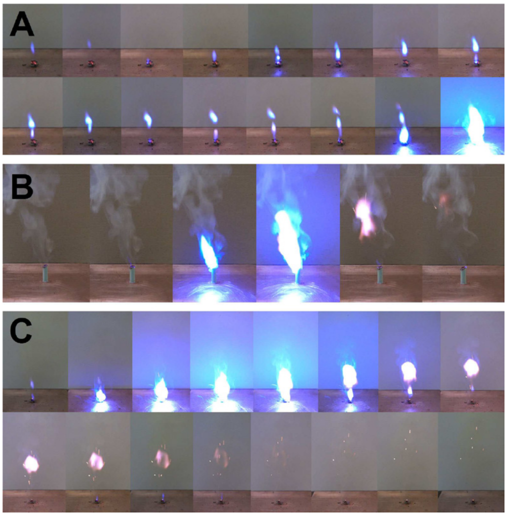

Figure 6. High speed camera footage of the oscillatory burning B composition. A) glowing gases appear at the reaction surface at all time (500 fps); bright flame spot appearing prior to the flash reaction can be seen in the fifth frame; in the last frame flash reaction starts. B,C) capture series of the occuring blue flash at 100 fps and 500 fps respectively. The blue color is associated to the emission of CuCl and redish tip to CuO.

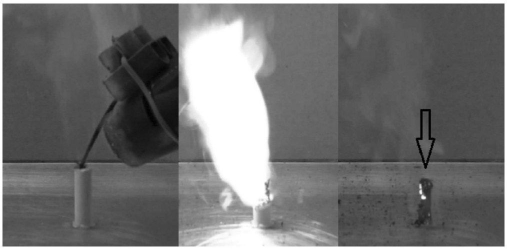

Figure 7. The ash scaffold is formed due to a strong heat loss to the surounding atmosphere during the combustion of 5 mm rod (comp. B). Partially red glowing ash scaffold in the last frame is observed.

Interestingly, being thin and fragile as the scaffold is, it did not fall apart due the strobe reaction that would make one expect to have a certain pressure fluctuation at the surface that is accompanied by the popping sound observed every time when testing compressed and uncompressed B composition. For example, a classical white strobe composition based on AP/MgAl/$BaSO_4$ [8] burns to produce flashes that are more similar to a small portions of flash powder deflagrating. This produces pressure fluctuations, that can be seen when such composition is compact into a cardboard casing, that eventually burns off and the remaining's of the paper casing are blown away by the pressure waves of the flashes. However, in the case of rod, the ash scaffold remained still, indicating that there are no significant pressure fluctuations at the burning surface, what supports the second assumption.

Moreover, in Figure 6B it can be seen, the erupted blue flash did not create pressure that would blow away the smoke cloud that had been formed from the beginning. This would indicate that the flame had spread through the flammable semi-reacted smoke above the pellet, consuming it, however not creating any significant pressure in the flame envelope. This also supports our personal observations during measurements. Visually, the combustion of the B comp. rod produced a rather steady flow of gases from the rod's surface that only flashed rapidly, and the flashes did not disturb the uniform flow of the gases. Also the popping sound was very distinct and observed all time for tests of Comp. B.

4 Conclusions

AGN was proved to be a suitable material in combination with AP and BCC for producing a blue strobe pyrotechnic pellet. The composition B burned producing sharp and well defined flashes accompanied by a popping sound.

The smolder reaction seems to be caused by the decomposition of AGN with a copper catalyst and the flash reaction is possibly a combination of an exothermic reaction at the surface and ignition of flammable gases above. However, the origin of the cycling burning is unclear.

Composition B powder showed sensitivity to moisture at RH = 58–75 %, and better resistance with RH = 75–94 % when tested in as a compressed pellet bind with PVC/MEK. In both cases the composition turned purple with a registered weight loss in the sample.

