New Trends in Sustainable Light- and Smoke-Generating Pyrotechnics

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für meine Eltern
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&

für meine liebste Oma
Hildegard Schlander
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Part I.

Introduction

1. Pyrotechnics

Colorful effects, crackling sounds, loud noises as well as the typical smell of new year's eve; these impressions are all associated with the popular field of pyrotechnics. Although pyrotechnic mixtures have been known since the early 11th century, they are still a very controversial topic in society.[1] On the one hand, they spread astonishment and joy during festive occasions; on the other hand, they pose an acute threat to environment and human's health.[2–4] Nevertheless, people are still fascinated by pyrotechnic effects, since they are designed to display bright light, loud sound, heat or colorful smoke.[5]

Figure 1.1: Firework display.

Pyrotechnic effects are not caused by a single molecule, rather a suitable ratio of various ingredients is crucial. A typical formulation consists of an oxidizer, reducing agent / fuel and other additives, which are mixed to a homogeneous powder.[2,6] Although pyrotechnics have been studied for centuries, there is still a lot of research potential: some of the applied chemicals are no longer state-of-the-art. Legal restrictions to limit the application of harmful compounds are one of the main reasons to rethink traditional compositions.[3,7,8] In order to meet today's awareness for safer, environmentally and health-friendly chemistry, a complete reformulation with harmless molecules is essential.[3] However, the expected color, burning behavior as well as other specific properties should be the same or even surpass the traditional ones. Pyrotechnics are entirely known to the general public as fireworks, though, application and research efforts are predominantly driven from military interest.[6,9–11]

1.1. Light-Generating Pyrotechnics

Light-generating pyrotechnics are applied exclusively at night, due to their ability to emit brightly colored flames. Even though this subclass is particularly popular as firework displays, the military remains the largest consumer. Here, they are not only used for illumination, but also for communication and signaling.[12,13] Unfortunately, the number of elements and compounds to create a colored flame is very limited.[5,14] To name a few examples, sodium is the ideal candidate for an intense yellow flame, while strontium results in deep crimson red.[6,15] Historically, green light was generated by barium salts and a chlorine source. Due to environmental issues, nowadays boron compounds are preferred.[16,17]

The reason for colored light is a basic physical process: By absorbing thermal energy, the metals' outer electrons can be excited to a higher energy level. Since the excited state is meta stable, the electrons quickly return to their ground state. During relaxation, the previously absorbed energy is emitted as visible light.[19] The difference between these two energy levels is characteristic and corresponds to the emitted spectral color.[1,2] For the exitation of the outer electron, heat from the ongoing reaction is necessary. Temperatures up to 3000 °C can be reached by using organic fuels, chlorates or perchlorates in combination with metal powders.[6,13]

Figure 1.2: Firework colors.[18]

The combustion of metal powders like magnesium or magnalium not only leads to very high temperatures, but also goes along with high intensities. At night, this guarantees perfect visibility and brightness. There are two other factors to characterize a light-generating formulation: First, spectral purity. The spectral purity is a measure to quantify the monochromaticity of a light sample.[20] However, light is almost never purely monochromatic. In truth, light-generating pyrotechnics comprise more complex emission spectra, with varying intensities over many different frequencies. In color science, the dominant wavelength is a way of describing non-spectral light mixtures in terms of the spectral light that evokes an identical perception of hue.[21] It is therefore closely related to the spectral purity; they are usually depicted in a so-called CIE chromaticity diagram for representation.[22,23] Different flame effects, color impressions or burning properties can be enabled by a well-balanced pyrotechnic composition. Therefore, there is an enormous potential of variation possibilities. For example, a constant burning flame with high color purity and intensity is called *flare*, whereas compositions that show an oscillatory combustion are referred to as *strobes*.[24–26]

Flares

For military research on hand-held signal flares, the focus is on the colors yellow, red and green. In the civil sector there is an additional blue formulation available.[3,4,6,27] Typical emitters are atomic sodium for yellow, strontium (I) chloride for red, barium (I) chloride for green or copper (I) chloride for blue.[15] Consequently, to obtain a saturated red, green or blue flame color, a chlorine source is mandatory. The classic composition is a colorant together with potassium perchlorate, polyvinyl chloride and a metal fuel; additional additives are adapted to the respective color.[1,5] Although this results in high-performing signal flares, they cause also environmental pollution and pose health risks. For this reason, research efforts have nowadays been made to particularly eliminate heavy metals and chlorine species.[3,4,27]

The perchlorate anion causes both soil and groundwater contamination, since it is highly persistent.[28,29] In the human body, perchlorates inhibit the iodine uptake and thus, the thyroid metabolism.[8,30] In addition, toxic and carcinogenic biphenyls, polychlorinated dibenzo-*p*-dioxins and dibenzofurans are formed during the combustion of perchlorate or polyvinyl chloride and organic materials.[31] Modern approaches avoid chlorine species by using nitrogen-rich compounds instead.[3,4,27] The research of Sabatini *et al.* on chlorine-free flares has shown, that an intense and saturated red flame can also be attributed to strontium (I) hydroxide and concomitant strontium (I) hydride emissions. In detail, the addition of 5-amino-1H-tetrazole or hexamine has a deoxidizing effect on the combustion flame, suppressing the formation of unwanted red-orange-emitting strontium (II) oxide, while promoting desirable strontium (I) hydroxide.[32,33]

Figure 1.3: Red hand-held signal flare. © Marcel Holler.

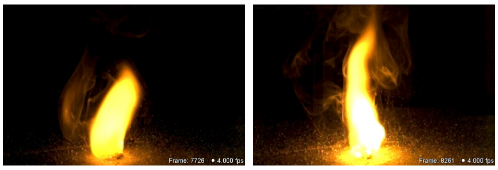
But strontium itself is also part of the problem: Due to its similarity to calcium, Sr^{2+} is able to substitute Ca^{2+} in the bones; the impact is the worst for children and adolescents.[34] The strontium concentrations in drinking water are correspondingly high, especially in areas with exhaustive pyrotechnic use.[35] In 2017, for the very first time strontium could be replaced by a nitrogen-rich lithium salt.[36] Previously, lithium was expected to be unsuitable as red colorant, since it suffers from hygroscopicity.

One of the most challenging tasks is blue light.[37] Until today, there is no sufficient alternative to copper-containing compounds and the associated emitter copper (I) chloride. In common firework displays also copper-arsenic salts are widely spread.[4,27,38,39] It is almost impossible to prevent the use of potassium perchlorate and polyvinyl chloride. To overcome this issue, recent results suggested other copper (I) halides CuX (X = Br, I) as blue light-emitting species.[38,40–42] From a toxicity point of view, especially the formulations based on copper (I) iodide are more advantageous. Potentially formed polyiodinated biphenyls are not believed to be harmful as they are applied in medicine.[43–46]

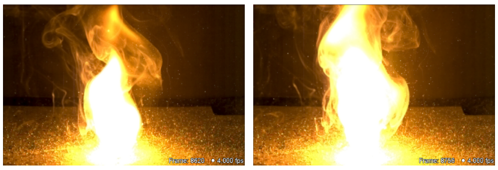
Strobes

In 1898, strobes were discovered coincidentally by the company Brocks Fireworks Ltd.[47] Up to now, the development of strobe systems heavily relies on trial and error methods as the underlying mechanism remains unclear.[26] Furthermore, they respond sensitively to preparational control parameters, so that for example, different grain sizes can make the difference between a flare or strobe system.[25]

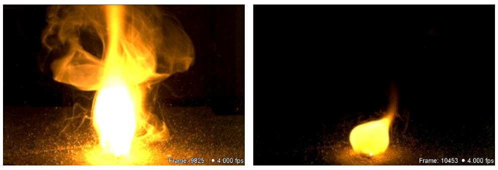
The mechanism behind these oscillating systems is not been completely understood yet. Since 1982, the hypothesis of Shimizu, which in turn is based on the work of Krone and Wasmann, is used to explain this phenomenon.[48–50] It states that the oscillatory combustion consists of a dark phase and a flash phase which alternates periodically. The trigger factor for the occurrence of a flash is the reaction temperature. At the beginning, the strobe mixture is ignited at the surface and the first dark phase starts. During the dark phase, the temperature is not uniformly distributed over the surface. For this reason, small hot spots appear on the top layer, which grow gradually as the temperature increases. Once the maximum has been reached, the flash phase is initialized. This leads to spontaneous ignition of the top layer causing a bright light flash. Since the subjacent layers have not reached the ignition temperature yet, the system returns to the dark phase again.[1,24–26,51]



(a) Dark phase. **(b)** Small hot spots.



(c) Large hot spots. **(d)** Flash phase.



(e) After flash. **(f)** Dark phase.

Figure 1.4: Oscillatory combustion of strobe formulations.[52]

The main parameter to characterize a strobe formulation is the frequency. More precisely, it should be possible to separate the produced flashes from each other while at the same time, the elapsed time between these flashes should be constant. It follows that the frequency need to be lower than 25 Hz in order to be perceived as an oscillating flame by the human eye.[24] Until now, a prediction of obtained frequency is not possible; however, there are some reliable methods for optimizing it: Most strobe formulations contain a metal powder like magnesium. It was observed that increasing the available surface area of the metal may also increases the frequency. As a consequence, the amount of metal as well as its particle grain size must be varied.[1,25] Furthermore, the frequency can be controlled by using toxicological questionable potassium dichromate as a stabilizer. The addition leads to a more homogeneous combustion.[25,26,53]

1.2. Smoke-Generating Pyrotechnics

In contrast to light-generating pyrotechnics, the benefits of smoke become visible during daytime. Obviously, on contrasting terrain backgrounds they serve higher visibility over greater distances.[54] In the past, smokes were applied exclusively by the military for signaling, communication as well as obscurant. Research efforts are only driven from military interest with the focus on white, red, violet, yellow and green smoke.[55,56] But today, smoke-generating pyrotechnics are increasingly known and accessible to a much broader group due to their application as colorful daylight firework or color effect during photo shootings.[57,58]

Figure 1.5: Daylight firework display. © Michael Plachetka (Feuerwerk-Fanpage.de).

White Smoke

White smoke-producing formulations are perfectly suited for self-protection as obscuration tool. Thus, a persistent and thick white aerosol cloud is brought into the line of sight between a target and an observer, which could be useful for troops to withdraw or regroup.[6] In the past, white smoke was produced by the AN-M8 hexachloroethane (HC) smoke grenade due to its outstanding efficiency. The typical HC mixture consisted only of aluminum, zinc oxide and HC, which forms hygroscopic zinc (II) chloride during combustion. $ZnCl_2$ rapidly undergoes further reactions with moisture from the air to give an immense dense smoke cloud.[3,5,6,59] However, Shinn indicated this kind of smoke as health and environmental disaster.[60] During combustion, chlorinated compounds such as CCl_4, C_2Cl_4, C_6Cl_6 may arise, which are known to be toxic and carcinogenic.[5,61]

Figure 1.6: Obscurant scenario.

Alternatively, white smoke can also be generated from white or red phosphorus.[62] The emerging aerosol also benefits from hygroscopicity; nonetheless, phosphorus compounds are also harmful as they are known for unpredictable spontaneous reactions.[6,63,64] White phosphorus itself is toxic and an incendiary, while red phosphorus suffers from hydrolysis. During combustion highly toxic phosphane or erosive phosphoric acid is formed.[63–66] Due to its calcium affinity, repeated exposure with phosphoric acid leads to tooth damage and bone loss.[62]

For this reason, smoke signals based on terephthalic acid (TA) are nowadays considered as less toxic and environmentally benign alternative.[6] However, the way of producing aerosol is completely different to hygroscopic ones: White smoke is also obtained by a straightforward sublimation-recondensation mechanism.[5,59,67] This kind of smoke composition usually consists of an organic dye, oxidizer, fuel and a coolant for temperature control.[68] The redox reaction of oxidizer and fuel provides the energy for dye sublimation, while the coolant ensures low combustion temperatures.[5,6,67] Otherwise, the dye would get destroyed rather than get sublimed.[1] The recondensed dye particles are finally dispersed by the gaseous combustion products.[67] It is mandatory to distinguish between hygroscopic and non-hygroscopic smoke generation, since it drastically affects the occurring smoke properties.[65,69–71] For this reason, the TA-based smoke will never be able to compete with the HC-based smoke in terms of thickness, smoke volume or optical properties, since it does not benefit from humidity.[3,5,6]

Colored Smoke

Especially colored smoke became very famous during the last few years, since it offers colorful effects during daytime.[57,58] However, research efforts are only of military interest. In this context the different colors are used for communication; for example, violet smoke is associated with medical evacuation.[6,9,10] The smoke generation is similar to non-hygroscopic TA-based formulations following a sublimation-recondensation process. Historically, a mixture of sulfur and potassium chlorate was applied for dye sublimation.[55,72] However, during combustion hazardous SO_2 is released perceiving a burning sensation in the lungs.[3] For this reason, today more environmentally benign formulations are based on sugar such as sucrose or lactose.[68,73]

Figure 1.7: Red smoke signal.

Although sulfur has already been successfully replaced, potassium chlorate remains the oxidizing agent of choice. It ensures the optimal temperature range for dye sublimation in smokes.[5,14,68] Potassium chlorate is highly reactive and tends to accidental reactions.[12,74,75] Especially the combustion products of chlorates and organic compounds are an underestimated risk, since – analogous to perchlorates – also toxic and carcinogenic chlorinated organic compounds can be formed.[8,30,31,45,76] Further, the chlorate anion is highly persistent and soluble in water causing problems to aquatic life as it is toxic.[77] Due to a lack of suitable alternative, potassium chlorate and its drawbacks has to be accepted by the energetic community until today.

There are several properties that should be taken into account when developing a smoke signal. One of the most important characteristics is the color impression.[11,19] Due to their use as reliable communication tool, the color must be clearly assignable.[6] Further, especially for white smoke optical properties should be considered to ensure the obscuration ability.[65] Regarding burning behavior, the duration of smoke generation as well as the time it takes for the aerosol to sedimentate are interesting.[5,55,56] To date, there exists only a limited number of literature on smoke-producing pyrotechnics. Characterizing smoke quality is therefore a relatively new area.[65,71,78] In detail, the produced particles during combustion are summarized as yield factor. However, this aerosol not only consists of dye but also other solid combustion products might be occurred.[6,9,10] In order to evaluate the efficiency, an HPLC analysis is mandatory to quantify the exact amount of dye present in the aerosol.[71,78] Therefore, the resulting transfer rate is a measure for effectiveness of smoke mixtures to be able to disperse the dye rather than to combust it.[71,78] A high dye content is desirable in order to guarantee a saturated bright color impression.

1.3. References

[1] K. Kosanke, B. Kosanke, B. Sturman, T. Shimizu, M. Wilson, I. Maltitz, R. Hancox, N. Kubota, C. Jennings-White, D. Chapman, D. Dillehay, T. Smith, M. Podlesak, *Pyrotechnic Chemistry*, Journal of Pyrotechnics Inc., UK, **2004**.

[2] F. Keller, *Chem. Unserer Zeit* **2012**, *46*, 248–265.

[3] J. Sabatini in *Advances Toward the Development of "Green" Pyrotechnics*, *Green Energetic Materials*, John Wiley & Sons Ltd, Inc., West Sussex, UK, **2014**.

[4] G. Steinhauser, T. Klapötke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3330–3347.

[5] J. Conkling, C. Mocella, *Chemistry of Pyrotechnics: Basic Principles and Theory*, CRC Press, Boca Raton, **2010**.

[6] T. Klapötke, *Chemistry of High-Energy Materials*, Boston: De Gruyter, Berlin, **2017**.

[7] European Chemicals Agency, `https://echa.europa.eu/de/home` (visited on May 27, 2020).

[8] Environmental Protection Agency, Contaminant Candidate List 3, `https://www.epa.gov/ccl/contaminant-candidate-list-3-ccl-3` (visited on July 1, 2019).

[9] C. Sterling, *Military Communications: From Ancient Times to the 21st Century*, ABC-CLIO, Santa Barbara, CA, USA, **2008**.

[10] H. Webster in *Inorganic red smoke compositions*, *Proceedings of the 8th International Pyrotechnics Seminar*, IPS, Steamboat Springs, CO, USA, **1982**.

[11] U. S. Army Material Command, *Engineering Design Handbook: Theory and Application*, Military Pyrotechnics Series, Part One, Washington, DC, USA, **1967**.

[12] H. Ellern, *Military and civilian pyrotechnics*, Chemical Pub. Co, New York City, NY, USA, **1968**.

[13] J. Akhavan, *The Chemistry of Explosives*, Royal Society of Chemistry, Cambridge, UK, **2011**.

[14] T. Shimizu, *Fireworks: The Art, Science, and Technique*, Pyrotechnica Publications, Austin, Texas, USA, **1996**.

[15] H. Webster, *Alkali Metal Emitters, 1. Analysis of Visible Spectra*, Naval Weapons Support Center, Indiana, USA, **1975**.

[16] T. Klapötke, M. Rusan, V. Sproll, *Z. Anorg. Allg. Chem.* **2014**, *640*, 1892–1899.

[17] J. Poret, J. Sabatini, *J. Energ. Mater.* **2013**, *31*, 27–34.

[18] What's happening inside those Fireworks, `http://www.worldsciencefestival.com/infographics/boom-science-behind-fourth-july-fireworks/` (visited on April 30, 2020).

[19] T. Shimizu, *Fireworks from a physical standpoint*, Pyrotechnica Publications, Austin, TX, USA, **1981**.

[20] R. Kingslake, *Applied Optics and Optical Engineering*, Academic Press, Rochester, NY, USA, **1980**.

[21] J. Guild, J. Petavel, *Phil. Trans.* **1931**, *230*, 149–187.

[22] L. Troland, *J. Opt. Soc. Am.* **1922**, *6*, 527–596.

[23] L. Jones, *J. Opt. Soc. Am.* **1943**, *33*, 534–543.

[24] J. Corbel, J. Lingen, J. Zevenbergen, O. Gijzeman, A. Meijerink, *J. Phys. Chem. B* **2012**, *116*, 4967–4975.

[25] J. Corbel, J. van Lingen, J. Zevenbergen, O. Gijzeman, A. Meijerink, *Propellants Explos. Pyrotech.* **2013**, *38*, 634–643.

[26] J. Corbel, J. van Lingen, J. Zevenbergen, O. Gijzeman, A. Meijerink, *Angew. Chem. Int. Ed.* **2013**, *52*, 290–303.

[27] G. Steinhauser, T. Klapötke, *Angew. Chem.* **2008**, *120*, 3376–3394.

[28] R. Srinivasan, G. Sorial, *Sep. Purif. Technol.* **2009**, *69*, 7–21.

[29] R. Gullick, M. Lechevallier, T. Barhorst, *J. Am. Water Works Assn.* **2001**, *93*, 66–77.

[30] P. Brandhuber, S. Clark, K. Morley, *J. Am. Water Works Assn.* **2009**, *101*, 63–73.

[31] P. Dyke, P. Coleman, *Organohalogen Compd.* **1995**, *24*, 213–216.

[32] J. Sabatini, E. Koch, J. Poret, J. Moretti, S. Harbol, *Angew. Chem. Int. Ed.* **2015**, *54*, 10968–10970.

[33] J. Sabatini, E. Koch, J. Poret, J. Moretti, S. Harbol, *Angew. Chem* **2015**, *127*, 11118–11120.

[34] S. Nielsen, *Bone* **2004**, *35*, 583–588.

[35] A. O'Donnell, D. Lytle, S. Harmon, K. Vu, H. Chait, D. Dionysiou, *Water Res.* **2016**, *103*, 319–333.

[36] J. Glück, T. Klapötke, M. Rusan, J. Sabatini, J. Stierstorfer, *Angew. Chem. Int. Ed.* **2017**, *56*, 16507–16509.

[37] A. Contini, *J. Pyrotech.* **2010**, 3–11.

[38] B. Douda, *Theory of Colored Flame Production*, Naval Sea Systems Command Crane, ADA951815, Crane, IN, USA, **1964**.

[39] B. Sturman, *Propellants Explos. Pyrotech.* **2006**, *31*, 70–74.

[40] E. Koch, *Propellants Explos. Pyrotech.* **2015**, *40*, 799–802.

[41] D. Juknelevicius, E. Karvinen, T. Klapötke, R. Kubilius, A. Ramanavicius, M. Rusan, *Chem. Eur. J.* **2015**, *21*, 15354–15359.

[42] T. Klapötke, M. Rusan, J. Sabatini, *Angew. Chem. Int. Ed.* **2014**, *53*, 9665–9668.

[43] K. Thomson, D. Varma, *Aust. Prescr.* **2010**, *33*, 35–37.

[44] W. Christmann, D. Kasiske, K. Klöppel, H. Partscht, W. Rotard, *Chemosphere* **1989**, *19*, 387–392.

[45] O. Fleischer, H. Wichmann, W. Lorenz, *Chemosphere* **1999**, *39*, 925–932.

[46] Agency for Toxic Substances and Disease Registry, *Toxicological profile for Polybrominated Biphenyls and Polybrominated Diphenyl Ethers*, Department of Health and Human Services, Public Health Service, Atlanta, GA, USA, **2004**.

[47] A. Brock, *Pyrotechnics: The History and Art of Fireworks Making*, Daniel O'Connor, London, UK, **1922**.

[48] U. Krone, *Pyrotechnical Mixtures: For Intermittent Emission of Light*, DE 2164437, **1973**.

[49] U. Krone in *A Non-toxic Pyrotechnic Screening Smoke for Training Purposes*, *Proceedings of the 15th International Pyrotechnics Seminar*, IPS, Boulder, CO, USA, **1990**.

[50] F. Wasman in *The Phenomen of Pulsating Burning in Pyrotechnics*, *Proceedings of the 5th International Pyrotechnics Seminar*, IPS, Vail, CO, USA, **1976**.

[51] T. Shimizu, *Studies in Strobe Light Pyrotechnic Compositions*, Pyrotechnica III, **1982**.

[52] J. Glück, T. Klapötke, T. Küblböck, *ACS Sustainable Chem. Eng.* **2018**, *6*, 4400–4404.

[53] A. Davies, J. Goddard, M. Hursthouse, N. Walker, *Dalton Trans.* **1986**, 1873–1877.

[54] Headquarters, *Field Manual 21-60, Visual Signals*, Department of the Army, US Government Printing Office, Washington, DC, USA, **1987**.

[55] Subcommittee on Military Smokes and Obscurants, National Research Council, *Toxicity of Military Smokes and Obscurants, Volume 3*, The National Academies Press, Washington, DC, USA, **1999**.

[56] *Engineering Design Handbook: Design of Ammunition for Pyrotechnic Effects*, Military Pyrotechnics Series, Part Four, Washington, DC, USA, **1974**.

[57] Everything You Need To Know About Smoke Photography, `https://www.format.com/magazine/resources/photography/smoke-bomb-photography-guide` (visited on March 13, 2020).

[58] UK Firework Review, `http://www.firework-review.org.uk/daytime-fireworks/` (visited on January 22, 2018).

