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This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record.

**To be cited as:** 10.1002/ejic.201601486

**Link to VoR:** <https://doi.org/10.1002/ejic.201601486>

# Study of ammonium perchlorate and tetramethylammonium nitrate based pyrotechnic blue strobe compositions

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*Dedicated to Professor Dr. Wolfgang Beck on the occasion of his 85<sup>th</sup> birthday*

**Abstract:** Pyrotechnic strobes, both colorless and colorful, are compositions that burn in an oscillatory behavior. 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 flame exclusively at temperatures

ranging from 1200-1500 °C. At higher temperatures the emitter is destroyed, or more specifically, a preferred trimer  $\text{Cu}_3\text{Cl}_3$  species are converted into monomers. As a result, the flame color fades and 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 Jennings-White's blue strobe No. 5 (55% AP, 30% TMAN and 15% copper) is considered the top of the line formulation, which

is described to be capable of producing a deep color blue strobe. However, its mechanism is not well understood and the formulation is not chemically compatible. This paper presents a research focused on improving the latter blue strobe formulation by Jennings-White.

**Keywords:** strobes • oscillatory combustion • flame spectra • pyrotechnics • energetic materials • colored flame • ammonium perchlorate • tetramethylammonium nitrate

## 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 – polyvinyl chloride  
 (K4 – K112) – Tested formulation numbers (full formulations are present in Appendix)

## 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 called 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 on 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, 65-75% of nitrates or perchlorates of the alkali-earth metals serving as oxidizers and additives gave a significant hint on the strobing mechanism: during a reaction phase he observed the formation of a partly solid, partly molten foam and he called it the „semi-slag“, which contained only small amounts of magnesium [4, 5]. This result led Krone to the conclusion that the oxidation of magnesium does mainly take place in the previous dark phase whereas aluminum is only oxidized in the presence of active gases during the „semi-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 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 periodical 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 differently hot dark zone with a small activation energy and small heat output [1] and 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 of the next cycle [8]. Obviously, in this case the temperature controls the reaction progress. 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 right. The black strobe consisting of 30% AP, 40% TMAN and 30% Cu can be as well 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 with 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 be not fully satisfactory and requires experiments in order 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 combustions of several strobe compositions by a high-speed camera [2] did not only confirm 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 Sal'nikov model [11] focuses on a binary composition of Mg and AP. Herein a set of compounds consisting of solid and liquid magnesium reacts 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 formulation keeps the concentration of the preferred copper(I) chloride emitter low.

The first blue strobes evolved from Jennings-White's studies in 1990, which were inspired by the existence of white strobe compositions containing AP, magnalium and some nitrogenous strobe material and 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 (Jennings-White's blue strobe No. 5, (Table 1)) showed outstanding burning characteristics: it produced flashes of a high-quality color which were separated well. Additionally, the ignition sensitivity of this blue strobe was sufficient. The combination of these two properties makes Jennings-White's blue strobe No. 5 a promising candidate for a practical use.

**Table 1.** Jennings-White's blue strobe formulation No. 5.

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

The aim of this work was to compose a formulation of blue strobe that possess lower strobe frequency and improved flash separation in comparison to Jennings-White's 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 Jennings-White's blue strobe No. 5 (Table 1) are sharp and of an exceptional blue color, but they occur in too small intervals [13]. Although the ignition sensitivity of Jennings-White's blue strobe No. 5 is relatively high, it does not stay reliably lit. Furthermore, the chemical stability which decides over possible degradation upon 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 Jennings-White's 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 understanding of strobe mechanism would greatly benefit in 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 ammonium perchlorate / tetramethylammonium nitrate binary system was analyzed in order to get an insight on 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 (Appendix 1). From above, 8 formulations were selected for discussion for their conspicuous performance (Table 2). These formulations were analyzed further by collecting additional

physical and chemical parameters. Physical parameters included measuring their emission spectra, strobe frequency and chemical analysis included DSC measurements and chemical stability tests of pressed formulations.