5 Abbreviations

AP	ammonium perchlorate
TMAN	tetramethylammonium nitrate
AGN	aminoguanidinium nitrate
GN	guanidinium nitrate
BCC	basic copper carbonate (malachite)
Cu	copper powder (electrolytic)
CuCl	copper (I) chloride
CuO	copper (II) oxide (black)
MgAl	magnalium powder (Mg and Al alloy 50:50)
NC	nitrocellulose powder
PVC	polyvinyl chloride
RH	relative humidity

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Paper 4

Study of Pyrotechnic Blue Strobe Compositions Based on Ammonium Perchlorate and Tetramethylammonium Nitrate

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Energetic Materials

Study of Pyrotechnic Blue Strobe Compositions Based on Ammonium Perchlorate and Tetramethylammonium Nitrate

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Dedicated to Professor Dr. Wolfgang Beck on the occasion of his 85th birthday

Abstract: Pyrotechnic strobes, both colorless and colorful, are compositions that burn in an oscillatory manner. They are used in military illumination devices and in fireworks as one of the most attractive pyrotechnic effects. Most colored strobes contain magnesium (Mg) or magnesium–aluminum (MgAl) alloy as a fuel. However, this is an issue for blue strobes since the choice of stable blue-flame emitters is extremely limited. In fact, copper halides have been observed to produce blue emissions in pyrotechnic flames exclusively at temperatures ranging from 1200 to 1500 °C. At higher temperatures, the emitter is destroyed, or more specifically, a preferred trimer Cu_3Cl_3 species is converted into monomers. As a result, the flame color fades and a whitish-blue flame is observed. Therefore, it was interesting to see whether blue pyrotechnic strobes can be made without using conventional high-temperature fuels, such as Mg or Al, in order to conserve a deep flame color. The formulation called the Jennings-White blue strobe No. 5 [55 % ammonium perchlorate (AP), 30 % tetramethylammonium nitrate (TMAN), and 15 % copper] is considered the top-of-the-line formulation, which is described as being capable of producing an intense blue strobe. However, its mechanism is not well-understood, and the formulation is not chemically compatible. This paper presents research focused on improving the blue strobe formulation by Jennings-White.

Abbreviations

AP: ammonium perchlorate
TMAN: tetramethylammonium nitrate
TMAP: tetramethylammonium perchlorate
GN: guanidinium nitrate
Cu: copper powder (electrolytic)
CuO: copper(II) oxide (black)
MgAl: magnalium powder (Mg and Al alloy 50:50)
EDN: ethylenediammonium nitrate
TMEDN: tetramethylethylenediammonium nitrate
PR: phenolic resin
NC: nitrocellulose powder
PVC: poly(vinyl chloride)
K4–K112: Tested formulation numbers (full formulations are present in the Supporting Information)

Introduction

The pyrotechnic-strobe effect is defined as a cyclic variation of emitted light intensity as a function of time produced by a light-emitting pyrobody.[1,2] The two conditions expressed by this definition are the production of at least two flashes separated by a "dark" phase and a strobe frequency sufficiently low for the human eye to distinguish between flashes.

Although the first pyrotechnic-strobe compositions were published under the name "Orion Flashing Guns" as early as 1898,[3] there has been little knowledge of how the strobing behavior of such compositions comes about until Krone's[4,5] and Wasmann's[6,7] studies during the 1970s. Krone's experiments, with compositions that comprised 20 % magnalium serving as fuel, and 65–75 % nitrates or perchlorates of the alkali-earth metals serving as oxidizers and additives, gave a significant hint about the strobing mechanism: during a reaction phase, he observed the formation of a partly solid, partly molten foam and he called it the semireacted slag, which contained only small amounts of magnesium.[4,5] This result led Krone to the conclusion that the oxidation of magnesium mainly takes place in the previous dark phase, whereas aluminum is only oxidized in the presence of active gases in the semireacted slag zone when the available surface area is higher. The oxidation of aluminum results in a light flash. However, the occurrence of competing chemical reactions with opposite reaction pathways (in this case, the slow oxidation of magnesium and the fast oxidation of aluminum)[2] is only one way to explain strobing behavior.

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Wasmann suggested that physical parameters essentially contribute to strobe reactions.[6,7] This hypothesis emerged from studies involving copolymers of unsaturated monomers, which contained nitrate groups with conventional unsaturated monomers and metal perchlorates that were soluble in the monomers. Due to the low thermal conductivity of the microporous residual mixture of the former reaction cycle, the heat inside the system built up in some areas until it reached the ignition temperature and light was emitted. Here, the periodic strobing behavior is controlled by the heat transfer from the burning surface into the interior of the system.