[59] W. Muse, J. Anthony, J. Bergmann, D. Burnett, C. Crouse, B. Gaviola, S. Thomson, *Drug Chem. Toxicol.* **1997**, *20*, 293–302.

[60] J. Shinn, *Smokes and Obscurants: A Guidebook of Environmental Assessment. Volume I. Method of Assessment and Appended Data*, DTIC Report, Acc. Num. ADA203810, **1987**.

[61] J. Eaton, R. Lopinto, W. Palmer, *Health Effects of Hexachloroethane (HC) Smoke*, DTIC Report, Acc. Num. ADA277838, **1994**.

[62] E. Koch, *Propellants Explos. Pyrotech.* **2008**, *33*, 165–176.

[63] E. Koch, S. Cudziło, *Angew. Chem. Int. Ed.* **2016**, *55*, 15439–15442.

[64] A. Shaw, J. Poret, R. Gilbert, J. Moretti, J. Sabatini, K. Oyler, G. Chen in *Pyrotechnic Smoke Compositions Containing Boron Carbide*, *Proceedings of the 38th International Pyrotechnics Seminar*, IPS, Denver, CO, USA, **2012**.

[65] J. Glück, T. Klapötke, A. Shaw, *Cent. Eur. J. Energ. Mater.* **2017**, *14*, 489–500.

[66] M. Hemmilä, M. Hihkio, J. Kasanen, M. Turunen, M. Jarvela, S. Suhonen, A. Pasanen, H. Norppa, *Mutat. Res. Genet. Toxicol. Environ. Mutagen.* **2010**, *701*, 137–144.

[67] S. Kaye, *Encyclopaedia of Explosives and Related Items*, US Army Armament Research and Development Command, Large Calibre Weapon Systems Laboratory, Dover, NJ, USA, **1978**.

[68] A. Eslami, S. Hosseini, *J. Therm. Anal. Calorim.* **2010**, *104*, 671–678.

[69] G. Lane, W. Smith, E. Jankowiak in *Novel Pyrotechnic Compositions for Screening Smoke*, *Proceedings of the 1st International Pyrotechnics Seminar*, IPS, Estes Park, CO, USA, **1968**.

[70] N. Sordoni, W. Heard, W. Rouse, *Pyrotechnical Smoke Analysis Volume 1*, Defense Technical Information Center, Fort Belvoir, VA, USA, **1993**.

[71] J. Glück, T. Klapötke, M. Rusan, A. Shaw, *Propellants Explos. Pyrotech.* **2017**, *42*, 131–141.

[72] D. Lundy, J. Eaton, *Occupational Health Hazards Posed by Inventory US Army Smoke / Obscurant Munitions*, US Army Medical Research Detachment, Wright-Patterson Air Force Base, for Walter Reed Army Institute of Research, Washington, DC, USA, **1994**.

[73] C. Fish, G. Chen in *Characterization of Magnesium Carbonate for Use in Pyrotechnic Smoke Composition as a Thermal Regulator*, *Proceedings of the 35th International Pyrotechnics Seminar*, IPS, Fort Collins, CO, USA, **2008**.

[74] M. Russell, *The Chemistry of Fireworks*, The Royal Society of Chemistry, Cambridge, UK, **2009**.

[75] U. S. Army Material Command, *Engineering Design Handbook: Safety, Procedures and Glossary*, Military Pyrotechnics Series, Part Two, Washington, DC, USA, **1966**.

[76] L. Wackett, M. Sadowsky, L. Newman, H. Hur, S. Li, *Nature* **1994**, *368*, 627–629.

[77] IFA, *GESTIS – Substance Database*, Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung, Sankt Augustin, Germany, **2018**.

[78] J. Glück, T. Klapötke, T. Küblböck, *New J. Chem.* **2018**, *42*, 10670–10675.

2. Motivation

All over the world, occasions like new year's eve are unimaginable without firework displays. This not only shows how popular pyrotechnics are, but also how far-reaching the impact on our environment and health is. The energetic materials community is slowly coming around to the notion that environmental and health impact needs to be considered. Ignoring this reality has led to widespread contamination of soil and ground water. In today's society, there is a claim for contemporary sustainable and environmentally benign chemistry. However, until today research efforts are mainly driven from a military position with respect to efficiency and performance, whereby public requirements have only a subordinate role. To face this issues, so-called "future pyrotechnics" should combine acceptable properties, economical manufacturing processes as well as safe application.

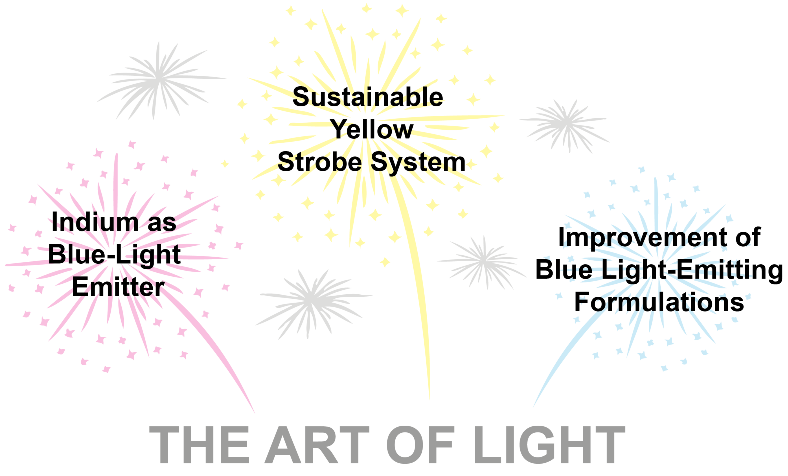
First, until today many mixtures are only applied as they are high-performing. In most cases, possible alternatives are insufficient and inefficient or there are even nonexistent. The performance should not suffer from state-of-the-art reformulations, since the intended application needs to be guaranteed. However, it might play a subordinate role to satisfy today's mindset for safety, environment and health. Second, in order to ensure economical manufacturing, the mixtures should be as simple as possible. Typical in-use formulations have to be optimized separately for each color or effect. For this reason, various different ingredients are required; the associated purchasing, storing and manufacturing is complex and expensive. Especially for producers and consumers, the availability and pricing of applied compounds is a central question. Therefore, a minimum of ingredients should be considered while maintaining consistent performance. This reduces not only the chemicals brought into circulation, but also the environmental pollution. Third, there are only few steps forward in pyrotechnics, even though it is present for centuries. It is essential to find modern approaches in the field of pyrotechnics in order to be able to substitute harmful compounds like halogens, heavy metals or questionable additives. It is mandatory to ensure safe handling and reduce exposure especially during the use by untrained people.

In the field of energetic materials, nitrogen-rich salts and compounds have prevailed in recent years. Because of the formation of mainly elemental nitrogen, their harmless combustion products are usually cool and inert. Through the use of nitrogen-rich compounds, great successes in modern pyrotechnics were achieved, such as halogen-free red light signals or more persistent white smoke clouds. However, it is ongoing research to find solutions for all requirements. To date, questionable compounds such as potassium chlorate have not been ruled out, not even through the use of nitrogen-rich compounds. Therefore, there are still numerous research opportunities and possibilities.

Part II.

Summary and Conclusion

3. Light-Generating Pyrotechnics



Sustainable Yellow Strobe System

The article "*Development of a Sustainable Perchlorate-Free Yellow Pyrotechnical Strobe Formulation*" discusses the investigation of an alternative yellow strobe system. Strobes are pyrotechnical mixtures, which periodically burn with alternating bright flashes and dark phases. Until today, the underlying mechanism remains unclear to the pyrotechnic society. In a typical in-use strobe formulation magnesium is coated with potassium dichromate to prevent a reaction with ammonium perchlorate. Further, potassium dichromate is expected to be a flash regulator. However, due to REACH and EPA dichromates are substances of very high concern as well as some perchlorates are kept under critical observation and therefore, should be avoided in modern pyrotechnics.

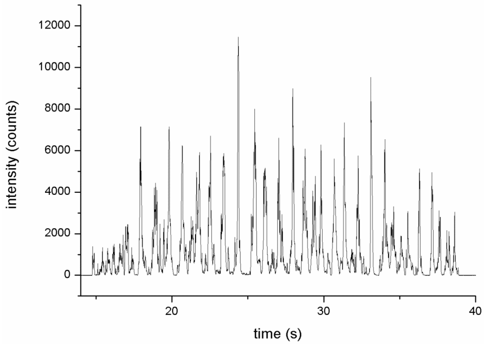


Figure 3.1: Frequency measurement of a sustainable yellow strobe system.

In order to meet today's awareness for sustainable pyrotechnics, these harmful compounds were excluded from reformulation. The authors applied sodium nitrate, magnesium, hexamine as well as an epoxy binder system or nitrocellulose. As a consequence, this strobe mixture was able to provide an alternating flash and dark phase with clear flash separation. The frequencies were in the range of 7–20 Hz and therefore, can be perceived by the eye. Moreover, the magnesium content affects both the burn time as well as the resulting frequency. Finally, the reformulation not only removed toxic chemicals, the desired strobe effect can also be achieved with less ingredients.

Indium as Blue Light Emitter

Since a saturated blue flame color is one of the most challenging task in pyrotechnics, in "*The Flame Emission of Indium from a Pyrotechnical View*" metallic indium was considered as alternative blue light emitter. From a commercial point of view, the blue light emitter of choice is copper (I) chloride, which is usually received during the combustion of copper compounds and perchlorates. However, due to toxicological and environmental issues the application of halogens and copper should be avoided.

Figure 3.2: Flame emission of indium.

Indium was supposed to be a halogen-free alternative to copper. However, indium would never be considered for mass production, since it is one of the most limited materials. For this reason, the flame emission was discussed from an academical point of view. Metallic indium was introduced as both colorant and fuel to a mixture of potassium / guanidine nitrate, magnesium, hexamine / 5-amino-1H-tetrazol and an epoxy binder system. The emission spectra of indium revealed the In_α and In_β bands at 410 nm and 451 nm. Unfortunately, only insufficient blue emission at the outer flame parts could be observed, while the main flame color was dominated by magenta and violet. It was concluded, that indium is unsuitable as blue emitter. Nevertheless, the emission spectra of indium was characterized for the first time.

Improvement of Blue Light-Emitting Formulations

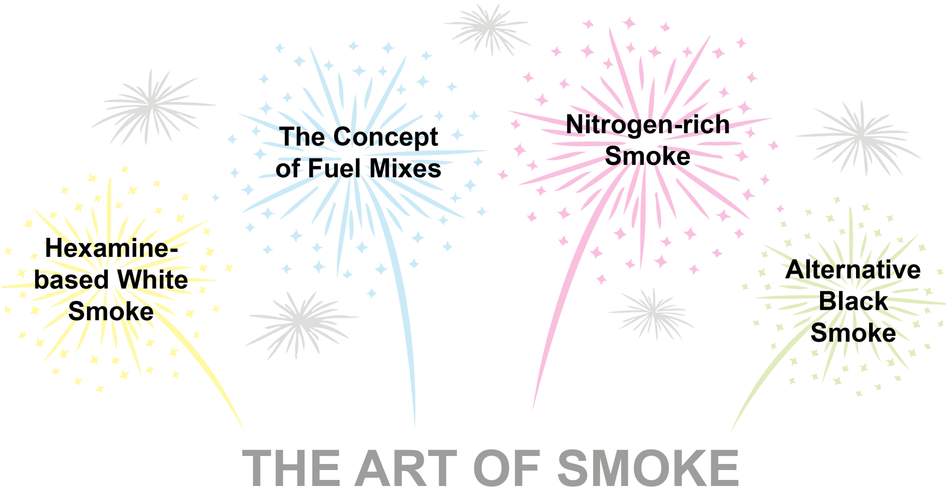
Since there is a lack of high-performing blue light-emitting species besides copper (I) chloride, the article "*Fine-Tuning: Advances in Chlorine-Free Blue-Light-Generating Pyrotechnics*" deals with further improvement of alternative copper (I) halides. Until today, halogens has to be accepted for blue light emission. Nevertheless, chlorine in combination with organic materials forms toxic and carcinogenic polychlorinated compounds. Modern approaches alternatively apply bromates or iodates to give copper (I) bromide or copper (I) iodide as blue emitter. The aim was to improve literature-known mixtures in terms of dominant wavelength and spectral purity to compete with copper (I) chloride.

Different strategies should lead to an improvement: First, the simultaneous use of copper (I) bromide or copper (I) iodide in the same mixtures was excluded from further investigation due to their high sensitivity. Next, a completely new approach is based on nitrogen-rich copper (I) complexes that combine colorant,

Figure 3.3: Blue light emission.

fuel and gas generator in one molecule. However, since the energetic properties of copper (I) complexes are often in a similar range to primary explosives, this strategy could not be pursued due to safety issues. Finally, the nitrogen-rich 1,2,4-triazole, 5-amino-1*H*-tetrazole and 3-nitro-1*H*-1,2,4-triazole were introduced to common copper bromate and copper iodate systems. While the copper iodate system suffered from stability problems, the performance of the copper bromate system could be significantly improved through the application of nitrogen-rich compounds.

4. Smoke-Generating Pyrotechnics



The Concept of Fuel Mixes

In the publication "*5-Amino-1H-Tetrazole-based Multi-coloured Smoke Signals Applying the Concept of Fuel Mixes*" the manufacturing process of colored smoke mixtures was simplified. Up to now, every single smoke dye needs its own optimized pyrotechnical formulation for sublimation and desired properties. Therefore, the manufacturing process of smoke signals is complex and expensive, since many different chemicals are required.

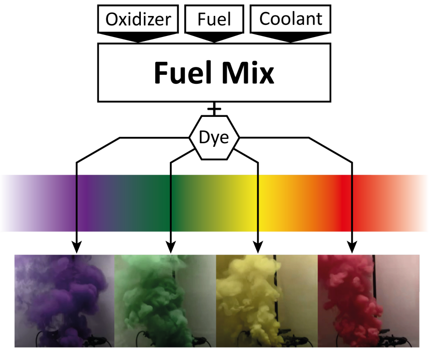


Figure 4.1: The concept of fuel mixes.

The concept of fuel mixes was developed to simplify manufacturing and to reduce the ingredients of colored smoke signals. First, all components such as oxidizing agent, fuel or coolant are pre-mixed to provide the so-called fuel mix. In a final step, the fuel mix is simply quick-mixed with a desired dye to obtain a multi-color approach for smoke signals. The great benefit for producers and consumers of having a certain number of different smoke formulations in stock is gone. Only the quick-mixing of only two powders (fuel mix + dye) is necessary to produce the desired smoke color with reliable smoke quality. Moreover, less energetic material needs to be stored in stock. As a consequence, required (safe) storage space is reduced, which is favored from a safety point of view. The application of nitrogen-rich 5-amino-1*H*-tetrazole-based fuel mixes also significantly improved the resulting smoke properties.

Hexamine-based White Smoke

The effect of hexamine as main fuel in non-hygroscopic white-smoking mixtures was examined in the cover story "*Combining Higher Efficiency with Lower Costs: an Alternative Hexamine-Based White Smoke Signal*". Until today, the efficiency of white smoke clouds is a challenging topic. Hygroscopic formulations benefit from atmospheric humidity, but are toxic and harmful. For this reason, non-hygroscopic less toxic alternatives based on sugar are applied nowadays, which are known to suffer from significantly low performance. Recent results revealed, that a more persistent and thick smoke cloud can be generated by using nitrogen-rich 5-amino-1*H*-tetrazole instead of sugar. However, hexamine can be favored from a cost point of view, since it is much cheaper than 5-amino-1*H*-tetrazole.

Hexamine was introduced to a simple four ingredients mixture in order to ensure economical manufacturing. As a result, higher decomposition temperatures were be observed, which further had a positive effect on the smokes' yield factor. It was possible to modify burning properties by varying the terephthalic acid content. In addition, in comparison to 5-amino-1*H*-tetrazole- and sugar-based formulations the application of hexamine resulted in superior obscuration properties. The occurring smoke cloud was more persistent to sedimentation. Finally, hexamine serves as low-cost alternative to 5-amino-1*H*-tetrazole that also lead to an improved smoke performance.

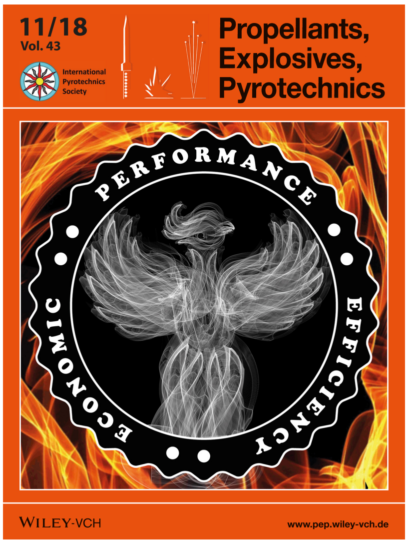


Figure 4.2: Cover picture: hexamine-based white smoke.

Alternative Black Smoke

The conference article "*Green is the new Black: An Environmentally Benign Black Smoke Fulfilling the Concept of Fuel Mixes*" provides an alternative method of black smoke generation. Black smoke is exclusively applied for training purposes in the Battlefield Simulator to indicate that a target has successfully been disabled or killed. Therefore, there is only subordinate research interest. A conventional mixture consists of naphthalene, potassium chlorate and a Laminac / Lupersol binder system. However, the components as well as their resulting combustion products are known to be harmful, toxic or carcinogenic. In order to reduce exposure during training, an alternative way of generating black smoke was developed.

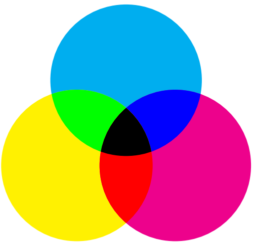


Figure 4.3: Subtractive color model.

In analogy to colored smoke, the black color impression was created by subtractive color mixing instead of burning naphthalene. In detail, a combination of green and red dye (2:1) is sufficient to give a black color. Black smoke can not only be produced in the same way as other colored smoke signals, it is also much healthier and more environmentally friendly.

Halogen-free Nitrogen-rich Smoke

Potassium chlorate seems to be the only oxidizing agent that provides the ideal temperature range for dye sublimation. However, several risks for health and environment arise from chlorates and their combustion products. The communication "*Guanidinium 5,5'-Azotetrazolate: A Colorful Chameleon for Halogen-free Smoke Signals*" presents an inventive method for modern halogen-free smoke generation.

The nitrogen-rich salt guanidinium 5,5'-azotetrazolate was mixed with organic dyes in order to provide a multi-color two-component system. Due to its desirable low combustion temperature, guanidinium 5,5'-azotetrazolate is able to sublimate the organic dye. In addition, the release of a large gas volume can disperse the emerging smoke dye particles. As a result, a dense and thick colored smoke cloud can be produced without any need of hazardous potassium chlorate. In comparison to chlorate-based formulations similar yield factors were be observed. However, only the transfer rates were slightly lower. The non-sensitive properties of guanidinium 5,5'-azotetrazolate smoke mixtures are advantageous as they are particularly safe to use. For the first time, halogens were completely avoided in smoke generation. These nitrogen-rich smoke signals not only open a completely new research topic, but it is also one breakthrough in environmentally benign pyrotechnics.

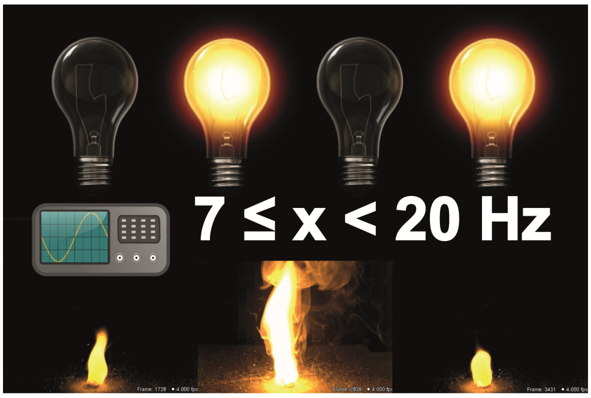
Figure 4.4: Guanidinium 5,5'-azotetrazolate as white smoke generator.

Part III.

Results and Discussion: Light-Generating Pyrotechnics

Development of a Sustainable Perchlorate-Free Yellow Pyrotechnical Strobe Formulation

by
Johann Glück, Thomas M. Klapötke and Teresa Küblböck



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Abstract Novel yellow-light-emitting pyrotechnical strobe formulations absent of any chlorine sources were developed. The five yellow strobe formulations cover a frequency range of 7 Hz $<$ x $<$ 20 Hz and do not use potassium dichromate, which is frequently applied as a stabilizer. Frequency measurements and a comparison to a literature-known state-of-the-art red reference strobe formulation revealed a comparable flash separation. In addition, the newly developed formulations meet the requirements of the U.S. Environmental Protection Agency and European regulation law REACH (Registration, Evaluation, Authorization and Restriction of Chemicals), as they do not contain any substances of very high concern, heavy metals, or chlorine atoms (*Interim Drinking Water Health Advisory for Perchlorate*; Office of Science and Technology, Office of Water, Health and Ecological Criteria Division, U.S. Environmental Protection Agency: Washington, DC, 2008). Potential resulting synergies with a proposed replacement candidate for the MK 144 yellow marine smoke and illumination signal might combine commercial and environmental sustainability, which enhances the chances for future application in both the military and civilian sectors.

5.1. Introduction

Firework displays are commonly used to celebrate national holidays or public events, such as New Year's Eve, the Fourth of July in the United States, or big sports events. Starting from early childhood, many people are attracted to fireworks due to characteristic special effects, the colorful lights, whistling sounds, and loud cracks. These impressive effects often outshine the negative concomitants such as the bad smell and smoke clouds. These smoke clouds consist of burned as well as unburned materials, which are capable of affecting human health even on a one-time exposure. In contrast to public opinion, the impact of a single event might not be neglectable. For example, Kulshrestra *et al.* showed that barium concentrations in air increased by more than a factor of 1000 over the course of the Indian Diwali festival.[1] Barium salts are the traditional colorants that produce the green color in pyrotechnical displays. Upon combustion, very poisonous water-soluble Ba (II) compounds, such as $BaCl_2$, BaO, and $Ba(OH)_2$, are formed. For the colors red and yellow, strontium and sodium salts are used, respectively. It is obvious that environmental risk increases with a higher frequency of events. In the United States, amusement parks such as Disney World and the U.S. Army training grounds show a high consumption of pyrotechnical formulations.[2]

In 1997, the critical concentration of the perchlorate anion in groundwater exceeded the maximum permissible level advised by the U.S. Environmental Protection Agency (EPA), which resulted in an all live fire training stop at Camp Edwards.[3,4] The main health threat of perchlorate oxidizers arises from the similar ionic radius compared to that of iodine, which results in an interference with iodine uptake in the thyroid gland.[5] For decades, perchlorates have been used as the oxidizer of choice, but with increasing environmental regulations, the need for alternatives has increased.[6] In contrast to the field of constant burning (*i.e.* flare) formulations, where perchlorate was already successfully replaced for the colors blue, green, red, and yellow to name only a few, there is a lack of perchlorate / chlorine- and heavy-metal-free options for strobe formulations.[4,6–11] Recently, we reported the development of a red strobe system based on lithium nitrate fulfilling the preset requirements.[12] Strobe formulations are characterized by a periodically alternating flash (big flame, bright light) and dark phase (small or no visible flame) reaction.[13] The first literature reported strobe formulations, the so-called "Orion flashing guns" (green light: mixture of sulfur, fine magnesium / aluminum pyroflakes, and barium nitrate) date back to 1898, the mechanisms involved have remained unclear until today.[14] A short historical review of developed formulations as well as a summary of the assumed underlying phenomena is given by Corbel *et al.*[13] Wasmann, Krone, and Shimizu did a lot of work trying to explain and solve the mechanism in the past, whereas our focus was on replacing toxic materials.[15–18]

In addition to the previously mentioned environmentally critical compounds, potassium dichromate is often applied to coat magnesium (the fuel in such formulations) and prevent the reaction with ammonium perchlorate.[17,19] It is also hypothesized that there is a regulating power on the flash frequency and improvement to their sharpness.[20] According to the European regulation law REACH (Registration, Evaluation, Authorization and Restriction of Chemicals), potassium dichromate is a substance of very high concern due to the high toxicity and correlated long-term effects.[21] It may cause genetic defects and cancer, damage fertility / unborn children, and damage organs through prolonged or repeated exposure and is very toxic to aquatic life.