**Table 2.** Selected strobe formulations for further analysis. K4 – Original formulation from ref. [13]; K25 – copper (II) oxide variation; K66 – copper (II) benzoate variation; K97 – basic copper carbonate variation; K102 – Non strobing, fast burning; K105 – sulphur containing; K108 – NC containing.

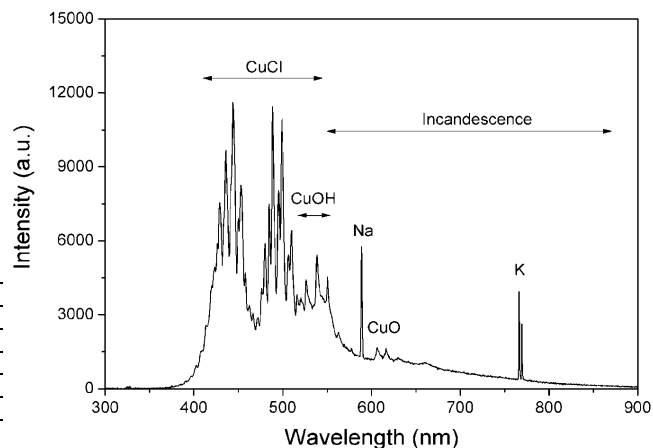
Ingredient (wt. %)	K4	K25	K66	K97	K102	K105	K108	Ref.	
AP	55	55	55	55	55	55	55	60	
TMAN	30	30	30	30		30	30		
CuO		15	7.5		15	15	15		
Cu	15								
Copper (II) benzoate			7.5						
Basic copper carbonate				15					
TMEDN					30				
MgAl (40-80 mesh)								25	
BaSO <sub>4</sub>								15	
Additive (add. %)						+2% Sulfur	+2% NC	+5% K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	
Sustainable combustion*	S	D	D	S	S	S	S	S	
Relative strobe frequency*	H	M	M	M	n/a	M	M	L	
Chemical (DSC), ° C stability	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

\* Abbreviations are described in the Appendix 1.

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 friction 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 strobe composition, accordingly there are two different emission spectra acquired during the measurement. Ideally, any strobe should produce minimum light during smolder stage and maximum light output during the flash stage. Therefore during smolder reaction the acquired emission spectra should be at the background level. Also these stages must be well separated. This makes the strobe process more easily distinguishable to a human eye. In case of colored strobes, another criterion adds – a good colored strobe must produce a preferred emission during the flash reaction so that the flash would be 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, which has the right parameters for both the strobe reaction and the blue flame production.