Another theory concerning the strobing mechanism comes from Shimizu.[8] Here, the ignition of a strobe composition on the surface triggers a reaction in the dark zone, which is at a different temperature, with a small activation energy and a small heat output,[1] and this leads to the formation of bright spots, which are glowing and moving on the surface.[9] The hot spots magnify with increasing temperature in these areas. When the temperature of the dark zone meets the ignition temperature, the flash reaction takes place. A small layer of the dark zone on the burning surface, in which the temperature remains below the ignition point, is left behind and is the starting point for the next cycle.[8] Obviously, in this case, the temperature controls the progress of the reaction. Furthermore, this mechanism suggests that strobe compositions consist of one dark composition, which gives rise to the dark reaction, and one flash composition, which gives rise to a flash reaction. Shimizu's hypothesis might be a useful criterion to decide whether a chemical composition is a possible strobe candidate or not.[1] However, theoretical and experimental analysis of diverse potential strobe compositions revealed that Shimizu's hypothesis does not always prove to be correct. The black strobe consisting of 30 % AP, 40 % TMAN, and 30 % Cu can also be referred to as a blue strobe, because the combustion gases produced during the "flash" phase may be ignited to generate a blue flame and increasing the amount of AP up to 40 % results in the ignition of these gases in air, of their own accord, to produce the blue flame. However, neither a dark reaction nor a flash reaction can be postulated that complies with the constant change of a slow and a fast smolder without the emission of visible light at any stage of the combustion. Vice versa, mixtures of a smolder composition and a flash composition do not generally show a strobing behavior. The breakdown of the Shimizu hypothesis to explain the strobe effect of some compositions can be justified by the fact that Shimizu did not claim the presence of a smolder composition and a flash composition as a sufficient condition for a strobe, but only as a necessary one. This implies that the description of the strobe mechanism by Shimizu might not be fully satisfactory. It also means that the mechanism requires experiments to detect the chemical changes occurring in different phases of the cycle as well as studies of the thermodynamics and kinetics involved.

Recordings of the combustion of several strobe compositions by a high-speed camera[2] not only confirmed the previous findings, but revealed the formation of gaseous species under the surface layer at the stage of the dark reaction. The latter escaped through the foam forming bubbles when the layer melted. When the layer remained partly solid, sometimes the gas escaped, breaking or even ejecting the layer due to the inflation underneath. When too much gas escaped, the flashes were irregular and less sharp. The concentration of the gaseous intermediate species oscillated due to their synthesis and consumption by competing chemical pathways.

The thermokinetic model developed by Davies,[10] which adapts a scheme created to model homogeneous oscillators and uses the Salnikov model,[11] focuses on a binary composition of Mg and AP. Herein, a set of compounds consisting of solid and liquid magnesium react in a slow reaction, thereby producing gaseous magnesium. The fast and exothermic flash reaction occurs only if the heat generated is sufficient and if the concentration of intermediate species has reached a critical level. The model claims not only thermal oscillations responsible for the regulation of the progress of strobe reactions, but also periodic variations in the concentration of gaseous intermediate species, which is more likely to explain strobe mechanisms.[2]

A common approach towards white, yellow, orange, red, and green strobe compositions is combining AP and magnesium, with a metal sulfate generating the desired color.[12] Blue strobes are not accessible in this system, since the high flame temperature during the combustion of such formulations keeps the concentration of the preferred copper(I) chloride emitter low.

The first blue strobes evolved from Jennings-White's studies in 1990 were inspired by the existence of white-strobe compositions containing AP, magnalium, and some nitrogenous strobe material, as well as Shimizu's observation of a good dark reaction produced by a mixture of AP and 2 % of copper powder.[8,13] In these experiments, among others, TMAN was tested in combination with AP and copper-substituting magnalium.[13] One composition [the Jennings-White blue strobe No. 5, (Table 1)] showed outstanding burning characteristics: it produced flashes of a high-quality color that were well-separated. Additionally, the ignition sensitivity of this blue strobe was sufficient. The combination of these two properties makes the Jennings-White blue strobe No. 5 a promising candidate for practical use.

Table 1. The Jennings-White blue-strobe formulation No. 5.