To tackle the above-described environmental and health concerns arising from the use of perchlorates, heavy metals, and potassium dichromate, we developed several new environmentally benign yellow strobe formulations based on sodium nitrate. We took the previously reported red strobe formulations based on lithium nitrate by Glück *et al.* as a starting point.[12] These new formulations contain no halogen source, which eliminates the risk of highly carcinogenic polychlorinated aromatic compounds such as polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs).[22] We determined the frequencies of the flash reactions and compared the regularity of the flashes to that of a literature-known red strobe formulation based on strontium salts, perchlorate, and potassium dichromate. In this paper, we present selected literature-known strobe formulations and compare them to the newly developed yellow strobe formulations in terms of components (known toxicity issues of the starting material) and performance values (*e.g.* frequency range, energetic properties). The potential application in both the military and civilian sectors will be discussed.

5.2. Results and Discussion

Ingredients of Yellow Strobe Formulations

A pyrotechnical formulation consists of an oxidizer, fuel, colorant (*e.g.* $Ba(NO_3)_2$, $SrSO_4$, Na_2SO_4), and sometimes additives to adjust the burning behavior. Typical applied oxidizers are potassium and ammonium perchlorate as well as nitrates (Table 5.1). The choice of fuel has a big influence on the resulting burn-

Table 5.1: Selected literature-known strobe compositions.[18]

	ingredient/wt%		
component	**A**	**B**^{a}	**C**^{a}
Mg (60 mesh, coated with $K_2Cr_2O_7$)		40	30
MgAl (coated with linseed oil)	12		
NH_4ClO_4		50	50
$Ba(NO_3)_2$	33		
KNO_3	7		
$SrSO_4$			20
Na_2SO_4		10	
BHC^b	11		
sulfur	27		
Sb_2S_3	5		
sodium oxalate	5		
$K_2Cr_2O_7$ (acting as a stabilizer)		5	5

^{a} Total amount = 100 wt% + 5 wt% stabilizer = 105 wt%. ^{b} BHC = benzene hexachloride.

ing temperature. For this reason, metal fuels such as magnesium or magnalium are applied if high burning temperatures are desired. Other options for lower burning temperatures are compounds such as sulfur, sugar, hexamine, 5-aminotetrazole, or nitrocellulose. Antimony sulfide (Sb_2S_3) may also act as a fuel; however, it is often used in flash formulations to promote the detonation inclination.[18] The application of Sb_2S_3 is alarming. There is limited evidence for the carcinogenicity of this compound, which makes it a suitable candidate for replacement.[23]

The corresponding metal sulfates and sodium oxalate are used as the colorant agent. Benzene hexachloride (BHC) is applied as a HCl source upon ignition. According to Shimizu, it is not as effective as the more commonly used poly vinyl chloride (PVC). The benefit of BHC is that it does not disturb the flickering of the flame.[18] The toxicological effects are immense, since BHC is bioaccumulative and is classified by the International Research Agency on Cancer (IARC) and the EPA as a probable human carcinogen.[24] The toxicological and environmental effects of potassium dichromate were already explained in the Introduction. A combination of Epon 813 / Versamid 140 was applied as the chlorine-free two-component binder system (Table 5.2). Sodium nitrate might be used as both an oxidizer and a colorant agent for yellow light.

Comparison of Regularity and Sharpness of Flashes

Corbel *et al.* reported that the strobe effect of formulation **C** was good with regard to the regularity and sharpness of the flashes.[25] The recorded frequency measurement is shown in Figure 5.1. The spectrum was recorded with a spectrometer maximum scan rate of $1\,\mathrm{ms\,scan^{-1}}$ (for details regarding the experimental setup, measurement procedure, and optical emission spectroscopy, please see the Supporting Information). In general, we observed a good separation of the flashes, which is indicated by an intensity value of 0 before

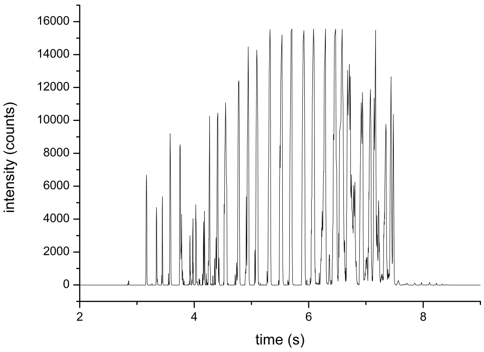


Figure 5.1: Frequency measurement ($1\,\mathrm{ms\,scan^{-1}}$) of formulation **C**.

the flash reaction (local intensity maximum) and after each local maximum for a series of events. Of the tested formulations by Corbel *et al.*, formulation **C** was reported to be within the best series. Examples of worse peak separation are given in the Supporting Information (Figures 5.7 and 5.9).

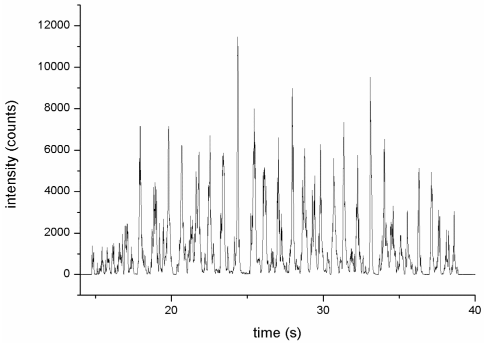


Figure 5.2: Formulation **4**.

The recorded frequency spectrum of formulation **4** (Figure 5.2) looks similar when compared to that of formulation **C**. The regularity of the single flash's maximum intensity looks similar, whereas a difference is observed for the peak separation. Approximately halfway through the burning, we were able to observe smaller, broad peaks between two peaks with high intensity (between 27–35 s). The number of these small peaks is significantly higher in formulation **4** compared to formulation **C**. A high scan rate ($5\,\mathrm{ms\,scan^{-1}}$ or lower) is essential to reveal the true time period of the flash reaction. Otherwise, two separate flashes might be mistaken for just one broad signal. At the same time, a fast flash reaction (Figure 5.1) results in a sharp signal which also contributes to a good peak separation. The peaks in formulation **4** are broadened, which provides us more information about the speed of the flash reaction. Since we did not observe the same behavior in formulation **C**, we conclude that the flash reaction of formulation **4** is slower than that of the reference formulation. High-speed video recording (Figure 5.3) proved this hypothesis. The time period of the bright flash of formulation **4** lasted approximately 290 ms, whereas it was 53 ms in the case of formulation **C** (see the Supporting Information, Figure 5.6). Another big difference is that formulation **C** shows a dark-phase reaction with absolutely no light output, whereas formulation **4** changes between a small flame (dark phase) and a bigger and brighter flame (flash reaction).

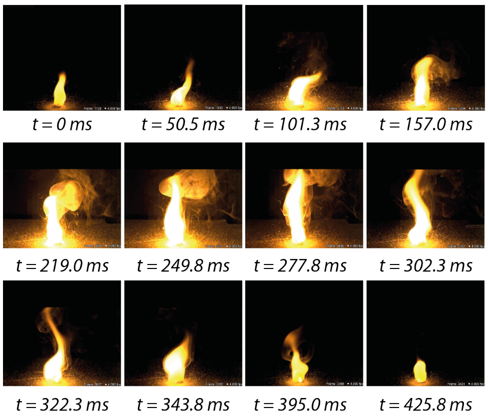


Figure 5.3: Time-resolved images of the burning of a strobe pellet (composition **4** in Table 5.2).

Our results indicate that the magnesium content directly affects both the burning time and the strobe frequency. Higher magnesium content resulted in a shorter burning time and a higher frequency (Table 5.3). The effect on the burning time is literature-known and can be easily explained by the heat-conducting properties of metals in general. A higher metal content promotes heat transfer and results in shorter burning times. Within the series of strobe formulations, formulation **2** had the shortest burning time, whereas formulations **4** and **6** had the longest. The obtained flare (*i.e.* constant burning, spectral purity 77 %) formulation **7** had an even shorter burning time, which can be explained by the lack of dark-phase reactions to generate the necessary heat for combustion. At the same time, a faster heat transfer from the top layer of the pellet to the next layer results in shorter dark phases. Since the dark-phase reaction is always followed by a flash-phase reaction in a strobe formulation, the overall flash frequency increases with shorter dark-phase reactions.

Energetic Properties

All newly developed formulations were tested toward their energetic properties regarding impact, friction, and shock sensitivity. According to the Bundesanstalt für Materialforschung (BAM) and the U.N. recommendations on the transport of dangerous goods, none of them were sensitive toward friction, which is crucial for both safe manufacturing and handling (see the Supporting Information for the classification ranges). The impact sensitivities of formulations **2**–**7** are categorized as sensitive. Formulation **1** is less sensitive toward impact. The ESD values are in the range of 1.5–0.65 J.

5.3. Conclusion

An environmentally benign yellow strobe formulation was presented, which according to REACH and the EPA does not contain any substances of very high concern and can therefore serve as a greener alternative to existing formulations. The frequency range covered by these formulations starts at 7 Hz and goes up to more than 15 Hz. We assume that, in the military sector, for training purposes as well as combat actions, the newly developed formulations can remedy the environmental impact while still providing a reliable signal formulation. Smaller variations or inconsistencies in the flash regularity might be neglectable, since strobe formulations are not expected to be as accurate as the Morse code. To our knowledge, small deviations in the frequency of the same colored strobe formulation do not transmit different information to the observer.

Almost all ingredients involved are applied by a recently published alternative yellow flare formulation by Miklaszewski *et al.*, which might promote synergies in the future, *e.g.* same supply chains and application of same materials.[4] For the application in the civilian sector, the reduced regularity of flashes might be an issue in big organized fireworks, which are often accompanied by music. Irregular flashing would impede the correct timing from an aesthetic point of view. One remaining question is whether it is also possible to change the frequency by changing the magnesium grain size instead of changing the ratio of ingredients. A better understanding of the mechanism involved, in this yellow system and the recently published red strobe system by our group, would strongly reduce the amount of extensive trial and error procedures.

Table 5.2: Formulations based on $NaNO_3$[a].

	ingredient/wt%						
component	**1**[b]	**2**	**3**	**4**	**5**	**6**	**7**
$NaNO_3$	51	51	51	51	51	51	47
Mg	12	23	15	12	15	12	21
Hexamine	33	22	30	33	30	33	28
Epon 813 / Versamid 140 (1:1)	4	4					
NC/mL			1	1	2	2	2

[a] Measured for a 1 g pellet. NC solution = 4–8 wt% in Et_2O / EtOH. [b] No constant burning.

Table 5.3: Properties of formulations **C** and **1**–**7**[a].

	BT/s	**DW**/nm	***f***/s^{-1}	**IS**/J	**FS**/N	**ESD**/J	$\mathbf{T_{onset}}$/°C
C	6.0	589–618	5.4	–	–	–	–
1	nd	583–589	–	40	>360	1.5	358
2	10.3	583–589	20 > x > 15	30	>360	1.5	338
3	13.4	583–589	12.1	15	>360	1.0	139
4	19.7	583–589	6.6	15	>360	0.75	137
5	10.3	583–589	11.4	15	>360	0.75	139
6	19.9	583–589	9.7	15	>360	0.65	138
7	7.4	588	–	10	>360	0.65	139

[a] Measured for a 1 g pellet. nd = not determined, formulation **1** showed no constant burning. The spectral purity (SP) of formulation **7** was 77 %. Key: BT = burning time, DW = dominant wavelength, *f* = frequency, IS = impact sensitivity, FS = friction sensitivity, ESD = electric spark discharge sensitivity.

5.4. 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 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 these materials.

Chemicals. The following materials were used: Mg (99 %), volume-based particle size in the range of 0.3 mm > x > 0.0 mm, Grüssing GmbH; hexamethylenetetramine (hexamine) (99.5 %), abcr; NH_4ClO_4 (reagent grade), Alfa Aesar; $SrSO_4$ (98 %), $K_2Cr_2O_7$, collodion solution (nitrocellulose solution in Et_2O / EtOH, 4–8 wt%), Sigma-Aldrich; MgAl (1:1), Omikron GmbH; $NaNO_3$ (98 %), AppliChem; Epon 813, Hexion; Versamid 140, BASF. A binder system (50 wt% Epon 813 / 50 wt% Versamid 140) was applied. All chemicals were used as provided without further purification. The literature states a maximum grain size of approximately 100 µm to observe the strobe effect.[16] However, we observed the strobe effect in our formulations by applying a mixture of different grain sizes covering the range of 300 µm and smaller.

Sample Preparation. All solid materials were weighed out into a mortar. After grinding, the binder solutions were added followed by a curing step. Before the powder was pressed into a cylindrical shape, the powder was ground again. For details regarding the sample preparation and Mg grain sizes / shapes, see Supporting Information (Figures 5.4 and 5.5).

5.5. References

[1] U. Kulshrestha, T. Nageswara Rao, S. Azhaguvel, M. Kulshrestha, *Atmos. Environ.* **2004**, *38*, 4421–4425.

[2] Along with Beauty, Fireworks Create a Beastly Mix of Pollutants, `http://www.latimes.com/local/la-me-fireworks4-2008jul04-story.html` (visited on June 6, 2017).

[3] Headquarters, *Field Manual 21-60, Visual Signals*, Department of the Army, US Government Printing Office, Washington, DC, USA, **1987**.

[4] E. Miklaszewski, J. Dilger, C. Yamamoto, *ACS Sustainable Chem. Eng.* **2017**, *5*, 936–941.

[5] U.S. Environmental Protection Agency, *Interim Drinking Water Health Advisory for Perchlorate*, Office of Water, Health and Ecological Criteria Division, Washington, DC, USA, **2008**.

[6] J. Brusnahan, A. Shaw, J. Moretti, W. Eck, *Propellants Explos. Pyrotech.* **2017**, *42*, 62–70.

[7] T. Klapötke, M. Rusan, J. Sabatini, *Angew. Chem. Int. Ed.* **2014**, *53*, 9665–9668.

[8] J. Glück, T. Klapötke, M. Rusan, J. Stierstorfer, *Chem. Eur. J.* **2014**, *20*, 15947–15960.

[9] J. Sabatini, E. Koch, J. Poret, J. Moretti, S. Harbol, *Angew. Chem. Int. Ed.* **2015**, *54*, 10968–10970.

[10] D. Juknelevicius, A. Dufter, M. Rusan, T. Klapötke, A. Ramanavicius, *Eur. J. Inorg. Chem.* **2017**, *2017*, 1113–1119.

[11] J. Glück, T. Klapötke, M. Rusan, J. Sabatini, J. Stierstorfer, *Angew. Chem. Int. Ed.* **2017**, *56*, 16507–16509.

[12] J. Glück, T. Klapötke, J. Sabatini, *Chem. Commun.* **2018**, *54*, 821–824.

[13] J. Corbel, J. Lingen, J. Zevenbergen, O. Gijzeman, A. Meijerink, *J. Phys. Chem. B* **2012**, *116*, 4967–4975.

[14] A. Brock, *Pyrotechnics: The History and Art of Fireworks Making*, Daniel O'Connor, London, UK, **1922**.

[15] F. Wasman in *The Phenomen of Pulsating Burning in Pyrotechnics*, *Proceedings of the 5th International Pyrotechnics Seminar*, IPS, Vail, CO, USA, **1976**.

[16] U. Krone, *Pyrotechnical Mixtures: For Intermittent Emission of Light*, DE 2164437, **1973**.

[17] T. Shimizu, *Studies in Strobe Light Pyrotechnic Compositions*, Pyrotechnica III, **1982**.

[18] T. Shimizu, *Fireworks: The Art, Science, and Technique*, Pyrotechnica Publications, Austin, Texas, USA, **1996**.

[19] C. Jennings-White, *J. Pyrotech.* **2004**, *20*, 7–16.

[20] M. Davies, *J. Pyrotech.* **2008**, *27*, 42–49.

[21] European Chemicals Agency: Hazard Classification and Labelling of Potassium Dichromate, `https://echa.europa.eu/substance-information/-/substanceinfo/100.029.005` (visited on April 13, 2020).

[22] W. Christmann, D. Kasiske, K. Klöppel, H. Partscht, W. Rotard, *Chemosphere* **1989**, *19*, 387–392.

[23] National Library of Medicine. Toxicity of Antimony Trisulfide, `https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1604` (visited on September 13, 2017).

[24] L. Reed, V. Buchner, P. Tchounwou, *Rev. Environ. Health* **2007**, *22*, 213–43.

[25] J. Corbel, J. van Lingen, J. Zevenbergen, O. Gijzeman, A. Meijerink, *Angew. Chem. Int. Ed.* **2013**, *52*, 290–303.

5.6. Supporting Information

Grain Size / Particle Shape

We discovered that the grain size after grinding was mainly influenced by the applied magnesium. The supplier of Mg (Grüssing GmbH, 99 %) reported the grain size in the range of 60–300 µm. This Mg was applied in formulations **1**–**7**. However, manually sieving revealed that even smaller grain sizes were present (Figure 5.4). For this reason we quantitatively determined the grain size distribution of a 10 g Mg sample applying different sieves. In addition, we used REM measurements (Figure 5.5) to determine the particle shape of the applied Mg. In formulation **C**, Mg (Grüssing GmbH, 99 %, 60 mesh) was applied.

Mg Grain Size Distribution

The applied Mg was sieved to determine the grain size fractions in the powder. Five different sieves with a size of 600 µm, 300 µm, 150 µm, 106 µm, 71 µm were applied. 99.8 % of the Mg powder passed through the biggest (600 µm) sieve. The obtained fractions are shown in Figure 5.4. The color code describes the weight percentage (wt%) of the powder that did not pass through the smaller sieve, *e.g.* 7.51 wt% are in between 300–150 µm. In this case the Mg powder did not pass through the 150 µm sieve. It is notable that 68.43 wt% of the applied Mg powder has a grain size smaller than 106 µm.

Mg Particle Shape

Scanning electron microscopy (SEM) measurements were done to determine the particle size and shape qualitative. The powder can be characterized as a mixture of course ground and fine ground Mg.

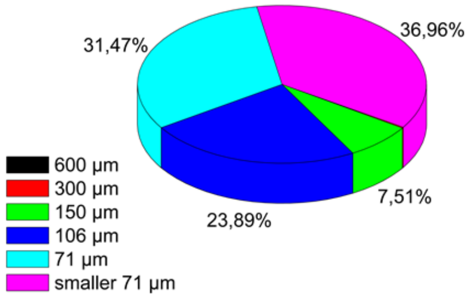


Figure 5.4: Mg grain size distribution.

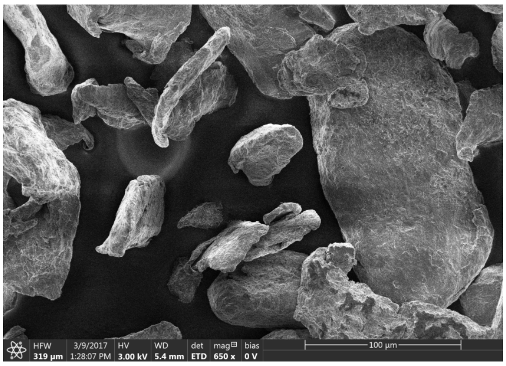
Sample Preparation

The samples were weighed out according to their weight percentages (max. 1 g) into a mortar. After grinding by hand for 3 min, both Epon 813 (20 mg mL^{-1}) and Versamid 140 solution (10 mg mL^{-1}) in ethyl acetate were added using a syringe. For nitrocellulose, we applied collodion solution (4–8 % ethanol / diethylether) to the pre-grinded solid materials. The mixture was blended with a spatula every 10 min until the solvent was evaporated. The solid material was stored over night at 70 °C in the drying oven for curing. Before consolidation, the pyrotechnic material was grinded again by hand for 3 min. The formulations were pressed with the aid of a tooling die (inner diameter 12.9 mm) into a cylindrical shape. The formulation powders were pressed at a consolidation dead load of 2 t with a dwell time of 3 s. A torch was used to ignite the pellets.

Optical Emission Spectroscopy

Dominant Wavelength / Spectral Purity / Luminous Intensity. Optical emissive properties were characterized using both an Ocean Optics HR 2000+ ES spectrometer with an ILX 511 B linear silicon CCD-array detector (190–1100 nm) and included software / calibration files from Ocean Optics. Spectra were recorded

(a) SEM of Mg (Grüssing GmbH, 99 %).



(b) Enlarged sector of (a).

Figure 5.5: Scanning electron microscopy measurements of Mg (Grüssing GmbH, 99 %).

with a detector-sample distance of 1 m. The acquisition time for the flare formulation was 20 ms scan^{-1}. The dominant wavelength (DW) and spectral purity (SP) were measured based on the 1931 CIE method using illuminant C as the white reference point. Four samples were measured for each formulation and all given values are averaged based on the full burn of the mixture. The controlled burn was filmed with a digital video camera recorder (SONY, DCR-HC37E).

Frequency Measurement. Frequency measurement were performed using an acquisition time of 1 ms scan^{-1}. Dominant wavelengths were measured based on the 1931 CIE method using illuminant C as the white reference point. The range selection for recording a signal was set the range from 560.11–610.14 nm. Calculation of the frequency was done by detecting the single peaks applying the Origin Pro 9.0 software and calculating the period of time between the single peaks (= flash reactions).