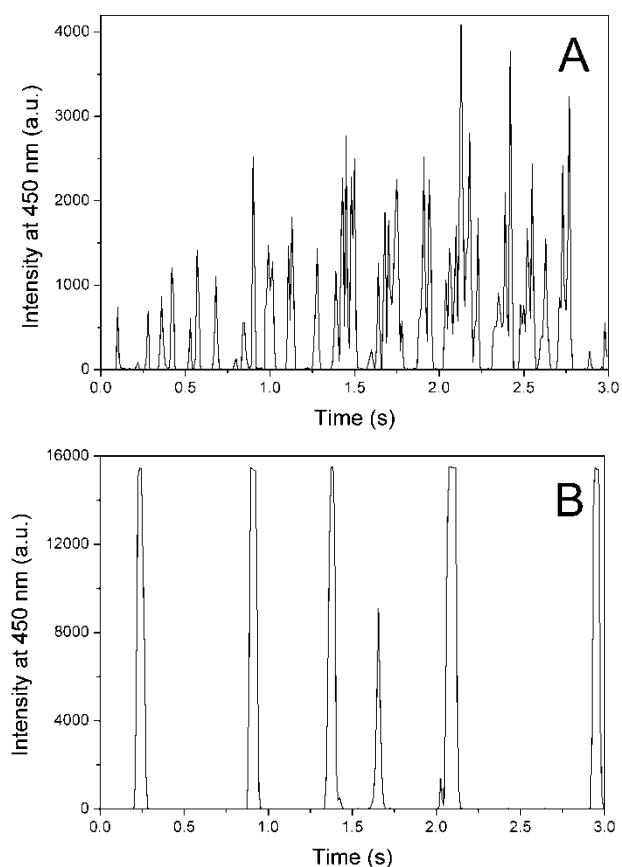


**Figure 1.** Emission spectrum of the blue strobe formulation K66.

As all pyrotechnic compositions presented herein contained AP as an oxidizer as well as some form of copper as 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. As an example the emission spectrum of K66 is shown (Figure 1). Dominating copper (I) chloride emissions are present in the 400 nm to 500 nm region, copper hydroxide produces a wide band in the 550 nm region, which overlaps with CuCl emissions. Copper oxide has two bands in the red region. Sodium and potassium impurities give sharp atomic lines at 589 nm and 767 nm, respectively. This pattern was visible in the emission spectra in all formulations that contained AP, TMAN and copper source. The only observed fluctuations were in the error limits that did not essentially influence the overall quality of the colored flame.

## Strobe frequencies

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



**Figure 2.** Light intensities at 450 over time. A graph represents the strobing pattern of formulation K25, B graph – reference (see table 2).

## Stroke mechanism

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

The formulation of AP and TMAN in ratio 2:1 is the base for this type of strobe formulations. However, the mixture of two only stays lit with the help of external heat source. The third component that is added to this mixture, in our case copper and its salts and oxides, act as catalysts in AP decomposition. This is what makes the composition to sustain combustion. Copper in this case acts as a double duty material as not only it has a catalytic effect on AP decomposition, but also it helps to sustain the reaction quite well (comp. K4). This could be related to the fact that copper acts as a fuel in either flash or smolder reaction. 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 have prepared the formulation K98, in which the ratio of AP and TMAN was original from the most of our tested formulations 11:6 (K98 contained: 64.7 % ammonium perchlorate, 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 formulation K98, it starts to produce gases due to low temperature

decomposition process that occurs for AP below 300<sup>o</sup> C. At the same time, it is visible how the pellet's surface starts to melt and turns dark yellow and upon further heating - brown. At the moment when 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 and 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 without any residue remaining on the test plate. From this experiment it was clear that without a presence of a third component, which acts as a catalyst or a low temperature fuel, smolder reaction does not occur. Also it was important to understand the chemical consistency of the slag as it would give an insight on the occurring reactions. So in one experiment when the slag was already formed and brown, just before the flash, butane torch was removed and the slag was allowed to cool. 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, remained within the slag. It was visible that formed slag is yellow or brown in color. This indicates a presence of unsaturated hydrocarbons, which are essentially formed from the partial decomposition of TMAN. In order to get more information of the slag's composition NMR measurement was 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. Elsewise being volatile they would have evaporated at temperatures close to 300<sup>o</sup> C. b) alkyl chains 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 decomposition reaction. 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 (strong exotherm). For K102 a 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 endotherm occurred at 185 °C which could be addressed to the oxidation of sulfur. An exotherm at 175 °C in the DSC curve of K108 indicated a start of 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 rapid burning blue flare formulation, with TMEDN as a fuel.

In addition to DSC test, a chemical stability test was performed. Pressed pellets were left to stand in a humid air at temperature ranging from 0 to 8°C. After 30 days pellets were inspected. All formulations have degraded over time by some degree. Pellet K4 containing copper completely changed its color as a result of metallic copper's reaction forming Cu<sup>2+</sup> 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 a 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 rises the temperature of 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. Elsewise they would vaporize and leave the slag.

3) When 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 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.