Ingredient (wt.-%)	No. 5
AP	55
TMAN	30
Cu (atomized, 40–100 mesh)	15

The aim of this work is to compose a blue-strobe formulation that possesses lower strobe frequency and improved flash separation than the Jennings-White blue strobe No. 5, without a significant loss in flame color quality or combustion properties, and also to tune the chemical stability of this strobe composition.

Results and Discussion

The flashes produced by the Jennings-White blue strobe No. 5 (Table 1) are sharp and of an exceptional blue color, but the interval between the flashes is too small.[13] Although the ignition sensitivity of the Jennings-White blue strobe No. 5 is rela-

Table 2. Selected strobe formulations for further analysis. K4: Original formulation (ref.[13]); K25: copper(II) oxide variation; K66: copper(II) benzoate variation; K97: basic copper carbonate variation; K102: Nonstrobing, fast-burning; K105: sulfur-containing; K108: NC-containing. Reference: AP white strobe.

Ingredient (wt.-%)	K4	K25	K66	K97	K102	K105	K108	Reference values
AP	55	55	55	55	55	55	55	60
TMAN	30	30	30	30		30	30	
CuO		15	7.5		15	15	15	
Cu	15							
Copper(II) benzoate			7.5					
Basic copper carbonate				15				
TMEDN					30			
MgAl (40–80 mesh)								25
$BaSO_4$								15
Additive (add. %)						+2 % sulfur	+2 % NC	+5 % $K_2Cr_2O_7$
Sustainable combustion[a]	S	D	D	S	S	S	S	S
Relative strobe frequency[a]	H	M	M	M	n/a	M	M	L
Chemical stability (DSC) (°C)	245	270	305	245	165	300	270	> 330
Sensitivity tests								
Impact (J)	6	7	5	15	7.5	4	7	7.5
Friction (N)	240	288	240	360	120	120	288	144

[a] Abbreviations are described in the Supporting Information.

tively high, it does not stay reliably lit. Furthermore, its chemical stability, which determines the susceptibility to degradation during storage, and thus, the potential of this composition for industrial use, leaves much to be desired. Therefore, the aim of this research project was to lower the strobe frequency, to improve the flash separation of the Jennings-White blue strobe No. 5 without a loss in color quality, to make the combustion sustainable, and to tune the chemical compatibility of this strobe composition. Also, an understanding of the strobe mechanism would greatly benefit the empirical evaluation method that was used for this experiment as the strobe mechanism of this particular system is not well-understood.[1,14] Parallel to the empirical optimization experiments, DSC measurements were performed and an ammonium perchlorate/tetramethylammonium nitrate binary system was analyzed to get an insight into the strobing mechanism. The empirical evaluation method was used in the experimental section, which led to some general conclusions on various strobe formulations that contained mostly AP and TMAN. During the experiment, a total of 112 formulations were tested (Supporting Information). From these, eight formulations were selected for discussion for their conspicuous performance (Table 2). These formulations were analyzed further by collecting additional physical and chemical parameters. Physical measurements include emission spectra and strobe frequencies, and chemical analysis includes DSC measurements and chemical stability tests of pressed formulations.

The sensitivity tests revealed that most formulations are stable up to 245 °C, except formulation K102, which contains TMEDN. The impact sensitivity is in the range of 4–15 J, and the friction sensitivity ranges from 120 to 360 N. According to U.N. recommendations on the transport of dangerous goods,[15] such formulations are classified as sensitive to very sensitive to shock and sensitive to friction.

Emission Spectra

Emission spectra were acquired during the combustion process of each strobe formulation. As there are two stages of combustion in the strobe composition, there are two different emission spectra acquired during the measurement. Ideally, any strobe should produce minimum light during the smolder stage and maximum light output during the flash stage. Therefore, during the smolder reaction, the acquired emission spectra should represent the background level. Also, these stages must be well-separated. This makes the strobe process more easily distinguishable to the human eye. In the case of colored strobes, another criterion is added – a good colored strobe must produce a preferred emission during the flash reaction so that the flash is colorful in and by itself. For blue strobes, copper halides must be excited during the flash reaction in the flame to produce dominating emissions in the blue region of the visible spectrum. For this reason, the system of AP and TMAN is one of the very few that have the right parameters for both the strobe reaction and blue-flame production.