High-Speed Camera

Setup. High-speed video recording was performed applying the "SpeedCam Visario G2 1500" by Weinberger AG with the accompanied "Visart 2.2" software package. The applied camera lens was purchased from Sigma (24–70 mm, 2.8 EX DG, Macro, diameter 82 mm). In addition, a Heliopan Filter UV SH-PMC 82 mm was applied. Following data is taken from the supplier data sheet:

Sensor: high-speed APS-CMOS sensor

Active Sensor Area: 16.89 mm × 11.26 mm

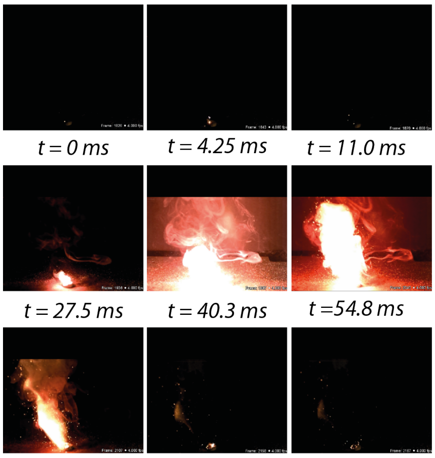
Active Pixel Size: 11 µm square

Image Formats: 768 px × 512 px,
up to 4000 frames s^{-1}

Shutter: electronic shutter down to 10 µs

Dynamic Range: color depth to 30 bit

High-Speed Video Recording. The bare pellet was placed in the fume hood and ignited by applying a torch. No prime composition was applied. The distance between the camera and the pellet (same height) was approximately 1 m. Due to the camera settings and applied lense / filter, additional halogen lamps to illuminate the fume hood were applied. A sequence of several seconds was recorded for selected formulations.



t = 0 ms t = 4.25 ms t = 11.0 ms

t = 27.5 ms t = 40.3 ms t = 54.8 ms

t = 70.3 ms t = 83.0 ms t = 85.3 ms

Figure 5.6: High speed video recording of formulation **C** (4000 frames s^{-1}).

Energetic Properties

The impact and friction sensitivities were determined using a BAM Drophammer and a BAM Friction Tester (method 1 of 6). The sensitivities of the compounds are indicated according to the UN Recommendations on the Transport of Dangerous Goods (+): impact: insensitive >40 J, less sensitive ≥ 40 J, sensitive >4 J, very sensitive <4 J; friction: insensitive >360 N, less sensitive $=360$ N, sensitive $360\ \mathrm{N} > x > 80\ \mathrm{N}$, very sensitive <80 N, extreme sensitive <10 N. Additionally all formulations were tested for sensitivity towards electrical discharge using an Electric Spark Tester ESD 2010 EN. Decomposition points were measured with an OZM Research DTA 552-Ex Differential Thermal Analyzer. Measurements were performed at a heating rate of 5 °C min^{-1}.

Recorded Spectra

The maximum recorded intensity was set to the value I = 10 (no light emission I = 0). All intensities are given relative to the highest value I = 10 in following style: Formulation (Intensity 1–10). A comparison of the maximum recorded relative intensities of all constant burning strobe formulations reveals following trend: **C** (10) > **2** (5.4) > **7** (3.2) > **3** (2.2) > **4** (2.0) > **5** (1.8) > **6** (1.7).

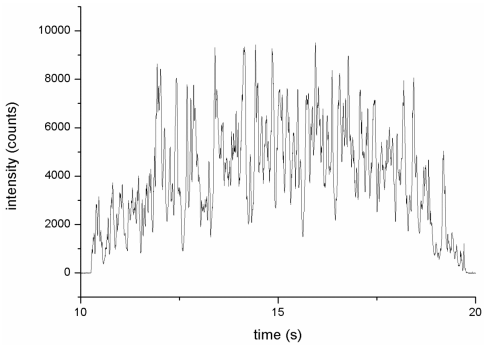


Figure 5.7: Formulation **3**.

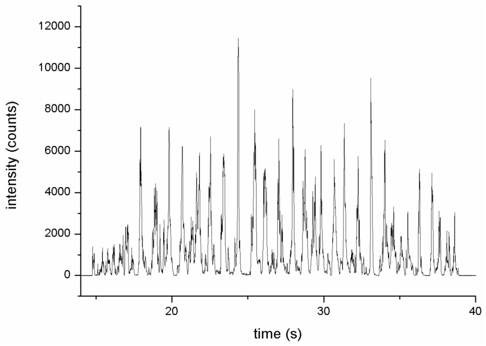


Figure 5.8: Formulation **4**.

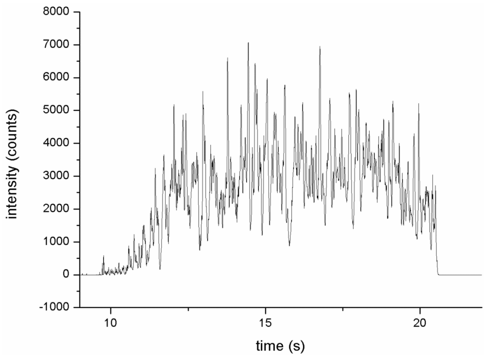


Figure 5.9: Formulation **5**.

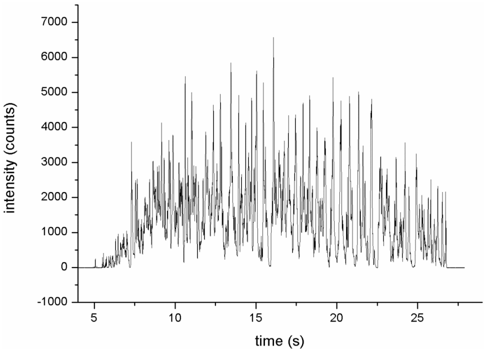


Figure 5.10: Formulation **6**.

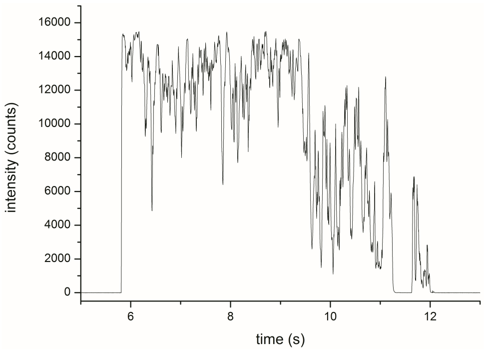


Figure 5.11: Formulation **2**.

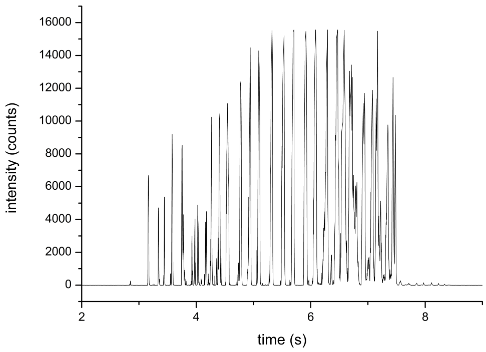


Figure 5.12: Sr red strobe reference **C**.

The Flame Emission of Indium from a Pyrotechnical View

by
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Abstract Until today, all blue-colored light-generating pyrotechnics are still based on copper and a halogen-source providing the blue-emitting species copper (I) chloride, copper (I) bromide or copper (I) iodide. The use of indium as a potential halogen-free blue light emitter in modern pyrotechnics is described. Therefore, metallic indium was introduced as both fuel and colorant in various pyrotechnical formulations including guanidine nitrate or potassium nitrate as oxidizing agent as well as magnesium, hexamine and 5-amino-1*H*-tetrazole as fuel. The effect of incandescence was examined by applying different magnesium contents within the mixtures. Emission spectra and occurring emission lines of indium-based pyrotechnical compositions were recorded and evaluated for the first time. Since the expected blue flame color could not be completely achieved, the emission of indium was discussed from an academic point of view.

6.1. Introduction

Since the earliest advances in pyrotechnical research, the most challenging task is the production of a saturated blue flame color.[1] Until now, there is no sufficient alternative material to copper and copper-containing chemicals.[2–4] In a typical blue flare formulation, these compounds were mixed with potassium perchlorate $KClO_4$ as oxidizing agent, some fuel and additional polyvinyl chloride (PVC) to generate the metastable copper (I) chloride as blue light emitter.[1,5,6] Blue colorants are for example Paris Green $Cu(CH_3COO)_2 \cdot 3\,Cu(AsO_2)_2$ or Scheele's Green $CuHAsO_3$. These components are high-performing and efficient, nevertheless, there are also high toxic according to their arsenic content.[7] Further, water soluble copper salts like copper nitrates suffer from aqueous toxicity and cause groundwater contamination.[8] The perchlorate anion is highly persistent in water, therefore it contaminates groundwater and soil each time it is used in fireworks or military approaches.[9] Because of its similar ionic radius as iodide, perchlorate inhibits the iodide uptake in the thyroid glade.[10] For this reason, the Environmental Protection Agency (EPA) added perchlorates to the Contaminant Candidate List, since this anion has been detected in both drinking water and groundwater affecting human's health.[11,12] Another problematic issue is the formation of toxic chlorinated organic compounds, such as polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) during the combustion of commonly used organic binders and a chlorine source.[13]

To overcome these issues, Koch evaluated copper (I) halides CuX (X = F, Br, I) by UV/Vis spectroscopy as alternative blue-emitting species as it has been suggested by Douda.[2,14] At the same time, Klapötke *et al.* reported on chlorine-free blue flare formulations based on copper (II) iodate.[15] The mixture with copper (I) iodide as blue light emitter provides a spectral purity (SP) of 64 % and dominant wavelength (DW) of 477 nm. More recent results apply a mixture of copper (I) bromide and potassium bromate for generating a blue color impression.[16] Unfortunately, these formulations suffer from impact and friction sensitivity and the resulting analogous polybrominated organic combustion products are also believed to be toxic.[17] There is

Table 6.1: Indium-based formulations (in wt%) applying guanidine nitrate.

	GN[a]	**In**[b]	**Mg**[c]	**Hexamine**	**Binder**[d]
1	50	5	35	5	5
2	50	5	30	10	5
3	50	5	25	15	5
4	50	5	20	20	5
5	50	5	15	25	5
6	50	5	10	30	5
7	50	10	30	5	5
8	50	10	25	10	5
9	50	10	20	15	5
10	50	10	15	20	5

[a] Guanidine nitrate [b] Indium (−100 mesh) [c] Magnesium (50/100 mesh) [d] Epon 813 / Versamid 140 (ratio 4:1).

insufficient information about the environmental and health impact of polyiodinated organic compounds given in the literature, however, it is expected to be similar to other polyhalogenated materials.[18] Regarding blue strobes, there is less information given in the literature.[19–22] A constant burning flame with high color purity and intensity is called flare, whereas compositions that show an oscillatory combustion are referred as strobes.[19,23,24] In 2017, the established Jennings-White blue strobe system consisting of 55 % ammonium perchlorate, 30 % tetramethylammonium nitrate (TMAN) and 15 % copper was modified with various ingredients and additives to study the effect on the resulting strobing behavior.[22]

Further research is mandatory to surpass the performance of the best performing flare formulations until now (DW = 465±20 nm and SP ≥65 %) and to meet the requirements for much environmentally benign compositions. The claim for so-called “next generation pyrotechnics that reduce the environmental impact” was also emphasized by a Statement of Need of the Strategic Environmental Research and Development Program (SERDP) in 2017.[25] Especially perchlorate oxidizers should be banned in modern formulations. An excessive literature research revealed two other postulated ways to generate blue light without the need of halogen and copper atoms. Some literature mentioned cesium salts to give a pale blue color, which unfortunately does not meet the requirement for blue illumination signals in terms of DW and SP.[2,26] The second hypothesis mentioned by Jennings-White is based on the observations published by Reich and Richter in 1863 about their discovery of indium.[27] They reported a violet color with two emission lines in the Bunsen burner and a blue light upon the addition of hydrochloric acid.

Indium is a silvery-white rare heavy metal. Its crustal abundance is similar to silver and mercury.[28,29] Unfortunately, it is produced exclusively as a by-product during the processing of tin and lead.[30,31] Due to the excessively high demand and at the same time low supply of indium, it is one of the scarcities raw materials on earth.[29,30,32] Obviously, indium would never be considered as a pyrotechnic colorant for mass production until now.[33] Today´s application of indium compounds is dominated by indium tin oxide (ITO) as an essential part of touch screen panels, flat screens and transparent layers in perovskite solar cells.[34,35] Next to Reich and Richter in 1863, the flame chemistry of indium was further studied by Paschen and Campbell later on, who detected additional emission lines and assigned them to the corresponding excitations.[36] Reich and Richter reported a blue light emission upon addition of hydrochloric acid. Due to the previously discussed health concerns, no chlorine source was considered for application in newly designed pyrotechnical formulations. Analogous to the copper (I) salts CuCl, CuBr and CuI, the corresponding indium (I) bromide or indium (I) iodide could be considered as potential colorants at first. Already in 1991, Singh *et al.* reported the main emission of InBr and InI to be in the green region (520 nm), which prohibits the application as blue colorant.[37] Consequently, it was concluded that it is not possible to generate deep blue light through the application of other halogen atoms. The high price and low availability of pure indium metal presumably explains why no further research was done on indium as a blue-light emitter in pyrotechnic formulations so far. Due to the known disadvantages of indium, the presented study to the emission of indium is mainly of academically interest.

6.2. Results and Discussion

Nevertheless, the idea was to investigate, if further tuning of the flame conditions in halogen-free indium-based formulations might shift the emission lines into the desired blue range. First experiments (Table 6.1) applied guanidine nitrate (GN) as a metal-free oxidizer (T_{dec}: $\geq$250 °C).[38] It's a favored oxidizing agent in gas- and smoke-generating pyrotechnical systems.[6] Further, in 2015 Sabatini *et al.* discovered nitrogen-rich fuels like hexamethylentetramine (hexamine) in red-colored halogen-free flares to have a deoxidizing effect on the flame entailing higher luminosity and spectral purity.[39] Indium served as both colorant and fuel. The two-component epoxy binder system was a mixture of Epon 813 and Versamid 140 (ratio 4:1).

The amount of oxidizer and binder were fixed at 50 wt% and 5 wt% respectively. Altering the magnesium / hexamine ratio had only little influence on the resulting color: Whereas formulation **1** was dominated by bright white light attributed to the highest magnesium percentage, all other formulations within this row showed a red-violet color with only little blue light emission in the outer flame parts (see Figure 6.1). Most of the formulations **1**–**10** achieved no constant burning after ignition and had to be re-ignited a few times. Potassium nitrate is a long-known, widely used component in pyrotechnics due to its availability in high purity and low costs, even though it suffers from hygroscopicity.[3,6] In contrast to guanidine ni-

Figure 6.1: Burning of formulation **4**.

Table 6.2: Indium-based formulations (in wt%) applying potassium nitrate.

	KNO_3	**In**[a]	**Mg**[b]	**Hexamine**	**Binder**[c]
11	50	5	35	5	5
12	50	5	30	10	5
13	50	5	25	15	5
14	50	5	20	20	5
15	50	5	15	25	5
16	50	5	10	30	5
17	50	10	30	5	5
18	50	10	25	10	5
19	50	10	20	15	5
20	50	10	15	20	5

[a] Indium (−100 mesh) [b] Magnesium (50/100 mesh) [c] Epon 813 / Versamid 140 (ratio 4:1).

trate, potassium nitrate decomposes at higher temperatures (T_{dec}: 400–700 °C).[38] Since the decomposition reaction is endothermic, the addition of metal fuels is mandatory to release enough energy for color emission.[3,40] Applying potassium nitrate as oxidizer in formulations **11**–**20** resulted in violet burning formulations (Table 6.2, Figure 6.2). No blue light was observed. Here again, formulation **11** had the shortest burning time (<1 s), which was due to the highest magnesium content.

Figure 6.2: Burning of flare formulation **19** (left) and strobe formulation **15** (right).

The frequency measurement of formulation **15** proofed a non-regular burning behavior, which was detected by visual examination earlier (Figure 6.3). After the first ignition and several flash reactions (= emission of light), the burning stopped and the pellet had to be re-ignited after a few seconds. This lack of the flash regularity as well as the insufficient flash separation, does not allow any potential application efforts. Another literature-known magenta strobe composition relies on cheaper compounds such as ammonium perchlorate, strontium nitrate, tetramethylammonium nitrate, hexamine and copper-aluminum alloy (50:50).[41] However, next to the application of cheaper but hazardous materials such as perchlorate, the color of this formulation was reported to substantially degraded in conditions of high humidity.

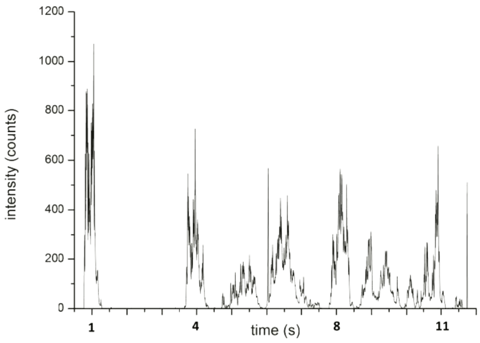

Figure 6.3: Frequency measurement of formulation **15** with 1 ms scan^{-1}.

Since the overall indium amount in formulations **11**–**20** (Table 6.2) was quite small compared to other colorants in existing formulations (typically more than 20 wt% up to 50 wt%), the effect of indium amounts up to 30 wt% was investigated next. Higher amounts of indium would result in even more expensive formulations, however, no blue light was observed for lower amounts. Formulations **21**–**29** applied 5-amino-1*H*-tetrazole (5-AT) instead of hexamine and potassium nitrate as an oxidizer (Table 6.3). This time, the effect of different oxidizer to metal fuel ratios was studied. Both 5-AT and hexamine were reported to give high spectral purities in light-producing pyrotechnical compositions before.[39] Magnesium is usually applied to increase the resulting burning temperature thus producing a higher incandescence level. Incandescence describes the phenomena of an emitted continuous spectrum covering the whole part of the visible spectrum (= white light), which can be observed for example with glowing steal ingots.[2] This gain in luminous intensity comes along with a loss in spectral purity as the white light diminishes the color quality. To study the effect of lower magnesium content and reduced incandescence, formulation **24** was developed as a completely magnesium-free formulation. All of the tested formulations **21**–**29** revealed constant burning with a violet flame.

Reich and Richter did not provide any comparable wavelength values; instead they referred to an older dimensionless scale. In this scale, Na was set to the value 50, Sr to 104 and $\text{In}_\alpha/\text{In}_\beta$ to 110/147.[27] To obtain standardized values, the emission of selected formulations was measured with a calibrated spectrometer. A look at the emission spectrum of formulation **4** revealed five sharp lines and one broad signal in the range of 364–400 nm (UV/Vis region, violet) (Figure 6.4). Next to this, two sharp emission lines in the violet (410 nm) and the blue region (451 nm) were detected and referred to the $\text{In}_\alpha/\text{In}_\beta$ band as described by Reich and Richter earlier.[27]

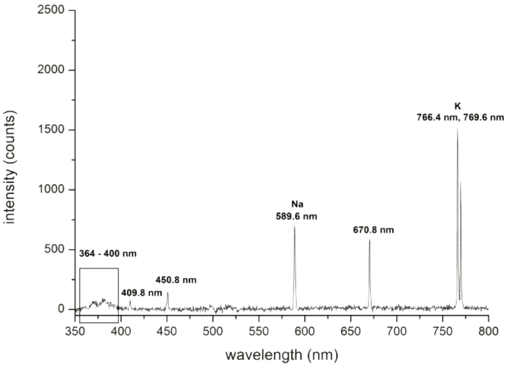

Figure 6.4: Emission spectrum of **4**.

The remaining signals at 590 nm and 766 nm were assigned as sodium and potassium impurities. The last remaining line (671 nm) would fit as the main lithium emission. However, the second emission of atomic lithium at 610 nm is missing and therefore, was ruled out. Due to the low intensity of the blue emission and the presence of the violet emission, it was concluded that it is not possible to achieve deep blue light with halogen-free indium-based formulations, since the impurities dominate the flame color.

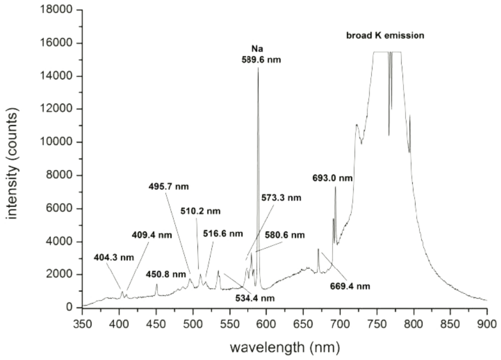

Figure 6.5: Emission spectrum of **19**.

Table 6.3: Indium-based formulations (in wt%) applying 5-amino-1*H*-tetrazole.

	KNO_3	**In**[a]	**Mg**[b]	**5-AT**	**Binder**[c]
21	60	20	10	5	5
22	55	25	10	5	5
23	50	30	10	5	5
24	70	20	–	5	5
25	60	25	5	5	5
26	55	30	5	5	5
27	50	20	20	5	5
28	50	25	15	5	5
29	50	30	10	5	5

[a] Indium (−100 mesh). [b] Magnesium (50/100 mesh). [c] Epon 813 / Versamid 140 (ratio 4:1).

A look at the emission spectrum of formulation **19** revealed higher intensities across the whole displayed wavelength range (Figure 6.5). The potassium line width increased and dominated the spectrum. This observation can be explained by a higher potassium concentration present in the flame, which is also known for other alkaline metals like lithium.[42,43] The broad emission at 496 nm was assigned to condensed MgO(s) particles.[44] Next to the identified emission lines of indium, sodium and potassium, several new unidentified lines at 404, 510, 517, 534, 581, 669 and 693 nm appeared. Again, the intensity of the emitted light in the blue region was too low to produce a blue color impression. Finally, the color points of formulations **4**, **15** and **19** are depicted in a CIE 1931 chromaticity diagram (Figure 6.6). As discussed before, the corresponding color impressions are in the violet region due to the high intensity of impurities.

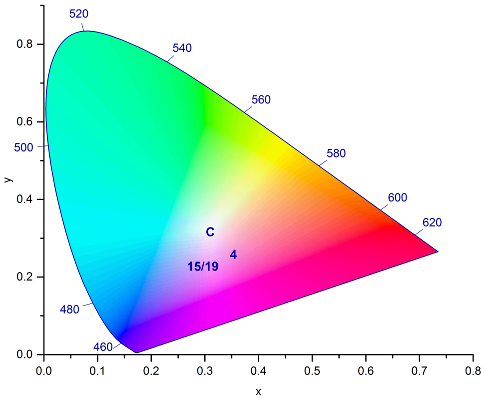

Figure 6.6: CIE 1931 chromaticity diagram of formulations **4**, **15** and **19**.

6.3. Conclusion

Besides the well-known drawbacks of indium such as price and availability, we decided to investigate the flame chemistry from an academically point of view. For this reason, indium was introduced as colorant to a typical pyrotechnical formulation consisting of magnesium, hexamine or 5-amino-1*H*-tetrazole, potassium nitrate or guanidine nitrate and an epoxy binder system. Unfortunately, none of the tested mixtures provided sufficient blue color emission. The main emission was dominated by magenta and violet, whereas only at the outer flame a blue color could be detected. Higher magnesium contents had higher luminous intensity, but at the same time a loss in spectral purity as a consequence. Due to the lack of existing flame emission spectra of indium, the author's measured emission spectra of selected indium-based pyrotechnical formulations. As a result, sharp lines at 410 nm and 451 nm could be detected, which were further referred to the In_α/In_β bands. However, the emission spectrum as well as the resulting flame color is dominated by impurities of sodium and potassium. In addition, the intensity of blue emission is insufficient and does not fulfill the quality demands for pyrotechnical formulations. Finally, it was concluded that it is not possible to observe a blue light with the provided indium-based halogen-free pyrotechnical system.