## Conclusions

The substitution of TMAN in Jennings-White's blue strobe No. 5 (55% AP, 30% TMAN and 15% Cu) by the less reactive fuels such as hexamine, TMAP, EDN or TMEDN caused the flash frequencies to rise so dramatically that the resulting compositions were either very fast strobing or constantly burning. As a consequence, formulations using the system AP/TMAN/Cu and/or CuO are still favorable over the analogous one 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 Jennings-White's blue strobe No. 5 by CuO resulted in a less consistent strobing behavior, but improved the flash separation. A complete substitution of Cu by CuO additionally lowered the strobe frequency. Substituting Cu by basic copper carbonate yielded a composition that produced very regularly occurring flashes and even sustained combustion. A replacement of half the amount of Cu by cupric benzoate increased the ignition sensitivity and resulted in a burning behavior superior to that of a formulation using CuO as the only colorant. In that sense, the substitution of copper in Jennings-White's blue strobe No. 5 by the less sensitive and cheaper colorants cupric oxide, cupric benzoate and basic copper carbonate is certainly possible and even improves the burning properties and physical characteristics of the pyrotechnic strobe.

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

The strobe frequencies mixtures containing AP, TMAN and CuO increased with an inclining 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 improved its strobing behavior. Higher amounts of this additive were not beneficial since they led to increased strobe frequencies. The same effect was observed upon addition of lactose to the same systems. The use of NC as 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 a binder to the formulation. The use of dextrin and phenolic resin in the system AP/TMAN/copper and/or

cupric oxide resulted in hardly ignitable or continuously burning compositions. Apart from sulfur, which caused the mixtures to stay lit thereby decreasing their ignition sensitivity; none of the tested additives were beneficial for the AP/hexamine/copper system.

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

## 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 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.

AP was employed as an oxidizer for most 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 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. As flame colorants, electrolytic -200 mesh copper powder, cupric oxide with a purity of 99+% (ACROS ORGANICS), basic copper carbonate (SIGMA ALDRICH,  $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ ) and cupric benzoate were tested. The latter 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), polyvinyl 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 primary composition was employed. To ignite strobe compositions K26 and K27 a droplet of a primary mixture consisting of 75% potassium perchlorate, 20% birch charcoal and 5% shellac was pasted on to the surface of the pellets. However, the poor ignitability of these formulations gave reason to improve the prime system. For all other pyrotechnic compositions presented herein a thin layer (0.1 g) of a primary formulation, which was composed by 65% of cupric oxide and 35% of 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 prime systems were wetted down with a 4% solution of collodion (MERCK) and homogeneous slurry was formed before pasting the primes on to 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 prime 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 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 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 which 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 non-metallic 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 <sup>1</sup>H NMR measurements in [D<sub>6</sub>]DMSO and [D<sub>2</sub>]H<sub>2</sub>O at 400 MHz, 25 °C using 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<sup>-1</sup>. The impact and friction sensitivities were determined using a BAM drophammer and a BAM friction tester. 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.

## Acknowledgements

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the Office of Naval Research (ONR) under grant no. ONR.N00014-16-1-2062, and the Bundeswehr – Wehrtechnische Dienststelle für Waffen und Munition (WTD 91) under grant no. E/E91S/FC015/CF049 is gratefully acknowledged. The authors acknowledge collaborations with Dr. Mila Krupka (OZM Research, Czech Republic) in the development of new testing and evaluation methods for energetic materials and with Dr. Muhamed Suceška (Brodarski Institute, Croatia) in the development of new computational codes to predict the detonation and propulsion parameters of novel explosives. We are indebted to and thank Drs. Betsy M. Rice, Jesse Sabatini and Brad Forch (ARL, Aberdeen, Proving Ground, MD) for many inspired discussions. The authors greatly acknowledge Dr. Wagner from Nitrochemie Aschau GmbH for providing nitrocellulose for the experiments and Dr. Jesse J. Sabatini from ARL for many inspiring discussions and support. The Erasmus plus program and DAAD (German academic exchange service) is gratefully acknowledged for the scholarship (D. Juknelevicius).