As all pyrotechnic compositions presented herein contain AP as an oxidizer, as well as some form of copper as a colorant, it can be assumed that copper(I) chloride is the only blue emitter formed during the burning processes of these formulations. For this reason, the emission spectra are expected to be very similar, which is indeed the fact. The emission spectrum of K66 is

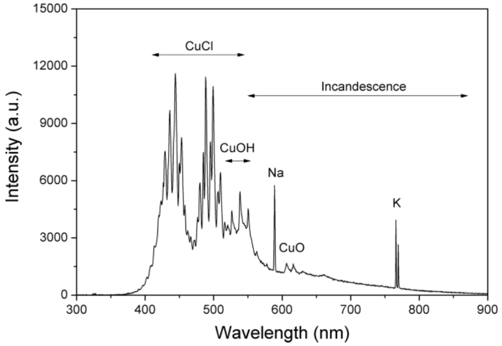

Figure 1. Emission spectrum of the blue strobe formulation K66.

shown as an example (Figure 1). Dominating copper(I) chloride emissions are present in the 400 to 500 nm region, and copper hydroxide produces a wide band in the 550 nm region, which overlaps with the CuCl emissions. Copper oxide has two bands in the red region. Sodium and potassium impurities give sharp atomic lines at 589 and 767 nm, respectively. This pattern is visible in the emission spectra of all formulations that contain AP, TMAN, and a copper source. The only observed fluctuations are within the error limits and do not essentially influence the overall quality of the colored flame.

Strobe Frequencies

Unsynchronized reaction zones progressing simultaneously through the pellet caused overlapping flashes that complicated these measurements. The strobe frequencies of the selected formulations are estimated to be between 5 and 15 Hz (Figure 2), with strobe frequencies of 1–2 Hz for the reference. According to Jennings-White,[13] strobe frequencies between 1 and 10 Hz are applicable in pyrotechnics; thus, the determined frequencies are within a good regime.

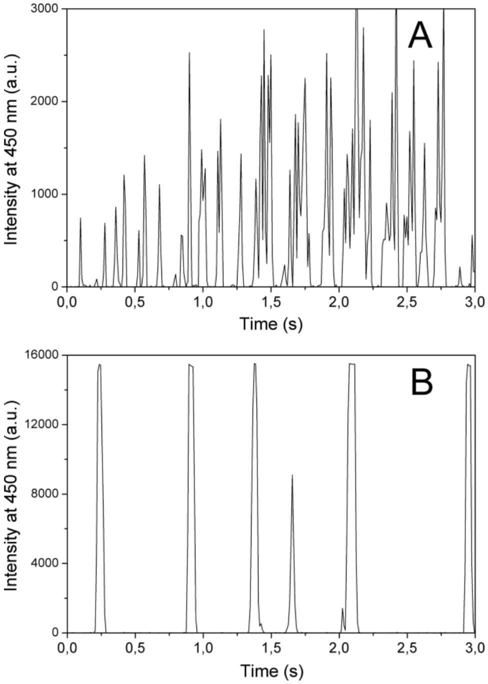

Figure 2. Light intensities at 450 nm versus time. (A) Strobing pattern of formulation K25; (B) strobing pattern of reference (see Table 2).

Strobe Mechanism

The effort to explain the AP/TMAN strobe reaction mechanism is an important part of this study. A more thorough understanding would lead to a more purposeful approach to the development of a good strobe that possesses a sustainable reaction, a distinguishable strobing effect, and good chemical stability.

Jennings-White has made a huge effort in the quest to elucidate certain strobe reaction mechanisms.[1] However, the AP/TMAN system was the most difficult to explain, since the occurring combustion reactions were uncertain. It is usually referred to as a “black strobe”, because the base of this formulation does not contain any strong pyrotechnic flame emitters. Therefore, the flame is pale white, due to weak incandescent emission.

The formulation of AP and TMAN in the ratio of 2:1 is the basis for this type of strobe formulation. However, the mixture only stays alight with the help of an external heat source. The third component added to this mixture, in our case, a mixture of copper and its salts and oxides, acts as catalysts in AP decomposition. This is what makes the composition sustain combustion. Copper, in this case, acts as a double-duty material, as it not only has a catalytic effect on AP decomposition, but also helps to sustain the reaction quite well (composition K4). This could be related to the fact that copper acts as a fuel in either flash or smolder reactions. In any case, the net heat produced during combustion is higher, thus increasing the energy feedback to the unburnt composition.