6.4. Experimental Section

Caution! The mixtures are potential explosives which are sensitive to environmental stimuli such as impact, friction, heat and electrostatic discharge. While 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 these materials.

Chemicals. The following materials were used as provided: Guanidine nitrate (98 %, Sigma-Aldrich); Potassium nitrate (99 %, Grüssing GmbH); Indium (99.9 %, −100 mesh, abcr Chemicals); Magnesium (99 %, 50/100 mesh, Grüssing GmbH); 5-Amino-1*H*-tetrazole (98 %, abcr chemicals); Hexamine (99 %, Acros Organics); Epon 813 (Hexion); Versamid 140 (BASF).

Sample Preparation. All pyrotechnic samples were prepared in 1.0 g scale using the same procedure in order to ensure reproducibility. Therefore, the ingredients were weighed into a sample glass according to their respective weight percentages in the formulations. Each sample was transferred into a porcelain mortar and carefully ground to a homogeneous powder. After grinding, the binder solutions were added followed by a curing step. The so-prepared compositions were ground again and then, pressed into a cylindrical shape with the aid of a tooling die using a hydraulic press with a dead load of 2.0 t for 3.0 s.

Optical Measurement. Optical properties were characterized using both an Ocean Optics HR 2000+ ES spectrometer with an ILX 511 B linear silicon CCD-array detector (190–1100 nm) and included software/calibration files from Ocean Optics. Spectra were recorded with a detector-sample distance of 1 m. The acquisition time for the flare formulation was $1\,\mathrm{ms\,scan^{-1}}$. The dominant wavelength (DW) and spectral purity (SP) were measured based on the 1931 CIE method using Illuminant C as the white reference point. Four samples were measured for each formulation and all given values are averaged based on the full burn of the mixture. The controlled burn was filmed with a digital video camera recorder (SONY, DCR-HC37E).

6.5. References

[1] A. Contini, *J. Pyrotech.* **2010**, 3–11.

[2] B. Douda, *Theory of Colored Flame Production*, Naval Sea Systems Command Crane, ADA951815, Crane, IN, USA, **1964**.

[3] T. Shimizu, *Fireworks: The Art, Science, and Technique*, Pyrotechnica Publications, Austin, Texas, USA, **1996**.

[4] G. Steinhauser, T. Klapötke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3330–3347.

[5] B. Sturman, *Propellants Explos. Pyrotech.* **2006**, *31*, 70–74.

[6] J. Conkling, C. Mocella, *Chemistry of Pyrotechnics: Basic Principles and Theory*, CRC Press, Boca Raton, **2010**.

[7] R. Ratnaike, *Postgrad. Med. J.* **2003**, *79*, 391–396.

[8] H. Bradl, *Heavy Metals in the Environment: Origin, Interaction and Remediation*, Academic Press, London, UK, **2005**.

[9] S. Susarla, T. Collette, A. Garrison, N. Wolfe, S. McCutcheon, *Environ. Sci. Technol.* **1999**, *33*, 3469–3472.

[10] L. Braverman, X. He, S. Pino, M. Cross, B. Magnani, S. Lamm, M. Kruse, A. Engel, K. Crump, J. Gibbs, *J. Clin. Endocrinol. Metab.* **2005**, *90*, 700–706.

[11] P. Brandhuber, S. Clark, K. Morley, *J. Am. Water Works Assn.* **2009**, *101*, 63–73.

[12] Environmental Protection Agency, Contaminant Candidate List 3, `https://www.epa.gov/ccl/contaminant-candidate-list-3-ccl-3` (visited on July 1, 2019).

[13] P. Dyke, P. Coleman, *Organohalogen Compd.* **1995**, *24*, 213–216.

[14] E. Koch, *Propellants Explos. Pyrotech.* **2015**, *40*, 799–802.

[15] T. Klapötke, M. Rusan, J. Sabatini, *Angew. Chem. Int. Ed.* **2014**, *53*, 9665–9668.

[16] D. Juknelevicius, E. Karvinen, T. Klapötke, R. Kubilius, A. Ramanavicius, M. Rusan, *Chem. Eur. J.* **2015**, *21*, 15354–15359.

[17] Agency for Toxic Substances and Disease Registry, *Toxicological profile for Polybrominated Biphenyls and Polybrominated Diphenyl Ethers*, Department of Health and Human Services, Public Health Service, Atlanta, GA, USA, **2004**.

[18] L. Wackett, M. Sadowsky, L. Newman, H. Hur, S. Li, *Nature* **1994**, *368*, 627–629.

[19] J. Corbel, J. Lingen, J. Zevenbergen, O. Gijzeman, A. Meijerink, *J. Phys. Chem. B* **2012**, *116*, 4967–4975.

[20] J. Glück, T. Klapötke, T. Küblböck, *ACS Sustainable Chem. Eng.* **2018**, *6*, 4400–4404.

[21] J. Glück, T. Klapötke, J. Sabatini, *Chem. Commun.* **2018**, *54*, 821–824.

[22] D. Juknelevicius, A. Dufter, M. Rusan, T. Klapötke, A. Ramanavicius, *Eur. J. Inorg. Chem.* **2017**, *2017*, 1113–1119.

[23] J. Corbel, J. van Lingen, J. Zevenbergen, O. Gijzeman, A. Meijerink, *Angew. Chem. Int. Ed.* **2013**, *52*, 290–303.

[24] J. Corbel, J. van Lingen, J. Zevenbergen, O. Gijzeman, A. Meijerink, *Propellants Explos. Pyrotech.* **2013**, *38*, 634–643.

[25] Strategic Environmental Research and Development Program (SERDP), *Novel Pyrotechnics that Reduce Environmental Impact*, SON Number: WPSON-19-C4, FY 2019 Statement of Need, Alexandria, VA, USA, **2017**.

[26] H. Ellern, *Military and civilian pyrotechnics*, Chemical Pub. Co, New York City, NY, USA, **1968**.

[27] F. Reich, T. Richter, *J. Prakt. Chem.* **1863**, *90*, 172–176.

[28] U. Schwarz-Schampera, P. Herzig, *Indium: Geology, Mineralogy, and Economics*, Springer-Verlag, Berlin, Germany, **2002**.

[29] K. Wedepohl, *Geochim. Cosmochim. Acta* **1995**, *59*, 1217–1232.

[30] M. Frenzel, C. Mikolajczak, M. Reuter, J. Gutzmer, *Resour. Policy* **2017**, *52*, 327–335.

[31] W. Morawietz, *Chem. Ing. Tech.* **1964**, *36*, 638–647.

[32] S. Behrendt, W. Kahlenborn, M. Feil, C. Dereje, R. Bleischwitz, R. Delzeit, M. Scharp, *Rare metals*, Umweltbundesamt, Dessau, Germany, **2007**.

[33] L. Oglesby, *Glitter, The Chemistry and Techniques*, American Fireworks News, Dingmans Ferry, PA, USA, **1989**.

[34] D. Cairns, D. Paine, G. Crawford, S. Kukureka, *SID Symp. Dig. Tech. Pap.* **2001**, *32*, 654–657.

[35] N. Giesbrecht, J. Schlipf, L. Oesinghaus, A. Binek, T. Bein, P. Müller-Buschbaum, P. Docampo, *ACS Energy Lett.* **2016**, *1*, 150–154.

[36] F. Paschen, J. Campbell, *Ann. Phys.* **1938**, *423*, 29–75.

[37] M. Singh, G. Ghodgaonkar, M. Saksena, *J. Quant. Spectrosc. Radiat. Transfer* **1991**, *46*, 583–586.

[38] IFA, *GESTIS – Substance Database*, Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung, Sankt Augustin, Germany, **2018**.

[39] J. Sabatini, E. Koch, J. Poret, J. Moretti, S. Harbol, *Angew. Chem. Int. Ed.* **2015**, *54*, 10968–10970.

[40] T. Shimizu, *Fireworks from a physical standpoint*, Pyrotechnica Publications, Austin, TX, USA, **1981**.

[41] C. Jennings-White in *Pyrotechnica XIV*, Pyrotechnica Publications, Austin, TX, USA, **1992**, pp. 30–32.

[42] D. Dillehay in *Proceedings of the 9th International Pyrotechnics Seminar*, IPS, Colorado Springs, CO, USA, **1984**, pp. 85–106.

[43] B. Douda in *Proceedings of the 5th International Pyrotechnics Seminar*, IPS, Vail, CO, USA, **1976**, pp. 212–222.

[44] E. Miklaszewski, J. Dilger, C. Yamamoto, *ACS Sustainable Chem. Eng.* **2017**, *5*, 936–941.

Fine-Tuning: Advances in Chlorine-Free Blue-Light-Generating Pyrotechnics

by
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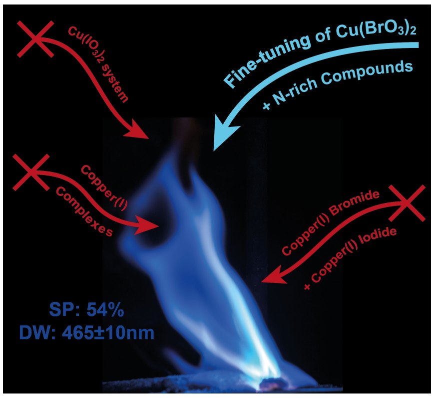

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Abstract One of the most challenging tasks in the field of light-producing pyrotechnics is the generation of saturated blue light with high spectral purity. Only copper salts in combination with chlorine seem to be high-performing blue light emitters. However, in modern pyrotechnics the application of chlorine should be avoided. Different strategies are presented to further fine-tune literature-known chlorine-free blue-light-emitting pyrotechnical compositions. The copper iodate as well as the copper bromate systems have been studied by using small amounts of nitrogen-rich compounds like 1,2,4-triazole, 5-amino-1*H*-tetrazole or 3-nitro-1*H*-1,2,4-triazole. To overcome sensitivity issues, a two-component epoxy binder system was introduced. The application of both copper (I) iodide and copper (I) bromide in the same pyrotechnical formulation were considered as blue-light-emitting species. Further, a quite new approach by using copper (I) nitrogen-rich coordination compounds was investigated to give a blue flame color. All relevant formulations were characterized with respect to their dominant wavelength and spectral purity as well as impact and friction sensitivity.

7.1. Introduction

Pyrotechnical disseminated blue light is supposed to be the most challenging color of all.[1] This assumption is not only supported by the limited number of publications, but also by the quite recent steps forward regarding a higher spectral purity (SP) and optimized dominant wavelength (DW).[2–4] Traditionally, a combination of copper salts and chlorine sources were applied to give the desired blue color.[5] Usually, ammonium perchlorate or potassium perchlorate fulfill both the role of an oxidizing agent and as chlorine source.[1,6,7] In the case of proper flame tuning, the combustion temperature is sufficient to produce the blue light emitter copper (I) chloride. As a result, blue emission in the visible spectrum ranging from 435–480 nm and 428–452 nm with additional peaks between 476–488 nm is observed.[4] If the temperature exceeds a certain level, the molecular emitter will decompose to give copper (II) oxide and copper (I) hydroxide.[8] CuO can sometimes be spotted as red tip on the top of flame, whereas CuOH emits in the green region of the visible spectrum and therefore, weakens the overall color quality.[5,9] The formation of the blue light emitter copper (I) chloride is limited by a maximum reaction temperature; for example, Conkling and Shidlovsky supposed 1500 K.[10] Several other temperatures were discussed in the literature, but according to Sturman they should be wrong.[10] Thermodynamic modelling applying the NASA Chemical Equilibria with Applications (NASA-CEA) computer code confirmed Shimizu´s hypothesis, that it should be possible to obtain blue compositions of high purity and color with copper (I) chloride up to 2500 K.[11,12] Further increased temperatures should lead to dissociation of copper (I) chloride.

For a long time it was believed, that copper (I) chloride is the only suitable emitter in the blue region. In 2014, Klapötke *et al.* reported on chlorine-free pyrotechnical mixtures with copper (I) iodide as the blue light emitter.[4] The best working formulation consisted of copper iodate, 5-amino-1*H*-tetrazole (5-AT), magnesium, copper (I) iodide, and an epoxy binder system (Epon 828 / Epikure 3140). To this date, these compositions achieved the highest recorded spectral purity (65 %) and dominant wavelength (473 nm).[4] In 2015, Juknelevicius *et al.* outlined another possible blue-light emitter – copper (I) bromide – which was found to achieve a SP $\leq$38 % and a DW = 479 nm.[3] From a toxicity point of view, especially the formulations based on copper (I) iodide are more advantageous, since the postulated formation of highly carcinogenic polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and analogous brominated compounds like polybrominated biphenyls (PBBs) can be avoided.[13–15] In 2004, the U.S. Department of Health and Human Services summarized earlier publications and indicated, that PBBs might accumulate in the environment and were found to cause cancer in selected animal studies.[15] Potentially formed polyiodinated biphenyls (PIBs) are not believed to be associated with health hazards as they are applied as contrast agents for radiological purposes in medicine, but there is insufficient information given in the literature.[16] Next to halogenated compounds and perchlorates, soluble copper salts tend to show aqueous toxicity and therefore, are considered as part of the problem to create environmentally friendly blue light-generating pyrotechnical formulations.[17] In 2019, the author's considered indium as a possible blue light emitter; however, the resulting flame color was dominated by sodium and potassium impurities.[18] Due to the lack of suitable alternatives, the application of copper salts has to be accepted by the military in illumination signals and civilian sector for firework displays or indoor pyrotechnics.[5,19,20]

The task of this presented study was to develop a new pyrotechnic composition that surpasses the performance of known formulations and yields a deep blue color with a DW of 465±20 nm and SP of $\geq$65 %. For this reason, the author's defined additional requirements for the improvement of newly developed pyrotechnics: The smoke formation should be significantly reduced compared to black powder and only little-produced ash is tolerated. Further, the avoidance of chlorates, perchlorates or other chlorine sources is mandatory. All applied compounds should be commercially feasible, which means sufficient availability to moderate prices. As a consequence, multi-step syntheses were not considered for the ongoing investigation. Since all mixtures should be safe in handling, storing and preparing, the sensitivity as well as toxicity should be considered. Regarding the toxicity requirements, compounds with known major toxicity issues were ruled out. Also high amounts of metals and metal salts should be avoided. The safety aspect mainly included the sensitivities towards mechanical stimuli such as impact (IS) and friction (FS). Only formulations which guarantee safe handling are likely to be produced on a larger scale. Different strategies were applied to achieve the abovementioned goals, which can be summarized as followed:

- Improvement of $Cu(IO_3)_2$ system
- Improvement of $Cu(BrO_3)_2$ system
- Copper (I) nitrogen-rich coordination compounds

Table 7.1: Blue reference formulation **S** by Shimizu (in wt%) and its resulting properties.[4]

	$KClO_4$	**Cu**	**PVC**	**starch**	**DW**/nm	**SP**/%	**IP**/J	**FS**/N
S	70	10	20	5	475	61	8	324

7.2. Results and Discussion

Improvement of $Cu(IO_3)_2$ System

The $Cu(IO_3)_2$ system by Klapötke *et al.* was chosen as starting point for further investigations. More accurate, the idea was to tune the flame conditions by applying small amounts of nitrogen-rich compounds to increase the spectral purity. The produced nitrogen gas would not only be beneficial to reduced smoke volume, and thus increased spectral purity, but also consumes heat to tailor the flame temperature. This literature-known and proofed concept was successfully applied earlier in numerous publications and seemed to be very promising at first.[21–25]

Figure 7.1: Burning and smoke generation of formulation **I7**.

However, initial experiments with $Cu(IO_3)_2$, hexamine, CuBr and nitrogen-rich compounds such as 1,2,4-triazole (Tr), 5-AT, and 3-nitro-1*H*-1,2,4-triazole (3-NT) only produced brown smoke (see ESI: Table 7.5, Figure 7.1). The hint of a small blue flame was only detected at the very beginning of ignition stage and disappeared quickly. Various other formulations applying guanidine nitrate, copper or urea suffered from stability issues and were not considered for further investigations. As a consequence, the focus shifted to the $Cu(BrO_3)_2$ system, which was supposed to show bigger potential for improvement regarding the spectral purity and dominant wavelength.

Improvement of $Cu(BrO_3)_2$ System

The introduced $Cu(BrO_3)_2$ system by Juknelevicius *et al.* achieved lower spectral purities (SP $\leq$38 %)[3] compared to Klapötke's $Cu(IO_3)_2$ system as well as the literature-known publication by Shimizu applying undesired potassium perchlorate, copper, polyvinyl chloride (PVC) and starch (Table 7.1).[4] Shimizu´s formulation show comparatively high impact sensitivity (8 J), but is less sensitive towards friction. To overcome the disadvantage of low spectral purity, the previously pursued strategy applied for the $Cu(IO_3)_2$ case was also applied for an analogous $Cu(BrO_3)_2$ system. In this context, the initial formulations consisted of $Cu(BrO_3)_2$, hexamine and CuBr only. In the next step, the effect of nitrogen-rich compounds such as Tr, 5-AT and 3-NT was investigated. The amount of introduced nitrogen-rich additive was either 5 % or 10 % (Table 7.2).

All developed formulations showed dominant wavelengths in the desired range of 465±20 nm. The three starting formulations **Br1**–**Br3** already exceeded the best formulation by Juknelevicius *et al.* without incorporating any nitrogen-rich compound.[3] The addition of Tr, 5-AT and 3-NT further increased the spectral purity up to 50–54 %. Only formulation **Br5** suffered from a reduced spectral purity compared to the formulations **Br1**–**Br3**. It is noteworthy, that upon burning of formulation **Br9** no residue was left at all (Figure 7.2).

Unfortunately, the sensitivities towards mechanical stimuli increased to a non-tolerable level (Table 7.2). According to the *Bundesanstalt für Materialforschung* (BAM), the friction sensitivity of formulations **Br1**–**Br3** was characterized as very sensitive and changed for the worse with the addition of nitrogen-rich additives.[26,27] It was discovered, that a higher amount of additive resulted in higher sensitivity and safety risk. Whereas formulations **Br2**–**Br6** were classified as sensitive towards impact, formulation **Br1** and **Br7**–**Br9** had to be classified as very sensitive. Upon preparation of these formulations, several accidently decompositions such as fast deflagration and sometimes crackling sounds occurred.

Figure 7.2: Burning of formulation **Br9**.

Since the best performance was obtained for formulations containing nitrogen-rich additives, further fine-tuning was undertaken to achieve even higher spectral purities and optimized burning behavior. Small changes in the ratio of oxidizing agent and hexamine in combination with a fixed amount of nitrogen-rich additives resulted in blue light emission within the required dominant wavelength range (see ESI: Table 7.7). Bigger variations were observed for the spectral purities differing in between 30–50 %. In contrast to former mixtures, the formation of unwanted CuO as red tip was observed in most cases. Only formulations **Br12**, **Br15** and **Br18** did not exhibit red flame impurities and were characterized towards their energetic properties. The sensitivities were classified as very sensitive towards friction and impact (Table 7.3, see ESI: Table 7.7).

Formulations **Br19**–**Br30** were further prepared to investigate the effect of slightly increased amounts of CuBr (max. 25 wt%), while keeping the oxidizer level constant (see ESI: Table 7.8). **Br19**, **Br20**, **Br22**–**Br25**, and **Br30** also showed a red tip and therefore, were excluded from further investigations. Only **Br21** was further characterized and classified as sensitive towards impact and friction (Table 7.3). During the grinding step, formulations **Br26** to **Br29** accidentally decomposed with a big flame and crackling sound. It was assumed, that these formulations were even more sensitive than previous compositions.

Even though the spectral purities of these formulations increased up to 54 % and also fulfilled the requirement for dominant wavelength, the resulting sensitivities were considered as a serious problem. One literature-known strategy to reduce the sensitivity of pyrotechnical formulations is the addition of non-energetic binder materials such as carbohydrates, oils or epoxy resins.[28,29] These binder materials usually do not only increase the mechanical

Table 7.2: $Cu(BrO_3)_2$-based formulations **Br1**–**Br9** (in wt%) and their resulting properties.

	$\mathbf{Cu(BrO_3)_2}$	**Hexamine**	**CuBr**	**Tr**	**5-AT**	**3-NT**	**DW**/nm	**SP**/%	**IP**/J	**FS**/N
Br1	70	10	20	–	–	–	465	44	2	30
Br2	70	15	15	–	–	–	468	40	7	36
Br3	65	15	20	–	–	–	466	46	8	40
Br4	65	10	20	5	–	–	468	52	10	20
Br5	65	10	20	–	5	–	464	39	8	20
Br6	65	10	20	–	–	5	467	54	5	24
Br7	60	10	20	10	–	–	468	53	3	16
Br8	60	10	20	–	10	–	468	50	1	16
Br9	60	10	20	–	–	10	470	53	1	18

Table 7.3: Selected$Cu(BrO_3)_2$-based formulations (in wt%) and their resulting properties.

	$\mathbf{Cu(BrO_3)_2}$	**Hexamine**	**CuBr**	**Tr**	**5-AT**	**3-NT**	**Binder**	**DW**/nm	**SP**/%	**IP**/J	**FS**/N
Br12	60	15	20	–	–	5	–	463	50	3	24
Br15	55	15	20	–	–	10	–	467	50	2	32
Br18	60	20	15	–	–	5	–	464	48	2	18
Br21	60	10	20	–	–	10		468	54	3	42
Br33	65	10	20	–	5	–	5	469	50	4	14
Br34	65	10	20	–	5	–	8	470	49	5	18
Br37	60	10	20	10	–	–	5	468	53	2	48
Br38	60	10	20	10	–	–	8	469	47	1	36
Br41	60	10	20	–	–	10	5	470	48	2	36
Br42	60	10	20	–	–	10	8	465	44	3	30

Annotation: Binder = Epon 813 / Versamid 140 (4:1); weight percentage in total = 100 wt% + 5–8 wt% binder = 105–108 wt% per formulation.

stability of the pressed pellet, but also coat the particles, which further should reduce the sensitivity by minimizing the emerging shearing forces.[29] However, the burning behavior as well as optical properties can also be influenced by binder systems. The binder itself can act as fuel providing more heat to the combustion process and thus, alter the resulting combustion temperature. **Br31**–**Br42** were prepared to study the effect of an epoxy binder system (Epon 813 / Versamid 140, 4:1) on the occurring properties (see ESI: Table 7.9).

The spectral purity of **Br31**, **Br32**, **Br35**, **Br36** and **Br40** dropped to 39–43 % and therefore, these formulations were excluded from further investigations. The same compositions with additional 5–8 wt% binder do not revealed the intended effect of reduced sensitivity (Table 7.3). Quite contrary to the expectations, the sensitivities of formulations **Br37** and **Br38** surprisingly increased with higher binder content. This phenomenon might be explained by the altered stoichiometry resulting in higher reactivity. A comparison of the pair **Br33** and **Br34** indicated only a slight loss in sensitivity, which might be neglectable due to measurement errors. For **Br41** and **Br42**, an increase of friction sensitivity was accompanied by a small decrease in the sensitivity towards impact. It is obvious, that in this case there is no connection between the binder content and the formulation's resulting sensitivity performance.