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Received: ((will be filled in by the editorial staff))  
Revised: ((will be filled in by the editorial staff))  
Published online: ((will be filled in by the editorial staff))

## Appendix

Summary of all experimental formulations. Ratios are given in weight %. Combustion: X – does not sustain combustion; D – sustains combustion, but with difficulties, sometimes extinguishes; S – sustains combustion. Strobe frequency (relative): L – low; M – medium; H – high; C – constant burning formulation (non-strobing). Other: A – acoustic strobe (exceptionally loud combustion), „~“ – Similar to (certain formulation stated before).

	K4	K5	K6	K7	K8	K9	K10	K11	K12	K13	K14	K15	K16	K17	K18
AP	55	25	55	55	55	60	60	55	55	55	65	55	60	60	60
GN		55													
TMAN	30			30	20			23	15	8	35				
Hexamine			30					8	15	23		30	25	23	21
Cu (electrolytic powder)	15	8	15	10	15		15	15	15	15			15	15	15
CuO		5													
PVC		8													
Mg (80 mesh, spherical)				5		25	10								
Mg (200 mesh, spherical)												15		2	4
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>					10	15									
K <sub>2</sub> SO <sub>4</sub>							15								
Comments	S,M,A	S,C	X	N	S,H	S,H	N	~K4	D, M	X	X	D, L	X	S, C	S, C

	K19	K20	K20'	K21	K22	K22'	K23	K24	K25	K26	K27	K28	K29	K30	K31
AP	55	55	55	50	65	65	55	55	55	55	55	55	65	85	75
TMAN	7						30	30	30	15	15	15	15		10
Hexamine	23	30	30	30	35	35				15	15	15			
Cu (electrolytic powder)	15	15	15				10	5		10	5		20	15	15
CuO							5	10	15	5	10	15			
Mg (200 mesh, spherical)				15											
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	5	5		5	5										
Bi <sub>2</sub> O <sub>3</sub>			5			5									
Comments	N	S,C	S,C	S,C	X	X	D, M	D, M	D, M	S,C	S,C	N	N	S,C	S,H

	K32	K33/K4	K34	K35	K36	K37	K38	K39	K40	K41	K42	K43	K44	K45	K46
AP	65	55	45	35	55	55	55	55	85	75	65	55	45	35	55
TMAN	20	30	40	50						10	20	30	40	50	
Hexamine					30	30	30	30							30
Cu (electrolytic powder)	15	15	15	15	15	15	15	15	8	8	8	7.5	8	8	15
CuO									8	8	8	7.5	8	8	
Sulfur				5											
NC					5										
Red gum						5									
Lactose							5								
Dextrin															5
Comments	S, H	S,M,A	S,M	S,C	D, M	S,C	S,C	D, M	S,C	S,C	S, H	S,M,A	S,M	S,C	X

	K47	K48	K49	K50	K51	K52	K53	K54	K55	K56	K57	K58	K66	K67	K68
AP	55	55	55	55	55	55	55	50	45	40	50	45	55	55	40
TMAN				25	25	25		20	10		30	30	30	30	
Hexamine	30	20	20												
Cu (electrolytic powder)	15	15	15	8	8	8	15	8	8	8	8	7.5			
CuO				8	8	8		8	8	8	8	7.5	8		15
PVC	5														
Sulfur		10		5											
Lactose			10		5										
Dextrin						5									
TMAP							30				5	10			
Guandinium nitrate								15	30	45					
Copper (II) benzoate													8	15	
Nitroguanidin															45
Constant	X	S,C	~K6	S,H	S,H	X	S, H	S,H	S,C	X	S,H	S,C	S, M	S,C	N