For the following experiment, we prepared formulation K98, in which the ratio of AP to TMAN was the most original of our tested formulations 11:6 (K98 contained 64.7 % ammonium perchlorate and 35.3 % TMAN). The external heat source was a butane torch. When the flame of the torch is pointed towards a 13 mm, 2 g pellet of the pressed K98 formulation, it starts to produce gases due to a low-temperature decomposition process that occurs for AP below 300 °C. At the same time, the pellet's surface starts to visibly melt and turns dark yellow, and upon further heating, brown. At the moment it turns brown, a certain temperature is reached and the molten residue reacts very rapidly, producing a flash with a big flame envelope. At this point, the molten layer is consumed in the flash reaction, the torch starts to heat up the next layer of the unreacted formulation, and the cycle repeats several times until the pellet is consumed. Finally, the pellet is fully combusted till no residue remains on the test plate. From this experiment, it is clear that, the smolder reaction does not occur without the presence of a third component, which acts as a catalyst or a low-temperature fuel. Also it was important to understand the chemical consistency of the slag, as it gave an insight into the occurring reactions. So, in one experiment when the slag was already formed and brown, just before the flash, the butane torch was removed and the slag was cooled. Then it was collected, with possibly a small amount of the remaining unburnt formulation, and analyzed.

Theoretically, during slag formation, volatile, low-molecular-mass species evaporate and high-molecular mass species, oligomers, and polymers, which are not volatile, remain within the slag. The formed slag is visibly yellow or brown in color. This indicates the presence of unsaturated hydrocarbons, which are essentially formed from the partial decomposition of TMAN. To get more information of the slag's composition, NMR measurements were performed. The results showed that the slag contains: (a) monosubstituted six-membered ring aromatic systems, which can be either benzene or pyridine moieties in an oligomer chain; otherwise, being volatile, they would have evaporated at temperatures close to 300 °C; (b) alkyl chains; and (c) carbonyl species.

DSC Measurement

Furthermore, differential scanning calorimetry was applied to estimate the decomposition temperature under ambient pressure. The first observed exothermic reaction peak was the indication of a decomposition reaction. The exact decomposition temperature of a formulation was sometimes hard to predict, because multiple decomposition points and phase transitions took place. K66, for example, started to decompose at 305 °C, but the final ignition point was at 365 °C (strongly exothermic). For K102, the first decomposition could be noticed at 165 °C, whereas the second one began at 350 °C. In the case of K97, an AP phase transition took place at 240 °C, before the actual decomposition started at 245 °C. In the DSC curve of K105, a slight endothermic reaction, which could be attributed to the oxidation of sulfur, occurred at 185 °C. An exothermic reaction at 175 °C in the DSC curve of K108 indicated the start of the decomposition of NC, which proceeded at 193 °C and reached its maximum at 200 °C. Generally, such formulations are stable up to 245 °C, except K102, which is not a strobe, but rather a rapidly burning blue-flare formulation, with TMEDN as the fuel.

In addition to the DSC test, a chemical stability test was performed. Pressed pellets were left to stand in humid air at temperatures ranging from 0 to 8 °C. After 30 days, pellets were inspected. All formulations had degraded over time to some degree. Pellet K4, containing copper, completely changed its color as a result of the metallic copper reaction forming Cu^{2+} salts. Small blue spots appeared on formulations containing copper oxide and the reference formulation showed the maximum resistance to degradation. It must be noted that even after the chemical stability test, all formulations still possessed the strobing effect.

Finally, with all data combined, the following explanation of the reaction mechanism in AP/TAMN strobe formulations is suggested:

(1) AP and TAMN decompose at temperatures close to 300 °C in a complex way.[16,17] One of the dominant reactions is exothermic (smolder reaction), which occurs at around 300 °C and increases the temperature of the reaction front further. Slag starts to form.

(2) TMAN partly decomposes to form a slag, which is stable at temperatures above 400 °C. Slag is composed of highly reactive resins, oligomers with phenyl or pyridyl moieties, and aromatics that possess low volatility. Otherwise, they would vaporize and leave the slag.

(3) When the temperature reaches 400 °C, due to an exothermic smolder reaction, the flash reaction's E_a is reached, the slag gets oxidized, and a flash occurs. The oxidizer for the flash reaction is possibly: (a) the partly decomposed oxidizers present in the slag; and (b) AP and TMAN from the pre-ignition layer.