It has to be stated, that especially the grinding process of all solid materials turned out to provide the highest risk for accidental decomposition. Other methods for safe sample preparation have to be considered in the future. Grinding and coating every single component separately before wet-mixing the ingredients might be an option for further investigations. However, the sensitivities in a dry state of these so-prepared formulations are questionable.

Finally, compositions applying a minimum content of metal or metals salts were developed to meet the above-introduced requirements for modern pyrotechnics. **BrI1** provides a blue formulation applying minimum amounts of copper or copper salts by using potassium bromate ($KBrO_3$) as an oxidizing agent (Table 7.4).The halogen source of choice was ammonium bromide NH_4Br as well as CuI. In combination with elemental copper, the blue light was generated by a mixture of two emitters – copper (I) bromide and copper (I) iodide. Unfortunately, the impact sensitivity was found to be one of the most hazardous ones; therefore, a spontaneous decomposition during the manufacturing process is very likely. As a result, these kind of pyrotechnical mixtures were excluded from further investigation, since they prevent safe sample preparation, storing as well as handling.

Copper (I) Coordination Compounds

The performance of pyrotechnical formulations is influenced by a lot of factors, *e.g.* environmental factors, sample preparation or material shape.[5,12] Small deviations in the production step, chemicals from another supplier or even different batches of the same supplier can cause big effects on the resulting performance and require a batch-to-batch reformulation.

To overcome the inconsistencies arising from mixing several powders, the idea was to reduce the number of ingredients by combining colorant, oxidizer and fuel in one molecule.[30] Analogue to the tetrakis(acetonitrile) copper (I) perchlorate complex published by Csöregh *et al.* in 1974, the first step was to synthesize the

Table 7.4: Formulation **BrI1** with a minimum amount of copper and its resulting properties.

	$KBrO_3$	**Hex**	**Cu**	**CuI**	**NH_4Br**	**Binder**	**DW**/nm	**SP**/%	**IP**/J	**FS**/N
BrI1	65	10	5	5	10	5	461	47	1	42

Annotation: Epon 813 / Versamid 140 (4:1); 100 wt% per formulation + 5–8 wt% binder = 105–108 wt% in total.

tetrakis(acetonitrile) copper (I) periodate complex (Scheme 1). In a second step, the corresponding tetrakis(acetonitrile) copper (I) periodate complex with various nitrogen-rich compounds as stabilizing ligands should be obtained via metathesis reaction.[31] A mixture of periodic acid and acetonitrile was provided. Subsequently, Cu_2O was added and heated until a clear solution was observed. This so-prepared solution was allowed to stand on air for crystallization. Unfortunately, all solutions turned blue and the intended complex could not be observed in the elemental analysis. The blue color already indicated the formation of copper (II) salts. In an attempt to overcome the occurring oxidation process, the nitrogen-rich ligands were first dissolved in periodic acid resulting in the same color shift (Scheme 2).

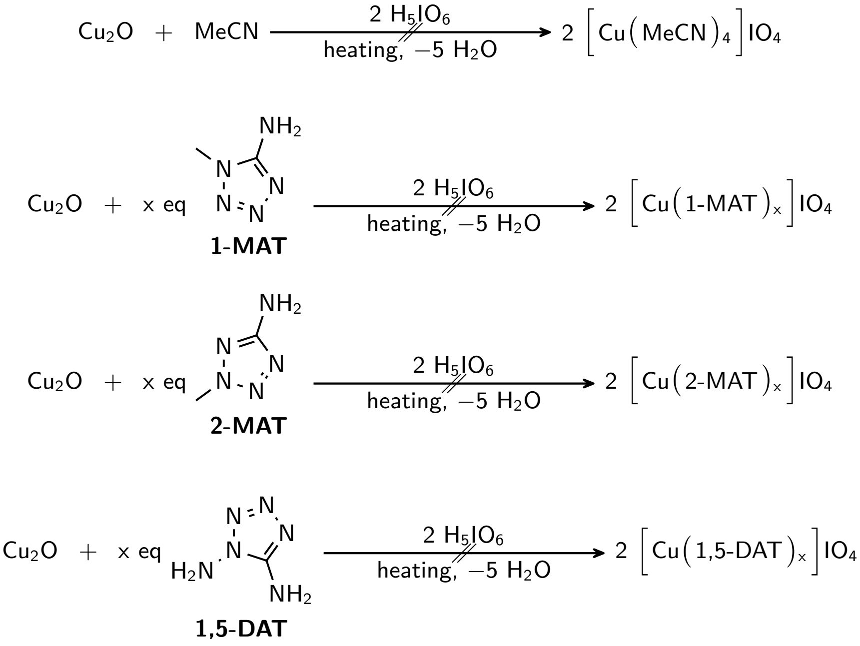
The tetrakis(acetonitrile) copper (I) periodate could not be isolated. Furthermore, 1,5-DAT instantly decomposed upon addition to the periodic acid solution, which was indicated by an instant gas formation. For the ligands 1-MAT and 2-MAT, a mixture of green and blue solid material was obtained after crystallization. The solution applying 1-MAT showed small colorless crystals in the glass vessel. X-ray analysis proofed the formation of the corresponding 1-MAT periodate salt instead of the intended product. It was concluded, that the formation of $[Cu(N\text{-rich ligands})_x]IO_4$ complexes is not possible by applying the literature-stated procedure for analogous perchlorate complexes. Due to the blue colored solution, the copper (I) ions were oxidized to copper (II) during the reaction. The oxidizing properties of periodic acid already decomposed one N-rich ligand upon addition, which further reduces the number of possible compounds for future investigations. Domyati *et al.* reported on copper (I) complexes with pincer *N*-heterocyclic carbene (NHC) ligands. The reaction started with $[Cu(MeCN)_4]PF_6$ or $[Cu(MeCN)_4]SbF_6$ and an *in situ* generated NHC at room temperature in the absence of air and moisture.[32] Consequently, other tetrakis(acetonitrile) copper (I) complexes with varying anions are known, which might serve as starting materials for simple metathesis reaction to obtain $[Cu(MeCN)_4]IO_4$. Some are already commercially available, *e.g.* $[Cu(MeCN)_4]^+ Y^-$ with $Y = SbF_6^-$, BF_4^-, ClO_4^-, PF_6^-. Acetonitrile (MeCN) is a weakly coordinated ligand, which can be substituted by stronger coordinating ligands such as triphenylphosphine (PPh_3) as well as bidentate ligands like diphenylphosphinomethane (dppm) or 1,10-phenanthroline (phen).[33] Most of the reported copper (I) complexes are also moisture- or air-sensitive; therefore, they cannot be considered in any pyrotechnical formulation.[34–37]

Further attempts to synthesize promising $[Cu(MeCN)_4]IO_4$ complexes starting from commercially available compound $[Cu(MeCN)_4]BF_4$ via metathesis reactions failed (Scheme 3). In

$$\mathrm{Cu_2O} + 2\,\mathrm{H_5IO_6} + \mathrm{MeCN} \dashrightarrow 2\,\left[\mathrm{Cu(MeCN)_4}\right]\mathrm{IO_4} + 5\,\mathrm{H_2O}$$

$$\left[\mathrm{Cu(MeCN)_4}\right]\mathrm{IO_4} + x\ \text{N-rich ligands} \dashrightarrow \left[\mathrm{Cu}\left(\text{N-rich ligands}\right)_x\right]\mathrm{IO_4} + \mathrm{MeCN}$$

Scheme 1: Planned synthetic route to [Cu(MeCN)$_4$]IO$_4$ with N-rich ligand = 5-amino-1-methyl-1*H*-tetrazole (1-MAT), 5-amino-2-methyl-2*H*-tetrazole (2-MAT); 1,5-diaminotetrazole (1,5-DAT).



Scheme 2: Copper (I) complexes attempts.

$$\left[\mathrm{Cu(MeCN)_4}\right]\mathrm{BF_4} + \mathrm{H_5IO_6} \cancel{\xrightarrow[\text{50 °C, } -2\,\mathrm{H_2O}]{\mathrm{MeCN}}} 2\,\left[\mathrm{Cu(MeCN)_4}\right]\mathrm{IO_4} + \mathrm{H^+} + \mathrm{BF_4^-}$$

$$\left[\mathrm{Cu(MeCN)_4}\right]\mathrm{BF_4} + \mathrm{NaIO_4} \cancel{\xrightarrow[\text{50 °C, } -2\,\mathrm{H_2O}]{\mathrm{MeCN}}} 2\,\left[\mathrm{Cu(MeCN)_4}\right]\mathrm{IO_4} + \mathrm{NaBF_4}$$

Scheme 3: Failed metathesis reactions applying [Cu(MeCN)$_4$]BF$_4$.

this study, it was not possible to successfully introduce copper (I) complexes in blue-light-emitting pyrotechnical formulations. Finally it was concluded, that copper (I) complexes need further research as well as improvement to meet the stability and sensitivity requirements for the application in modern pyrotechnical systems.

7.3. Conclusion

In the presented work, three different strategies are discussed to further fine-tune the performance of literature-known blue-light-emitting pyrotechnical compositions. The author's defined several requirements for these modern mixtures. The most important one is that the formulation should provide a deep blue color with a dominant wavelength of 465±20 nm and spectral purity of $\geq$65 %. The first approach was the improvement of the most-promising $Cu(IO_3)_2$ system, however, it was not possible to generate a blue flame and most of the mixtures suffer from stability issues. As a result, the focus shifted to the fine-tuning of the $Cu(BrO_3)_2$ system. The author's summarized the optical performance and the corresponding impact and friction sensitivity of discussed formulations together with Shimizu's blue reference and Juknelevicius' $KBrO_3$ system in an overview (Figure 7.3).[3,5]

The literature-known $KBrO_3$-based formulation reached only a spectral purity of $\leq$38 %. The flame conditions were tailored with nitrogen-rich compounds – 1,2,4-triazole, 5-amino-1*H*-tetrazole and 3-nitro-1*H*-1,2,4-triazole – to reduce smoke generation, increase spectral purity and control temperature. With this strategy spectral purities up to 54 % could be observed. Unfortunately, these mixtures suffer from impact and friction sensitivity (IS: 1–5 J, FS: 14–48 N), whereby a safe manufacturing process cannot be guaranteed. Also the addition of a two-component binder system was not able to reduce the sensitivity against mechanical manipulation. However, the author's proofed that it is possible to reach the optical performance of Shimizu's perchlorate-based blue reference formulation (SP: 61 %, DW: 475 nm, IS: 8 J, FS: 324 N) with the fine-tuning of bromate-based mixtures. The application of both blue-light-emitters copper (I) bromide and copper (I) iodide was excluded from further investigation, because of sensitivity issues.

The last concept to improve the performance of blue-light-emitting pyrotechnics was the addition of copper (I) nitrogen-rich coordination compounds served as colorant, fuel and gas generator in one molecule. Due to stability and sensitivity issues, it was not possible to introduce copper (I) complexes to pyrotechnical mixtures.

7.4. Experimental Section

Caution! The described pyrotechnical mixtures might explode during preparing, handling or manipulating! They are potential explosives, which are sensitive to environmental stimuli such as impact, friction, heat, and electrostatic discharge. Please handle these materials with care! Precautionary measures are mandatory and protective equipment like safety glasses, face shields, leather coats, Kevlar® gloves, and ear protectors is highly recommended.

Chemicals. The following materials were used as provided without further purification: 5-Amino-1*H*-tetrazole (98 %), abcr Chemicals; 1,2,3-triazole (99.5 %), Acros Organics; 3-nitro-1*H*-1,2,4-triazole (97 %), Sigma Aldrich; Hex-

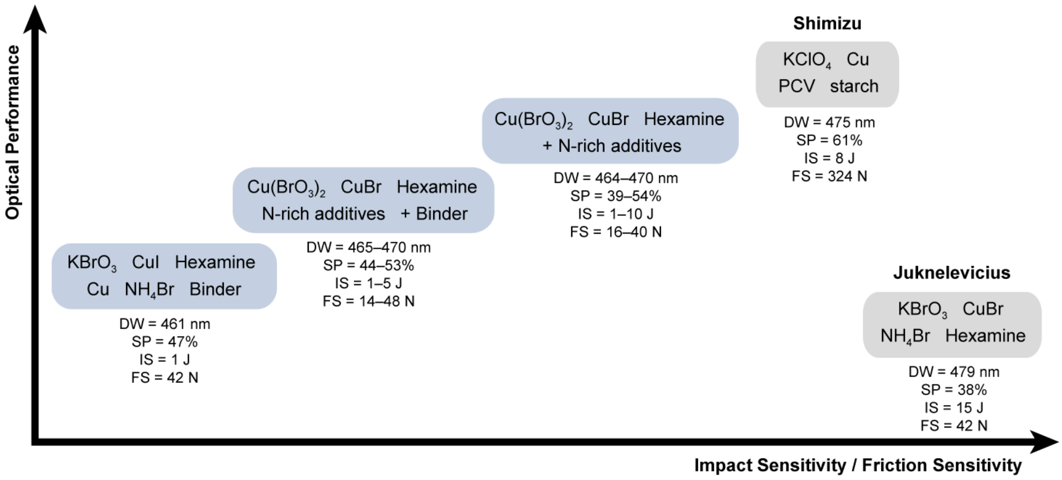


Figure 7.3: Optical performance (DW and SP) and sensitivities (IS and FS) of $Cu(BrO_3)_2$-based formulations in comparison with Shimizu's blue reference and Juknelevicius' $KBrO_3$ system.[3,5]

amethylenetetramine (99.5 %), abcr Chemicals; copper (−40+100 mesh, 99.5 %), Alfa Aesar; ammonium bromide (99 %), Sigma Aldrich; copper bromide (99 %), Sigma Adrich; copper iodide (98 %), Sigma Aldrich; copper iodate (95 %), Alfa Aesar; potassium bromate (99 %), Sigma Aldrich; Epon 813, Hexion; Versamid 140, BASF. All other compounds were synthesized according to literature procedures or provided at the laboratory stock.

Sample Preparation. All pyrotechnic samples were prepared in 1.0 g scale using the same procedure to ensure the reproducibility. Therefore, the different ingredients were weighed into a sample glass according to their respective weight percentages as given in the formulations. Each sample was transferred into a porcelain mortar and carefully ground to a homogeneous powder. After grinding, the binder solutions were added followed by a curing step. The so-prepared compositions were ground again and then, pressed into a cylindrical shape with the aid of a tooling die using a hydraulic press with a dead load of 2.0 t for 3.0 s.

Optical Measurement. Optical properties were characterized using both an Ocean Optics HR 2000+ ES spectrometer with an ILX 511 B linear silicon CCD-array detector (190–1100 nm) and included software/calibration files from Ocean Optics. Spectra were recorded with a detector-sample distance of 1 m. The acquisition time for the flare formulation was 1 ms scan^{-1}. The dominant wavelength (DW) and spectral purity (SP) were measured based on the 1931 CIE method using Illuminant C as the white reference point. Four samples were measured for each formulation and all given values are averaged based on the full burn of the mixture. The controlled burn was filmed with a digital video camera recorder (SONY, DCR-HC37E).

Synthesis of Copper (I) Complexes

Route (I): A mixture of periodic acid (2 M, 5 mL) and acetonitrile (15 mL) was prepared. Subsequently, Cu_2O (71.6 mg, 0.05 mmol) was added and heated (50 °C) until a clear solution was observed. After crystallization on air, the solution turned blue. A blue-greenish precipitate was obtained after removal of the solvent. **EA** ($C_8H_{12}N_4O_4CuI$, 418.7 g mol^{-1}): calc. C 22.95, H 2.89, N 13.38 %; found: C 0.00, H 0.00, N 0.00 %.

Route (II)–(IV): The nitrogen-rich ligands (200 mg, 4 eq) were dissolved in a mixture of periodic acid (2 M, 5 mL) and acetonitrile (15 mL). After addition of Cu_2O (1 eq), the solution was heated (50 °C) until all solid material was dissolved. The solution was allowed to stand on air for crystallization. A blue-greenish precipitate was obtained after removal of the solvent. **EA** ($C_8H_{20}N_{20}O_4CuI$, 650.8 g mol^{-1}): calc. C 14.76, H 3.01, N 43.04 %; found: C 7.14, H 2.03, N 20.33 %.

Route (V)–(VI): $[Cu(MeCN)_4]BF_4$ (200 mg, 0.62 mmol) was dissolved in an excess of acetonitrile (15 mL) and heated (50 °C) until a clear solution was observed. Upon addition of one droplet of H_5IO_6 (2 M), a green precipitate occurred immediately. **EA** ($C_8H_{12}N_4O_4CuI$, 418.7 g mol^{-1}): calc. C 22.95, H 2.89, N 13.38 %; found: C 0.00, H 0.85, N 0.00 %.

Applying $NaIO_4$ (133 mg, 0.62 mmol) instead resulted in the same product. The formation of a green precipitate was observed approximately 2 min after the addition of $NaIO_4$. **EA** ($C_8H_{12}N_4O_4CuI$, 418.7 g mol^{-1}): calc. C 22.95, H 2.89, N 13.38 %; found: C 0.00, H 0.00, N 0.00 %.

Sensitivity Data. Impact and friction sensitivity were determined using a BAM Drophammer and a BAM Friction Tester. The sensitivities of the compositions are indicated according to the UN Recommendations on the Transport of Dangerous Goods (+). Impact: insensitive >40 J, less sensitive ≥40 J, sensitive >4 J, very sensitive <4 J; friction: insensitive >360 N, less sensitive =360 N, sensitive 360 N > x > 80 N, very sensitive <80 N, extreme sensitive <10 N. Electrostatic discharge was measured with an OZM small-scale electrostatic spark X SPARK 10. ESD: sensitive <0.1 J, insensitive >0.1 J. The thermal stability was carried out using an OZM Research DTA 552 Ex Differential Thermal Analyzer with a heating rate of 5 °C min^{-1}.[26,27]

7.5. References

[1] R. Lancaster, *Fireworks, Principles and Practice*, Chemical Publishing Company, New York City, NY, USA, **1998**.

[2] D. Juknelevicius, A. Dufter, M. Rusan, T. Klapötke, A. Ramanavicius, *Eur. J. Inorg. Chem.* **2017**, *2017*, 1113–1119.

[3] D. Juknelevicius, E. Karvinen, T. Klapötke, R. Kubilius, A. Ramanavicius, M. Rusan, *Chem. Eur. J.* **2015**, *21*, 15354–15359.

[4] T. Klapötke, M. Rusan, J. Sabatini, *Angew. Chem. Int. Ed.* **2014**, *53*, 9665–9668.

[5] T. Shimizu, *Fireworks: The Art, Science, and Technique*, Pyrotechnica Publications, Austin, Texas, USA, **1996**.

[6] A. Hardt, B. Bush, T. Shimizu, B. Neyer, *Pyrotechnics*, Pyrotechnica Pubns, Corozal, PR, USA, **2001**.

[7] R. Webb, A. von Oertzen, S. Myatt, D. Chapman, P. Chapman, M. van Rooijen, W. Colpa, G. Colpa, E. de Jong, C. de Ruiter, *Literature review of fireworks compositions, propagation mechanisms, storage legislation and environmental effects*, Bundesanstalt für Materialforschung und -prüfung, EVG1-CT-2002-00074 CHAF, Berlin, Germany, **2003**.

[8] B. Douda, *Theory of Colored Flame Production*, Naval Sea Systems Command Crane, ADA951815, Crane, IN, USA, **1964**.

[9] M. Russell, *The Chemistry of Fireworks*, The Royal Society of Chemistry, Cambridge, UK, **2009**.

[10] B. Sturman, *Propellants Explos. Pyrotech.* **2006**, *31*, 70–74.

[11] NASA Glenn Research Center, *NASA Computer program CEA (Chemical Equilibrium with Applications) Code*, `https://www.grc.nasa.gov/www/CEAWeb/`, Cleveland, OH, USA, **2017**.

[12] T. Shimizu, *Fireworks from a physical standpoint*, Pyrotechnica Publications, Austin, TX, USA, **1981**.

[13] W. Christmann, D. Kasiske, K. Klöppel, H. Partscht, W. Rotard, *Chemosphere* **1989**, *19*, 387–392.

[14] O. Fleischer, H. Wichmann, W. Lorenz, *Chemosphere* **1999**, *39*, 925–932.

[15] Agency for Toxic Substances and Disease Registry, *Toxicological profile for Polybrominated Biphenyls and Polybrominated Diphenyl Ethers*, Department of Health and Human Services, Public Health Service, Atlanta, GA, USA, **2004**.

[16] K. Thomson, D. Varma, *Aust. Prescr.* **2010**, *33*, 35–37.

[17] G. Weingart, *Pyrotechnics*, Bloomfield Books, Portland, ME, USA, **1998**.

[18] J. Glück, T. Klapötke, T. Küblböck, *Z. Anorg. Allg. Chem.* **2019**, 133–137.

[19] J. Conkling, C. Mocella, *Chemistry of Pyrotechnics: Basic Principles and Theory*, CRC Press, Boca Raton, **2010**.

[20] T. Klapötke, *Chemistry of High-Energy Materials*, Boston: De Gruyter, Berlin, **2017**.

[21] D. Chavez, M. Hiskey, *J. Pyrotech.* **1998**, 11–14.

[22] D. Chavez, M. Hiskey, D. Naud, *J. Pyrotech.* **1999**, 17–36.

[23] I. Drukenmüller, T. Klapötke, Y. Morgenstern, M. Rusan, J. Stierstorfer, *Z. Anorg. Allg. Chem.* **2014**, *640*, 2139–2148.

[24] J. Glück, T. Klapötke, M. Rusan, J. Stierstorfer, *Chem. Eur. J.* **2014**, *20*, 15947–15960.

[25] T. Klapötke, T. Müller, M. Rusan, J. Stierstorfer, *Z. Anorg. Allg. Chem.* **2014**, *640*, 1347–1354.

[26] BAM Bundesanstalt für Materialforschung und -prüfung, *Empfehlungen für die Beförderung gefährlicher Güter - Handbuch über Prüfungen und Kriterien*, Bundesanstalt für Materialforschung und -prüfung, Berlin, **2015**.

[27] Committee of Experts on the Transport of Dangerous Goods, *UN Recommendations on the Transport of Dangerous Goods*, United Nations Economic and Social Council, New York City, NY, USA, **2019**.

[28] F. Betzler, V. Hartdegen, T. Klapötke, S. Sproll, *Cent. Eur. J. Energ. Mater.* **2016**, *13*, 289–300.

[29] J. Sabatini, C. Freeman, J. Poret, A. Nagori, G. Chen, *Propellants Explos. Pyrotech.* **2011**, *36*, 145–150.

[30] L. Blair, A. Colakel, R. Vrcelj, I. Sinclair, S. Coles, *Chem. Commun.* **2015**, *51*, 12185–12188.