	K69	K70	K71/ K25	K72	K73	K74	K75	K76	K77	K78	K79	K80	K81	K82	K83
AP	35	35	55	55	55	55	40	40	40	50	45	40	55	40	55
TMAN			30	30	30	30				30	30	30			30
Hexamine															30
Cu (electrolytic powder)	15	15					15			8	8	7.5			
CuO			15	10	5			15		8	8	7.5			
GN	45	45					45	45	45						45
Sulfur	5														
Lactose		5													
Copper (II) benzoate				5	10	15			15						15
NH <sub>4</sub> Cl										5	10	15			
CuCl															15 15
Comments	S,C	S,H	D,M	D,M	S,M	S,M	X	X,M	X,M	S,H	S,C	S,C	X	S,H	S,C

	K84	K85	K86	K87	K88	K89	K90	K91	K92	K93	K94/ K25	K95	K96	K97	K98
AP	45	22	20	50	55	55	40	40	62	58	55	52	49	55	65
TMAN				30	25	25		25	34	32	30	28	27	30	35
Hexamine															
Cu (electrolytic powder)		17	15												
CuO				15	15	15	15	10	5	10	15	20	25		
GN		47	60				35								
Sulfur		14													
Lactose	15														
Copper (II) benzoate								5							
NH <sub>4</sub> Cl	40														
PVC			5	5											
Mg (80 mesh, spherical)					5		10	5							
MgAl (40-80 mesh)						5									
Basic copper carbonate															15
Comments	X	D, L	S,C	S,C	S,C	S,C	S,C	S,C	X,L	D,M	D,M	X	X	S,M	X

	K99	K100	K101	K102	K103	K104	K105	K106	K107	K108	K109	K110	K111	K112
AP	55	45	35	55	45	35	55	55	55	55	10	20	30	40
TMAN							30	30	30	30				
Hexamine														
Cu (electrolytic powder)											23	20	18	15
CuO	15	15	15	15	15	15	15	15	15	15				
GN											45	40	35	30
Sulfur							2				23	20	18	15
Lactose								2						
Phenolic resin									2					
NC										2				
EDN	30	40	50											
TMEDN				30	40	50								
Comments	S,C	S,C	S,C	S,C	S,C	X	S,M	S,M	S,C	S,M	X,C	D,M	D,M	N

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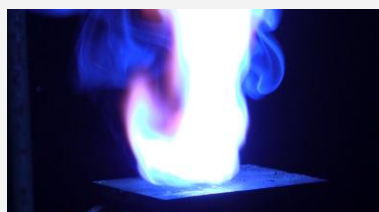
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### Study of ammonium perchlorate and tetramethylammonium nitrate based pyrotechnic blue strobe compositions

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*Dominykas Juknelevicius, Alicia Dufter, Magdalena Rusan, Thomas M. Klapötke, Arunas Ramanavicius, \** ..... Page – Page

### Study of ammonium perchlorate and tetramethylammonium nitrate based pyrotechnic blue strobe compositions



### Study of ammonium perchlorate and tetramethylammonium nitrate based pyrotechnic blue strobe compositions:

Pyrotechnic stobes, both colorless and colorful, are compositions that burn in an oscillatory behavior. They are used in military illumination devices and in fireworks as one of the most attractive pyrotechnic effects. Most colored stobes contain magnesium (Mg) or magnesium-aluminum (MgAl) alloy as a fuel. However this is an issue for blue stobes since the choice of stable blue flame emitters is extremely limited. In fact, copper halides have been observed to produce blue emissions in pyrotechnic flame exclusively at temperatures ranging from 1200-1500 °C. At higher temperatures the emitter is destroyed, or more specifically, a preferred trimer  $\text{Cu}_3\text{Cl}_3$  species are converted into monomers. As a result, the flame color fades and whitish-blue flame is observed. Therefore it was interesting to see whether blue pyrotechnic stobes 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 Jennings-White's blue strobe No. 5 (55% AP, 30% TMAN and 15% copper) is considered the top of the line formulation, which is described to be capable of producing a deep color blue strobe. However, its mechanism is not well understood and the formulation is not chemically compatible. This paper presents a research focused on improving the latter blue strobe formulation by Jennings-White.

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