(4) After the flash reaction, the smolder reaction progresses to the depth of the pellet and the cycle repeats until the pellet is completely combusted.

Conclusion

The substitution of TMAN in the Jennings-White blue strobe No. 5 (55 % AP, 30 % TMAN and 15 % Cu) by the less reactive fuels, such as hexamine, TMAP, EDN, or TMEDN, causes the flash frequencies to rise so dramatically that the resulting compositions are either very fast-strobing or they burn constantly. As a consequence, formulations using the AP/TMAN/Cu system and/or CuO are still favorable over the analogous ones with the tested fuels, with regard to the strobing behavior. Nevertheless, it should be mentioned that the use of TMEDN as a fuel in pyrotechnics is suggested due to its outstandingly high burning rate with ammonium perchlorate.

Replacing Cu in the Jennings-White blue strobe No. 5 by CuO results in a less consistent strobing behavior, but it improves the flash separation. A complete substitution of Cu by CuO additionally lowers the strobe frequency. Substituting Cu by basic copper carbonate yields a composition that produces very regularly occurring flashes and even sustains combustion. A replacement of half the amount of Cu by cupric benzoate increases the ignition sensitivity and results in a burning behavior superior to that of a formulation using CuO as the only colorant. In that sense, the substitution of copper in the Jennings-White blue strobe No. 5 by the less sensitive and cheaper colorants, cupric oxide, cupric benzoate, and basic copper carbonate, is certainly possible, and it even improves the burning properties and physical characteristics of the pyrotechnic strobe.

When the percentages of AP and TMAN deviate from the 11:6 ratio used in the Jennings-White blue strobe No. 5, the strobing behavior of the compositions gradually transitions to a constant burning. Therefore, the ratio 11:6 between AP and TMAN is suggested as the optimum ratio for all investigated blue strobe systems.

The strobe frequencies of mixtures containing AP, TMAN, and CuO increase with an increasing percentage of this color imparter.

Sulfur proved to be a dark-reaction sustainer for the system AP/TMAN/Cu and/or CuO. The addition of 2 % sulfur to the system AP/TMAN/CuO even improves its strobing behavior. Higher amounts of this additive are not beneficial, since they lead to increased strobe frequencies. The same effect was observed upon the addition of lactose to the same systems. The use of NC as an additive for compositions containing AP, TMAN, and cupric oxide did not only improve the performance and promote a sustainable combustion for these formulations, but also proved to be a binder for the formulation. The use of dextrin and phenolic resin in the system AP/TMAN/copper and/or cupric oxide results in hardly ignitable or continuously burning compositions. Apart from sulfur, which causes the mixtures to stay alight, thereby decreasing their ignition sensitivity, none of the tested additives are beneficial for the AP/hexamine/copper system.

The strobe reaction has been explained in the last section of this work. The mechanism, by itself, is closely related to the strobe theory by Shimizu,[1] which emphasizes that any strobe formulation can be deconstructed to smolder and flash formulations.

Experimental Section

CAUTION! *The mixtures described here are potential explosives, which are sensitive to environmental stimuli such as impact, friction, heat, and electrostatic discharge. While we encountered no problems in handling these materials, appropriate precautions and proper protective measures (safety glasses, face shields, leather coats, Kevlar gloves, and ear protectors) should be taken when preparing and manipulating them.*