[31] I. Csöregh, P. Kierkegaard, R. Norrestam, *Acta Crystallogr. Sect. B: Struct. Sci.* **1975**, *31*, 314–317.

[32] D. Domyati, S. Hope, R. Latifi, M. Hearns, L. Tahsini, *Inorg. Chem.* **2016**, *55*, 11685–11693.

[33] T. Murahashi, T. Nagai, T. Okuno, T. Matsutani, H. Kurosawa, *Chem. Commun.* **2000**, 1689–1690.

[34] V. de Lucca Neto, A. Mauro, V. Sargentelli, M. Ionashiro, *Thermochim. Acta* **1995**, *260*, 235–241.

[35] H. Liang, K. Karlin, R. Dyson, S. Kaderli, B. Jung, A. Zuberbühler, *Inorg. Chem.* **2000**, *39*, 5884–5894.

[36] H. Liang, E. Kim, C. Incarvito, A. Rheingold, K. Karlin, *Inorg. Chem.* **2002**, *41*, 2209–2212.

[37] T. Sorrell, D. Jameson, *J. Am. Chem. Soc.* **1982**, *104*, 2053–2054.

7.6. Supporting Information

Table 7.5: $Cu(IO_3)_2$-based formulations **I1**–**I9** (in wt%).

	$Cu(IO_3)_2$	**Hexamine**	**CuBr**	**Tr**	**5-AT**	**3-NT**
I1	70	10	20	–	–	–
I2	70	15	15	–	–	–
I3	65	15	20	–	–	–
I4	65	10	20	5	–	–
I5	65	10	20	–	5	–
I6	65	10	20	–	–	5
I7	60	10	20	10	–	–
I8	60	10	20	–	10	–
I9	60	10	20	–	–	10

Table 7.6: $Cu(BrO_3)_2$-based formulations **Br1**–**Br9** (in wt%) and their resulting properties.

	$Cu(BrO_3)_2$	**Hex**	**CuBr**	**Tr**	**5-AT**	**3-NT**	**DW**/nm	**SP**/%	**IP**/J	**FS**/N
Br1	70	10	20	–	–	–	465	44	2	30
Br2	70	15	15	–	–	–	468	40	7	36
Br3	65	15	20	–	–	–	466	46	8	40
Br4	65	10	20	5	–	–	468	52	10	20
Br5	65	10	20	–	5	–	464	39	8	20
Br6	65	10	20	–	–	5	467	54	5	24
Br7	60	10	20	10	–	–	468	53	3	16
Br8	60	10	20	–	10	–	468	50	1	16
Br9	60	10	20	–	–	10	470	53	1	18

Table 7.7: $Cu(BrO_3)_2$-based formulations **Br10**–**Br18** (in wt%) and their resulting properties.

	$\mathbf{Cu(BrO_3)_2}$	**Hex**	**CuBr**	**Tr**	**5-AT**	**3-NT**	**DW**/nm	**SP**/%	**IP**/J	**FS**/N
Br10	60	15	20	5	–	–	466	47	–	–
Br11	60	15	20	–	5	–	468	47	–	–
Br12	60	15	20	–	–	5	463	50	3	24
Br13	55	15	20	10	–	–	459	50	–	–
Br14	55	15	20	–	10	–	462	30	–	–
Br15	55	15	20	–	–	10	467	50	2	32
Br16	60	20	15	5	–	–	467	42	–	–
Br17	60	20	15	–	5	–	464	34	–	–
Br18	60	20	15	–	–	5	464	48	2	18

Table 7.8: $Cu(BrO_3)_2$-based formulations **Br19**–**Br30** (in wt%) and their resulting properties.

	$\mathbf{Cu(BrO_3)_2}$	**Hex**	**CuBr**	**Tr**	**5-AT**	**3-NT**	**DW**/nm	**SP**/%	**IP**/J	**FS**/N
Br19	60	10	20	10	–	–	463	47	–	–
Br20	60	10	20	–	10	–	463	43	–	–
Br21	60	10	20	–	–	10	468	54	3	42
Br22	60	10	25	5	–	–	465	52	–	–
Br23	60	10	25	–	5	–	466	47	–	–
Br24	60	10	25	–	–	5	471	47	–	–
Br25	60	5	25	10	–	–	468	50	–	–
Br26	60	5	25	–	10	–	–	–	–	–
Br27	60	5	25	–	–	10	–	–	–	–
Br28	60	5	20	15	–	–	–	–	–	–
Br29	60	5	20	–	15	–	–	–	–	–
Br30	60	5	20	–	–	15	471	46	–	–

Table 7.9: $Cu(BrO_3)_2$-based formulations **Br31**–**Br42** (in wt%) and their resulting properties.

	$Cu(BrO_3)_2$	**Hex**	**CuBr**	**Tr**	**5-AT**	**3-NT**	**Binder**	**DW**/nm	**SP**/%	**IP**/J	**FS**/N
Br31	65	10	20	5	–	–	5	469	42	–	–
Br32	65	10	20	5	–	–	8	465	43	–	–
Br33	65	10	20	–	5	–	5	469	50	4	14
Br34	65	10	20	–	5	–	8	470	49	5	18
Br35	65	10	20	–	–	5	5	459	42	–	–
Br36	65	10	20	–	–	5	8	468	39	–	–
Br37	60	10	20	10	–	–	5	468	53	2	48
Br38	60	10	20	10	–	–	8	469	47	1	36
Br39	60	10	20	–	10	–	5	463	42	4	20
Br40	60	10	20	–	10	–	8	464	40	–	–
Br41	60	10	20	–	–	10	5	470	48	2	36
Br42	60	10	20	–	–	10	8	465	44	3	30

Annotation: Binder = Epon 813 / Versamid 140 (4 : 1); weight percentage in total = 100 wt% + 5–8 wt% binder = 105–108 wt% per formulation.

Table 7.10: Formulation **BrI1** with a minimum amount of copper and its resulting properties.

	$KBrO_3$	**Hex**	**Cu**	**Cu (I)I**	**NH_4Br**	**Binder**	**DW**/nm	**SP**/%	**IP**/J	**FS**/N
BrI1	65	10	5	5	10	5	461	47	1	42

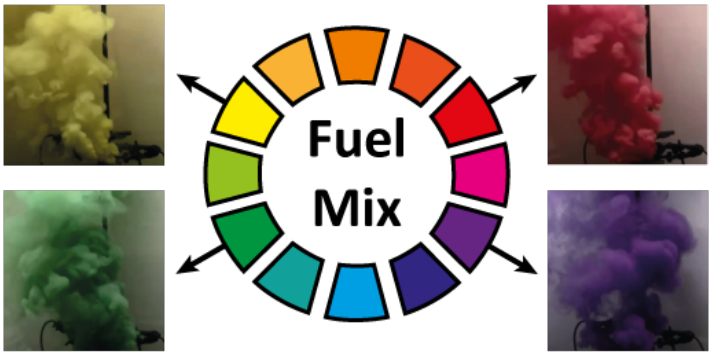
Annotation: Binder = Epon 813 / Versamid 140 (4:1); weight percentage in total = 100 wt% + 5–8 wt% binder = 105–108 wt% per formulation.

Part IV.

Results and Discussion: Smoke-Generating Pyrotechnics

5-Amino-1*H*-Tetrazole-based Multi-coloured Smoke Signals Applying the Concept of Fuel Mixes

by
Johann Glück, Thomas M. Klapötke and Teresa Küblböck



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New Journal of Chemistry **2018**, *42*, 10 670–10 675
(doi:10.1039/c8nj01786g)

Abstract The development of sugar-free multi-coloured smoke formulations, so-called fuel mixes is reported. These simple four ingredient-based mixtures of dye, potassium chlorate, 5-amino-1*H*-tetrazole and a magnesium carbonate derivative are able to produce a variety of colours by applying the same pyrotechnical system. All components except the dye are pre-mixed; the dye is added in the final step. Based on previous results which indicated an overall higher smoke performance in terms of efficiency and persistence by applying 5-amino-1*H*-tetrazole as fuel in smoke formulations, we developed new coloured smoke formulations. For big producers as well as consumers, the concept of fuel mixes is an effective way to reduce costs and provide a higher degree of safety. In this article, the focus was on dyes applied in the U.S. M18 coloured smoke grenades.

8.1. Introduction

Coloured smoke signals are a non-electronic communication tool for both ground as well as ground-to-air signalling.[1–4] During daytime, the big benefit compared to light-emitting signals is the high visibility over greater distances, when employed against a terrain background of contrasting colour.[2] In this context, the most perceptible colour contrast displaying optimum visibility at a considerable distance is offered by red, green, yellow and violet, thereby creating great research interest.[5] A rather new segment in the market for coloured smokes is the so-called daylight firework.[6] Similar to classical firework displays at night, these formulations create visible effects such as smoke trails or fountains at daytime. Daylight fireworks might be used for any daytime events like sport competitions, religious celebrations and cultural events like museum openings.[6] So far, the biggest consumer of smoke signals still remains the military sector. For decades, coloured smoke signals are valuable in the military for marking unit flanks, target locations, drop zones, and medical evacuation landing sites.[2,3,7–10] This also includes marine distress signals, which are an essential part of any safety equipment inventory in the shipping industry as well as sport activities.[11,12] For both civilian and military application, the formulation compounds remain the same. Typically, smoke-generating compositions consist of an oxidizer / fuel pair providing the heat to vaporize the dye.[13,14] The coolant keeps the reaction temperature in the desired range, while other additives may be used to modify the mechanical or burning properties.[15] Historically, the old M18 coloured smoke grenades contained an anthraquinone-based dye mixed with sulfur, potassium chlorate and sodium bicarbonate. Further, an optional amount of refined kerosene and tricalcium phosphate for control of dusting and caking could be added.[16,17]

However, due to toxicity and health issues, these smoke compositions are no longer produced, since they are suspected to release hazardous SO_2 during combustion. An indication for this is provided by soldiers perceiving a burning sensation in their lungs when inhaling such smoke.[9] For this reason, these early smoke signals, which were already applied during the World War II era, do not meet today's environmental demands anymore and are therefore under constant evaluation for reformulation.[9,18–23] Sugar was considered as a less toxic alternative to the widely applied sulfur-containing formulations.[18,24] Compared to former produced sulfoxides, the resulting combustion products derived from sugars contain only harmless H_2O and CO_2.[9]

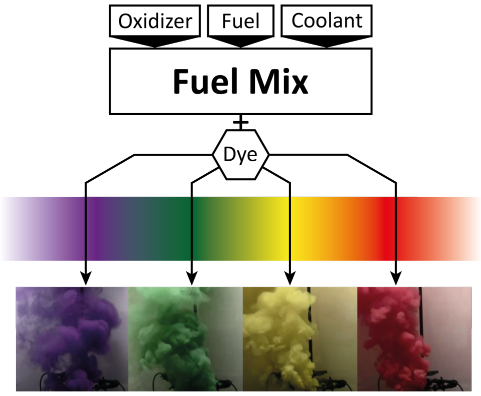


Figure 8.1: The concept of fuel mixes.

A look in the literature revealed, that there is only a limited number of information provided about the percentage of dye actually sublimed upon combustion of the signal.[25,26] The question arises, whether it is possible to apply alternative fuels, which might improve the smoke dispersal, efficiency, and persistence. As a consequence, the amount of hazardous dyes could be reduced to its minimum, while providing the same colour impression. Unfortunately, each coloured smoke dye has a different enthalpy of sublimation affecting the resulting behaviour and performance of a coloured smoke formulation.[9] For this reason, up to now every single dye needs its own optimized pyrotechnical formulation to meet the requirements for burn time and colour quality. A possible solution to this circumstance might be the development of so-called fuel mixes (Figure 8.1).[8] Essentially, fuel mixes are combinations of certain components such as the oxidizer/fuel pair and further, other additives like coolant or minor fuels. These ingredients are pre-mixed and subsequently combined with a smoke dye.

The great benefit for producers and consumers is that the need to have a certain number of different smoke formulations in stock serving each colour is gone. In comparison to the conventional smoke signals, the quick-mixing of only two premixed powders (fuel mix + dye) with known quality produces the desired smoke colour. As a result, not only the required space for safe storage is reduced dramatically, but also the total amount of energetic materials stored in the same place drops accordingly. Based on previous work carried out within our group, we investigated the effect of applying 5-amino-1*H*-tetrazole (5-AT) as main fuel in so-called fuel mixes.[25,26] Hereby, the main combustion product of the fuel would be N_2.[27] The slightly higher decomposition temperature compared to sucrose allowed the application as alternative fuel. The small temperature difference itself might be partially explained by the existence of non-oxidized bonds in 5-AT. $KClO_3$ in combination with 5-AT served as the oxidizer/fuel pair; magnesium carbonate hydroxide pentahydrate (MCHP) was the coolant. Most of the applied dyes belong to the anthraquinone group. Disperse Red 9 ((1-methylamino) anthraquinone) was applied for red, Solvent Green 3 (1,4-di-*p*-toluidino-9,10-anthraquinone) for green and Solvent Yellow 33 (2-(2-quinolyl)-1,3-indandione) for yellow. Moreover, to obtain a violet smoke signal the Violet Smoke Dye Mix consisting of the two dyes Disperse Red 9 and Solvent Violet 47 (1,4-diamino-2,3-dihydroxyanthraquinone) were applied.[8]

In a first step different ratios of the pre-mixed powders (oxidizer + fuel + coolant = fuel mix)

Table 8.1: Properties of yellow-, green-, red- and violet-coloured smoke formulations based on fuel mixes **FM1**, **FM2**, **FM3** and **Ref-FM**.

	BT/s	**Y**/%	**T%**/%	$\mathbf{m_{HPLC}}$/mg	**ESD**/J	$\mathbf{T_{onset}}$/°C
Y1	15	29	59	354	1.0	184
Y2	26	21	56	233	0.4	189
Y3	29	30	49	292	0.5	187
Ref-Y	13	33	73	435	0.3	178
G1	20	36	–	–	0.4	192
G2	45	24	–	–	0.2	198
G3	31	31	–	–	0.5	194
Ref-G	19	32	–	–	0.2	172
R1	20	29	76	457	0.5	184
R2	75	25	58	351	0.7	182
R3	41	28	72	432	0.5	189
Ref-R	21	36	86	514	0.6	172
V1	23	29	–	–	0.2	182
V2	27	26	–	–	0.3	186
V3	27	29	–	–	0.3	180
Ref-V	15	32	–	–	0.7	178

Annotation: measured for 2.0 g pellet; BT = burn time; Y = yield; T% = transfer rate; m_{HPLC} = dye content present in aerosol; ESD = electric discharge sensitivity; T_{onset} = onset temperature of decomposition; impact sensitivity = 40 J for all measured formulations (only Ref-G / Ref-V = 30 N); friction sensitivity = 360 N for all measured formulations; see ESI for summary of all properties.

and the dye were tested to give a coloured smoke cloud. The second step focused on adapting the colour. Diviacchi stated earlier, that the actual colour impression of the emerging smoke may be different from the labeled colour.[8] To overcome this issue, we applied a dye mixture in case the colour was too dark or brighter than intended. The focus of the herein presented results was on the dyes applied in the U.S. M18 coloured smoke grenades and mixtures thereof.[28] At this point, we were not interested in investigating the toxicity issues arising from the dyes or resulting combustion products.[8,17,28–32]

Instead, we developed three different 5-AT-based fuel mixes (**FM1**, **FM2**, **FM3**) and compared them towards a sucrose-based reference formulation (**Ref-FM**) of the same dye in terms of performance and smoke persistence. HPLC measurements were carried out to quantify the effective amount of dye present in the collected aerosol.

8.2. Results and Discussion

Developtment of Coloured Smokes

A suitable starting point to fulfil the concept of fuel mixes is an exactly stated testing protocol as outlined by Domanico (see ESI).[7] Due to the existing differences in terms of physical behaviour and chemical stability, a screening of several different fuel mix ratios was performed. Therefore, the amount of dye (30 %) was fixed, while the remaining 70 % was the respective fuel mix. The first step of this presented study was the investigation of working smoke compositions for each dye separately. Subsequently, the optical performance evaluation included the emerging colour impression, smoke thickness as well as burning behaviour. The most advanced formulations were selected for further testing and evaluation, such as yield, burn time and rate, transfer rate and sensitivity towards mechanical stimuli as well as thermal stability (Table 8.1).

A fuel mix might be more sensitive than the final coloured smoke formulation. To ensure safe handling in every single manufacturing step, *e.g.* the mixing and grinding of fuel mixes starting from the single components or the final coloured smoke formulations, the sensitivities have to be determined also for all intermediate steps. The most promising fuel mixes for further characterization are illustrated within a ternary diagram (Figure 8.2). The first fuel mix **FM1** consisted of 50 wt% 5-AT, 30 wt% $KClO_3$ and 20 wt% MCPH and therefore, contained the highest amount of oxidizer. **FM2** had a ratio of 50 wt% 5-AT to 20 wt% $KClO_3$ to 30 wt% MCPH and **FM3** had the highest amount of the fuel 5-AT (60 wt%) and equal contents of $KClO_3$ and MCPH (20 wt%). The reference fuel mix **Ref-FM** contained 40 wt% sucrose, 40 wt% $KClO_3$ and 20 wt% MCPH (see ESI for a complete listing of formulation ingredients and weight percentages). Further, the properties of the resulting coloured smoke formulations (Tables 8.2 and 8.3) based on these fuel mixes are summarized in Table 8.1.

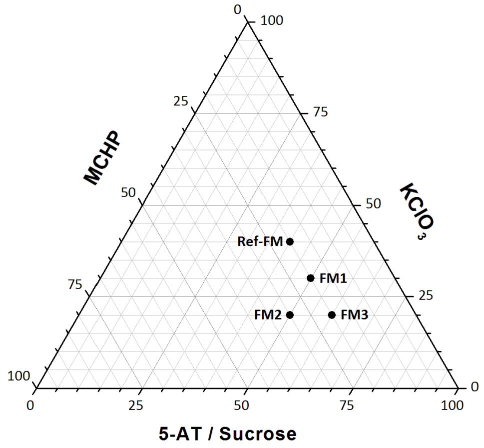


Figure 8.2: Developed fuel mixes. **FM1** = 5-AT (50 wt%), $KClO_3$ (30 wt%), MCHP (20 wt%); **FM2** = 5-AT (50 wt%), $KClO_3$ (20 wt%), MCHP (30 wt%); **FM3** = 5-AT (60 wt%), $KClO_3$ (20 wt%), MCHP (20 wt%); **Ref-FM** = sucrose (40 wt%), $KClO_3$ (40 wt%), MCHP (20 wt%). See Tables 8.2 and 8.3 for a complete listing of formulation ingredients, weight percentages and ESI for brief explanation of the triangle diagram.

Properties of Smoke Formulations

In this context, formulations **Y1**, **G1**, **R1** and **V1** were referred to **FM1**, while **FM2** was the basis for **Y2**, **G2**, **R2** and **V2**. The compositions **Y3**, **G3**, **R3** and **V3** were based on **FM3** and fuel mix **Ref-FM** resulted in coloured reference formulations. In detail, **FM1**- and **Ref-FM**-based formulations resulted in rapid, strong smoke generation, while **FM2**- and **FM3**-based compositions produced smoke continuously over a longer period of time. This trend was also reflected in terms of burn time (**FM1** or **Ref-FM**: 12–23 s compared to **FM2** or **FM3**: 26–45 s) as well as burn rate. An exception was **R2** with the overall longest burn time of 75 s. All tested smoke formulations were insensitive towards impact and friction except of **Ref-G** and **Ref-V**, which were classified as less sensitive. Moreover, they all were insensitive towards electrostatic discharge. The decomposition temperatures were in the range of 172–198 °C. The measurements of all coloured smoke formulations and their references were carried out on approximately similar humidities (see ESI). More precisely, the performance and in particular the yield Y of hygroscopic smoke

Table 8.2: Yellow- and green-colored smokes based on **FM1**, **FM2**, **FM3** and **Ref-FM** (in wt%).

	Y1	**Y2**	**Y3**	**G1**	**G2**	**G3**	**Ref-Y**	**Ref-G**
$KClO_3$	21	14	14	21	14	14	28	28
5-AT	35	35	42	35	35	42	–	–
MCPH	14	21	14	14	21	14	14	14
Sucrose	–	–	–	–	–	–	28	28
Solvent yellow 33	30	30	30	10	10	10	30	10
Solvent green 3	–	–	–	20	20	20	–	20

Table 8.3: Red- and violet-colored smokes based on **FM1**, **FM2**, **FM3** and **Ref-FM** (in wt%).

	R1	**R2**	**R3**	**V1**	**V2**	**V3**	**Ref-R**	**Ref-V**
$KClO_3$	21	14	14	21	14	14	28	28
5-AT	35	35	42	35	35	42	–	–
MCPH	14	21	14	14	21	14	14	14
Sucrose	–	–	–	–	–	–	28	28
Disperse Red 9	30	30	30	–	–	–	30	–
Violet Smoke Dye Mix	–	–	–	30	30	30	–	30

mixtures is strongly dependent on the relative humidity, since at higher humidity levels higher yields are obtained.[26] It is noticeable, that the yield of **FM2** was significantly worse for all tested dyes in the range of 21–26 %. In contrast, formulations based on **FM3** were approximately as efficient as **FM1** (28–31 %) with the exception of **G1** (36 %). However, the yield of **Ref-FM**-based smokes was slightly higher for yellow, red and violet smoke in the range of 32–33 %.

It has to be stated, that not all produced aerosol disseminated by coloured smoke formulations is in fact the implemented dye. More precisely, the term aerosol describes the total amount of produced non-gaseous reaction products including soot, water, dye and all other resulting combustion products. Whereas the information about the collected aerosol is sufficient for obscurants to calculate the yield (quotient between the amount of collected aerosol divided by the pyrotechnical payload), we were interested in the exact amount of dye present in the aerosol.

The so-obtained values were used for the calculation of the previously introduced term of the transfer rate by the authors (quotient between the amount of actually dispersed dye divided by the amount of dye in the pellet).[26] Dye which remains in the pyrotechnical device or is consumed by the flames does not contribute to the optical performance. The optimized ratio between the amount of applied dye and successfully dispersed dye would contribute to a more sustainable material life-circle, since less unburned material is spread into the environment. Due to the high solubility in organic solvents, HPLC analysis of the collected aerosol was performed and revealed the dye concentration in the aerosol (Table 8.1).

Table 8.4: Sensitivity data of fuel mixes **FM1**, **FM2**, **FM3** and **Ref-FM**.

	IS/J	**FS**/N	**ESD**/J	$\mathbf{T_{onselt}}$/°C
FM1	6	252	1.5	331
FM2	20	360	0.3	342
FM3	20	360	0.1	337
Ref-FM	20	360	1.5	172

Annotation: IS = impact sensitivity; FS = friction sensitivity; ESD = electric discharge sensitivity; T_{onset} = onset temperature of decomposition.