AP was employed as an oxidizer for most of the pyrotechnic compositions described in this report and was synthesized in Prof. Klapötke's energetic materials research group (LMU, München) by neutralizing perchloric acid with ammonia solution. A fine, 50 mesh powder of the fuel TMAN was used as received. Hexamine was purchased from Sigma–Aldrich. Tetramethylammonium perchlorate (TMAP) was synthesized according to the following protocol: perchloric acid (5.79 g, 0.0576 mol) was diluted with distilled water, and tetramethylammonium hydroxide (5.25 g, 0.0576 mol) was cooled down, separately, in an ice bath while stirring. Merging the two solutions resulted in the flocculation of the white metathesis product. Water was evaporated at 150 °C to form a crystalline product which was then placed in a drying cabinet. The fuels ethylenediammonium nitrate (EDN) and tetramethylethylenediammonium nitrate (TMEDN) were prepared by reacting ethylenediamine or tetramethylenediamine with an excess of nitric acid in ethanol. The precipitate products were filtered and washed with diethyl ether. As flame colorants, electrolytic 200 mesh copper powder, cupric oxide with a purity of 99+ % (Acros Organics), basic copper carbonate [Sigma–Aldrich, $CuCO_3{\cdot}Cu(OH)_2$], and cupric benzoate were tested. The last one was synthesized by reacting potassium benzoate with Cu^{II} chloride dihydrate in aqueous media. Sulfur flower, lactose, nitrocellulose (NC) with a nitrogen content of 13.25 % (Nitrochemie Aschau GMBH), dextrin, phenolic resin (Blikas Ltd., Lithuania), poly(vinyl chloride) (PVC), and red gum were used as received. All chemicals used were ground and sieved through a 50 mesh screen before conducting experiments.

After mixing the components for each strobe composition in a mortar and pestle, pellets of 1 g (13 mm in diameter, 4.0 mm to 4.5 mm in height) were pressed in one increment by a consolidation dead load of 2000 kg. For initial assessment of strobe formulations K75, K92 to K96, K98 to K101, K103 and K104, K106 and K107, and K109 to K112, no priming composition was employed. To ignite strobe compositions K26 and K27, a droplet of a priming mixture consisting of 75 % potassium perchlorate, 20 % birch charcoal, and 5 % shellac was pasted onto the surface of the pellets. However, the poor ignitability of these formulations gave reason to improve the priming system. For all other pyrotechnic compositions presented herein, a thin layer (0.1 g) of a priming formulation, which was composed of 65 % cupric oxide and 35 % magnesium, was applied to the surface of the pellets, and a droplet of a mixture consisting of 75 % potassium perchlorate and 25 % birch charcoal was placed on top. Both priming systems were wetted down with a 4 % solution of collodion (Merck), and homogeneous slurry was formed before pasting the primers onto the top of the pellets. Finished test units were dried for at least 1 h at room temperature. Ignition was imparted by touching the tip of the primer with a butane torch flame. The combustion process was filmed with a digital video camera recorder (Sony, DCR-HC37E) and the burning processes of the most promising strobe formulations K25, K66, K97, K102, K105, and K108 were recorded with a high-speed camera. The performance of each composition was evaluated with respect to flame color, smoke generation, and the amount of solid residues. Spectrometric measurements were carried out by using a HR2000+ES spectrometer with an ILX511B linear silicon CCD-array detector controlled by software from Ocean Optics. The integration time for recording the emission spectra was set to 20 ms, whereas it was 10 ms for the frequency measurements. The detector–sample distance was 1 m. Three samples were taken for each of the blue strobes K25, K66, K97, K102, K105, and K108 and all measured values were averaged. Averaging was based on the full burn of the mixture. Strobe compositions that were not pressed, primed, and burned on the day of manufacture were stored under dry conditions. For studying the strobing mechanism, formulation K98 was chosen, because it was the base mixture for the majority of nonmetallic strobe compositions studied, and it did not sustain combustion. Each time the formulation extinguished, a yellow-brownish combustion product containing a mixture of intermediate reaction products was scratched off the white pellet. The latter was then investigated by means of ^1H NMR measurements in $[D_6]DMSO$ and $[D_2]H_2O$ at 400 MHz, 25 °C with a JEOL Eclipse: 400 NMR instrument. The decomposition points of K25, K66, K97, K102, K105, and K108 were measured with a LINSEIS PT10 DSC apparatus at heating rates of 5 °C min^{-1}. The impact and friction sensitivities were determined using a BAM drop hammer and a BAM friction tester. The sensitivities of the compounds are indicated according to the definitions in the U.N. Recommendations on the Transport of Dangerous Goods. The degrees of impact sensitivity are defined as: insensitive for values greater than 40 J, less sensitive for values between 40 and 35 J, sensitive for values between 35 and 4 J, and very sensitive for values below 4 J. The degrees of friction sensitivity are defined as: insensitive for values greater than 360 N, less sensitive for a value of 360 N, sensitive for values between 360 and 80 N, very sensitive for values between 80 and 10 N, and extremely sensitive for values below 10 N.

A summary of all experimental formulations is given in Table S1.

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