Discussion Transfer Tate / HPLC

HPLC measurements revealed a transfer rate of 49–73 % for the yellow smoke formulations. **Ref-Y** based on sucrose achieved the highest transfer rate, followed by **Y1** with 59 %. Compared to the yellow smoke compositions, an increase of the transfer rate was observed for the red dye. Formulations **R1**–**R3** and **Ref-R** displayed transfer rates in the range of 58–86 %. Here again, the sucrose-based fuel mix achieved the best value followed by **R1**.

A change of the solution colour was observed for the violet dye mix in acetonitrile upon measurement. Re-running the measurements in darkened glass showed the same result displaying additional peaks. It was concluded, that the dye mix is not stable in solution and was therefore excluded from the HPLC measurements. The green formulations applying a mixture of two dyes proofed to be more difficult than expected and will be addressed in the future.

Properties of Fuel Mixes

The characterization of sensitivity data is mandatory for producers as well as consumers, since the handling, preparing and in particular storing of such fuel mixes need to be safe. Therefore, the sensitivities were determined additionally for the novel fuel mixes (Table 8.4).

In detail, the tested fuel mixes were sensitive towards impact, where the impact sensitivity of **FM1** was comparatively higher with 6 J. It is literature known that higher amounts of $KClO_3$ lead to higher sensitivities. Besides that, the exothermic decomposition process of $KClO_3$ causes an acceleration to the rate of reaction.[33] In contrast to this, **FM2**, **FM3** and **Ref-FM** were classified as insensitive towards friction, while **FM1** was sensitive. All samples were insensitive towards electrostatic discharge except of **FM3** reaching the transition between sensitive and insensitive material. The onset temperatures of decomposition of 5-AT-based fuel mixes were significantly higher in the range of 331–342 °C in comparison with the sucrose-based reference **Ref-FM** (172 °C). Therefore, these fuel mixes are potentially sensitive energetic materials and must be handled with care and caution.[34]

8.3. Conclusions

The successful demonstration of 5-AT-based fuel mixes to produce green, yellow, red and violet smoke is presented. The developed formulations revealed that non-traditional high-nitrogen fuels can produce smoke of high colour quality. More precisely, **FM1**-based mixtures resulted in a rapid, strong smoke generation in a short time, while **FM3**-based compositions were characterized by a slow, continuous smoke generation over a much longer period of time. 5-AT is only one of the potential candidates, which should be considered for future investigations. Sensitivity measurements revealed that all developed formulations are insensitive towards friction. In addition, all developed 5-AT-based coloured smoke formulations are completely insensitive towards impact. The fuel mixes were more sensitive towards mechanical stimuli. A comparison of the collected aerosol revealed similar yields for **FM1**-based and sugar-based formulations. The superiority of prepared sugar-based reference formulations was displayed by the measured transfer rates. The obtained baseline (yield, transfer rate) are the first literature-reported values for sugar- and 5-AT-based coloured smoke formulations. Future investigations in our group will focus on providing even more coloured smoke formulations, *e.g.* blue and black, applying the same fuel mixes. To secure a proper evaluation, new strategies to characterize aerosol produced by a mixture of two dyes (*e.g.* green dye mix) has to be established.

8.4. Experimental Section

Chemicals and Sample Preparation. Sucrose ($\geq$99 %), and magnesium carbonate hydroxide pentahydrate (BioXtra) were purchased from Sigma-Aldrich. 5-AT (98 %) was purchased from abcr chemicals. Potassium chlorate ($\geq$99 %) was purchased from Grüssing GmbH. Disperse Red 9, Solvent Green 3, Solvent Yellow 33 and the Violet Mix Smoke Dye were purchased by Nation Ford Chemical. For initial testing, small mixtures (2 g) were carefully mixed manually for 4 min in a mortar by combining the dry compounds. If those tests were successful, larger mixtures (40 g) were prepared by combining the dry components in a cylindrical rubber barrel and rolling for 120 min. The rotatory rock tumbler (model 67631) was built by Chicago Electric Power Tools and operated with steel balls. To remove any clumps, the compositions were passed through an 800 µm screen. 2 g of this so-prepared composition was pressed into a cylindrical steel compartment (diameter 2 cm), with the aid of a tooling die and a hydraulic press. The used consolidation dead load of 3 t was applied for 3 s, if not stated otherwise. Each pellet was ignited using a resistance heating Kanthal® A1 wire (FeCrAl, 0.8 mm diameter, $2.9\,\Omega\,\mathrm{m}^{-1}$). For each composition, three pellets were tested and the results were averaged.

Aerosol Quantification. The setup to collect the aerosol was described previously.[25,26] In detail, a Thermo Scientific™ DIONEX™ UltiMate™ 3000 HPLC System accucore RP-MS column (3 mm × 150 mm, particle size 2.6 mm) with a DAD-3000 photometer and Chromeleons® 7.2 Chromatography Management Software was used to quantify the amount of dye (see ESI for exact method). The measurements were performed in cooperation with the CBRN Defense, Safety and Environmental Protection School of the German Bundeswehr (CDSEP-School), Sonthofen (Germany).

Burn Rate. The testing protocols as well as pellet sizes are given in the ESI. However, we were facing serious problems to determine the burn rate at different pellet sizes. Some formulations which produced smoke on a rather small height / diameter ratio burned with an open flame at higher height / diameter ratios. The collected data is provided in the ESI.

Sensitivities and Thermal Stability. The impact and friction sensitivities were determined using a BAM Drophammer and a BAM Friction Tester (method 1 of 6). The sensitivities of the compositions are indicated according to the UN Recommendations on the Transport of Dangerous Goods (+): impact: insensitive >40 J, less sensitive ≥40 J, sensitive >4 J, very sensitive <4 J; friction: insensitive >360 N, less sensitive =360 N, sensitive 360 N > x > 80 N, very sensitive <80 N, extreme sensitive <10 N.[1] Thermal stability measurements: onset temperatures were measured with an OZM Research DTA 552-Ex Differential Thermal Analyzer at a heating rate of 5 °C min^{-1}. Electrostatic discharge was measured with an OZM small-scale electrostatic spark X SPARK 10. ESD: sensitive <0.1 J, insensitive >0.1 J.

8.5. References

[1] T. Klapötke, *Chemistry of High-Energy Materials*, Boston: De Gruyter, Berlin, **2017**.

[2] Headquarters, *Field Manual 21-60, Visual Signals*, Department of the Army, US Government Printing Office, Washington, DC, USA, **1987**.

[3] C. Sterling, *Military Communications: From Ancient Times to the 21st Century*, ABC-CLIO, Santa Barbara, CA, USA, **2008**.

[4] H. Webster in *Inorganic red smoke compositions*, *Proceedings of the 8th International Pyrotechnics Seminar*, IPS, Steamboat Springs, CO, USA, **1982**.

[5] *Engineering Design Handbook: Design of Ammunition for Pyrotechnic Effects*, Military Pyrotechnics Series, Part Four, Washington, DC, USA, **1974**.

[6] Chinese artist creates daytime firework display, `http://www.dailymail.co.uk/news/article-2072514/Cai-Guo-Qiang-Chinese-artist-creates-fireworks-display-daytime.html` (visited on March 1, 2020).

[7] J. Domanico in *Using a Standard Testing Protocol to Qualify Candidate Low Toxicity Colored Smoke Dyes*, *Proceedings of the 35th International Pyrotechnics Seminar*, IPS, Fort Collins, CO, USA, **2008**.

[8] G. Diviacchi in *Evaluation of Low Toxicity Colored Smoke Dyes*, *Proceedings of the 35th International Pyrotechnics Seminar*, IPS, Fort Collins, CO, USA, **2008**.

[9] J. Sabatini in *Advances Toward the Development of "Green" Pyrotechnics*, *Green Energetic Materials*, John Wiley & Sons Ltd, Inc., West Sussex, UK, **2014**.

[10] H. Ellern, *Military and civilian pyrotechnics*, Chemical Pub. Co, New York City, NY, USA, **1968**.

[11] Safety Marine - Marine Safety Equipment, `http://www.rms.nsw.gov.au/maritime/safety-rules/safety-equipment/index.html` (visited on November 1, 2017).

[12] Safety Marine - Marine Safety Equipment, `http://www.safety-marine.co.uk/` (visited on November 1, 2017).

[13] J. Conkling, C. Mocella, *Chemistry of Pyrotechnics: Basic Principles and Theory*, CRC Press, Boca Raton, **2010**.

[14] J. Conkling, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons Ltd, Inc., West Sussex, UK, **2000**.

[15] K. Kosanke, B. Kosanke, B. Sturman, T. Shimizu, M. Wilson, I. Maltitz, R. Hancox, N. Kubota, C. Jennings-White, D. Chapman, D. Dillehay, T. Smith, M. Podlesak, *Pyrotechnic Chemistry*, Journal of Pyrotechnics Inc., UK, **2004**.

[16] D. Lundy, J. Eaton, *Occupational Health Hazards Posed by Inventory US Army Smoke / Obscurant Munitions*, US Army Medical Research Detachment, Wright-Patterson Air Force Base, for Walter Reed Army Institute of Research, Washington, DC, USA, **1994**.

[17] I. Rubin, M. Buchanan, J. Moneyhun, *Chemical characterization and toxicologic evaluation of airborne mixtures. Chemical characterization of combusted inventory red and violet smoke mixes*, U.S. Army Medical Research and Development Command, Fort Detrick, Maryland, USA, **1982**.

[18] G. Chen, S. Showalter, G. Raibeck, J. Wejsa, *Environmentally Benign Battlefield Effects Black Smoke Simulator*, **2006**.

[19] J. Moretti, J. Sabatini, A. Shaw, G. Chen, R. Gilbert, K. Oyler, *ACS Sustainable Chem. Eng.* **2013**, *1*, 673–678.

[20] J. Moretti, J. Sabatini, A. Shaw, R. Gilbert, *ACS Sustainable Chem. Eng.* **2014**, *2*, 1325–1330.

[21] A. Shaw, J. Poret, R. Gilbert, J. Domanico, E. Black, *Propellants Explos. Pyrotech.* **2013**, *38*, 622–628.

[22] A. Shaw, J. Brusnahan, J. Poret, L. Morris, *ACS Sustainable Chem. Eng.* **2016**, *4*, 2309–2315.

[23] N. Caldwell, N. Hutslar, T. Clements in *Developmental coloured smoke systems based on azide-containing polymeric binders*, *Proceedings of the 20th International Pyrotechnics Seminar*, IPS, Colorado Springs, CO, USA, **1994**.

[24] G. Raibeck, G. Chen in *Assessment of Organic Fuels for Use in Environmentally Benign Colored Smoke Formulations*, *Proceedings of the 35th International Pyrotechnics Seminar*, IPS, Fort Collins, CO, USA, **2008**.

[25] J. Glück, T. Klapötke, A. Shaw, *Cent. Eur. J. Energ. Mater.* **2017**, *14*, 489–500.

[26] J. Glück, T. Klapötke, M. Rusan, A. Shaw, *Propellants Explos. Pyrotech.* **2017**, *42*, 131–141.

[27] A. Lesnikovich, O. Ivashkevich, S. Levchik, A. Balabanovich, P. Gaponik, A. Kulak, *Thermochim. Acta* **2002**, *388*, 233–251.

[28] Subcommittee on Military Smokes and Obscurants, National Research Council, *Toxicity of Military Smokes and Obscurants, Volume 3*, The National Academies Press, Washington, DC, USA, **1999**.

[29] G. Bondy, C. Armstrong, B. Dawson, C. Héroux-Metcalf, *Toxicol. In Vitro* **1994**, *8*, 329–335.

[30] M. Hemmilä, M. Hihkiö, K. Linnainmaa, *Propellants Explos. Pyrotech.* **2007**, *32*, 415–422.

[31] T. Marrs, H. Colgrave, P. Rice, J. Edginton, B. Morris, *J. Hazard. Mater.* **1989**, *21*, 73–88.

[32] M. van Hulst, J. Langenberg, W. de Klerk, M. Alblas, *Propellants Explos. Pyrotech.* **2016**, *42*, 17–23.

[33] R. Wharton, A. Barratt, *Propellants Explos. Pyrotech.* **1993**, *18*, 77–80.

[34] BAM Bundesanstalt für Materialforschung und -prüfung, *Empfehlungen für die Beförderung gefährlicher Güter - Handbuch über Prüfungen und Kriterien*, Bundesanstalt für Materialforschung und -prüfung, Berlin, **2015**.

8.6. Supporting Information

Explanation of Triangle Diagrams

The illustration as a triangle diagram (Figure 8.3) is a powerful tool to summarize the results of all kind of pyrotechnical formulations. In detail, this diagram includes three axes representing three different components from 0–100 %. Every point defines an unique ratio of the components applied.

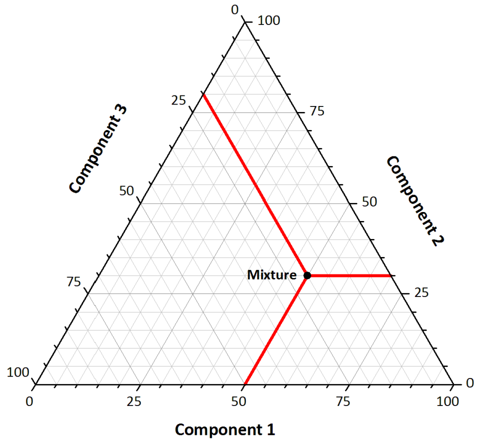


Figure 8.3: Triangle diagrams: how to read.

Since the reading direction is unintuitive for diagrams with three axes, it is marked with red lines in Figure 8.3 for a mixture containing 50 % of component 1, 30 % of component 2 and 20 % of component 3. Therefore, it is mandatory that the percentages of all three components results in 100 %. The artificial lines at the scale of every axe additionally support the given reading direction. Triangle diagrams offer promising advantages for pyrotechnics. They can discover hidden trends and relationships between different ratios of components, and for this reason, lead quickly to an optimum pyrotechnical formulation. A more detailed explanation and study exercises is given by Kosanke (K. L. Kosanke, B. J. Kosanke, *Selected pyrotechnic publications of K. L. and B. J. Kosanke*, Journal of Pyrotechnics, Whitewater, CO, USA, **1995**).

Testing Protocol

The testing protocol includes eight preliminary fuel mixes for initial burning tests. Therefore, the resulting smoke formulations have a fixed amount of 30 % dye, while the remaining 70 % is one of the specific fuel mixes consisting of various ratios of oxidizer, fuel and coolant (Figure 8.4).

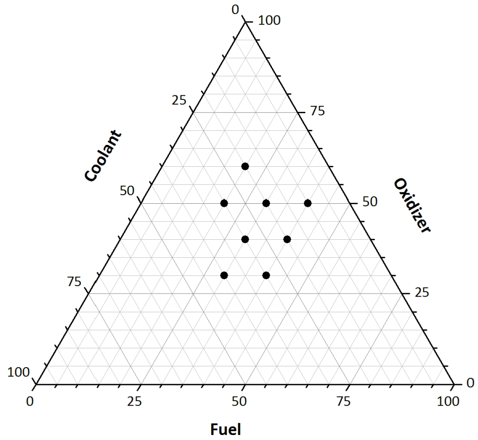


Figure 8.4: Initial burning tests.

A more detailed explanation and study exercises is given by Domanico (J. A. Domanico, *Using a Standard Testing Protocol to Qualify Candidate Low Toxicity Colored Smoke Dyes*, 35th International Pyrotechnics Seminar, Fort Collins, CO, USA, **2008**)

Aerosol Determination

The arising aerosol of four pellets (2.0 g) per formulation was collected and averaged.

Table 8.5: Aerosol of multi-colored smoke formulations based on **FM1**, **FM2**, **FM3** and **Ref-FM**.

	Y1	**Y2**	**Y3**	**G1**	**G2**	**G3**	**Ref-Y**	**Ref-G**
Aerosol/g	0.584	0.418	0.593	0.720	0.486	0.636	0.670	0.642
	R1	**R2**	**R3**	**V1**	**V2**	**V3**	**Ref-R**	**Ref-V**
Aerosol/g	0.499	0.590	0.574	0.575	0.522	0.578	0.729	0.652

HPLC Strategy

A Thermo Scientific™ Dionex™ UltiMate™ 3000 HPLC System accucore RP-MS column (3 mm × 150 mm, particle size 2.6 mm) with a DAD-3000 photometer and Chromeleons® 7.2 Chromatography Management Software was used to quantify the amount of dye. The single component devices were: SRD-3400 4-channel degaser eluenten-rack, HPG-3400SD gradient pump, WPS-3000TSL (Analytical) autosampler, TCC-3000SD column oven.

Mobile phase: A = water/acetonitrile (95/5), B = water/acetonitrile (5/95)

Gradient: 0 min (50 % A), 5 min (0 % A), 8 min (0 % A), 14 min (50 % A)

Flow rate: 0.3 mL min^{-1}

Injection volume: 5 µL

DAD: 220 nm, 250 nm; 3D-area: 190–800 nm

Column temperature: 30 °C

Sample temperature: 20 °C

Smoke Characterization

The solution of violet smoke dye mix in acetonitrile already degraded during measurement. A change of the coloured solution was observed within a few hours. The green formulations applying two dyes will be addressed in the future.

Burn Rate

Compositions were pressed into cardboard tube for burn rate studies. The cardboard rolls, cylindrical and open on both ends, had a 2.5 cm inner diameter, 3.0 cm height, and a 1.6 mm wall thickness. The compositions (10 g) were pressed with a consolidation dead load of 3 t for 10 s. The pellets were ignited at the top using a resistance heating Kanthal® A1 wire (FeCrAl, 0.8 mm diameter, 2.9 Ω m^{-1}). Upon testing of formulations with 3 g pyrotechnical payload and cylindrical pellet sizes of 1.0 cm diameter and 2.8 cm height, some of those formulations burned with an open flame and produced no smoke anymore. The so-obtained values should be treated with care, since a lot of factors such as the surface, pressure, humidity and the pellet size influence the observed burn rate. Large deviations are obtained for different pellet sizes / payloads (Table 8.6).

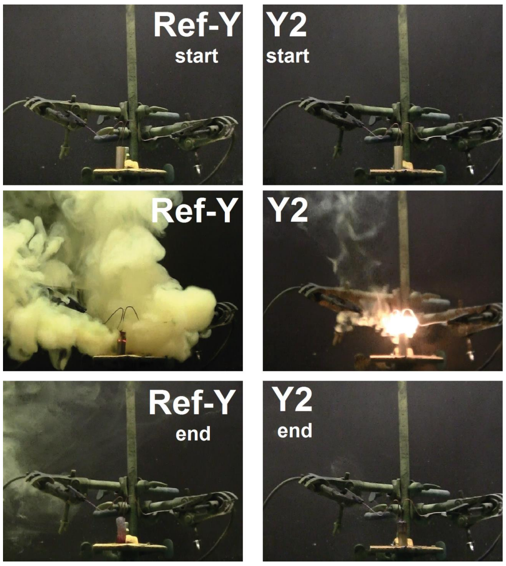


Figure 8.5: Burning of **Ref-Y** and **Y2** with a pellet size of 3 g.

Table 8.6: Burn rate of yellow-, green, red- and violet-colored smoke formulations based on fuel mixes **FM1**, **FM2**, **FM3** and **Ref-FM**.

	BT/s 10 g pellets	**BR**/g s^{-1} 10 g pellets	**BR**/g s^{-1} 3 g pellets	**BT**/s 3 g pellets
Y1	15	0.34	0.10	25
Y2	26	0.10	flame	–
Y3	29	0.10	flame	–
Ref-Y	13	0.43	0.08	37
G1	20	0.32	0.09	38
G2	45	0.08	–	–
G3	31	0.12	–	–
Ref-G	19	0.41	–	–
R1	20	0.29	–	–
R2	75	0.07	–	–
R3	41	0.07	–	–
Ref-R	21	0.29	–	–
V1	23	0.28	–	–
V2	27	0.07	–	–
V3	27	0.08	–	–
Ref-V	15	0.43	–	–

Table 8.7: Properties of yellow-, green, red- and violet-colored smoke formulations based on fuel mixes **FM1**, **FM2**, **FM3** and **Ref-FM**.

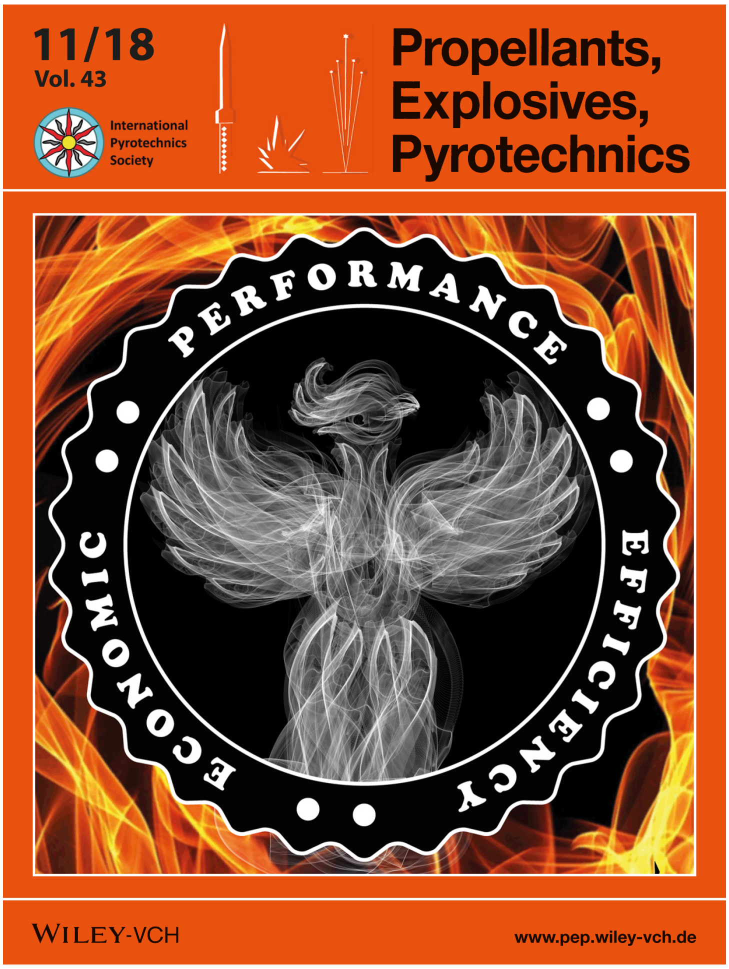
	BT/s	**BR**/g s^{-1}	**Y**/%	**RH**/%	**T%**/%	$\mathbf{m_{HPLC}}$/mg	**IS**/J	**FS**/N	**ESD**/J	$\mathbf{T_{onset}}$/°C
Y1	15	0.34	29	26	59	354	40	360	1.0	184
Y2	26	0.10	21	23	56	233	40	360	0.4	189
Y3	29	0.10	30	33	49	292	40	360	0.5	187
Ref-Y	13	0.43	33	29	73	435	40	360	0.3	178
G1	20	0.32	36	33	–	–	40	360	0.4	192
G2	45	0.08	24	34	–	–	40	360	0.2	198
G3	31	0.12	31	33	–	–	40	360	0.5	194
Ref-G	19	0.41	32	28	–	–	30	360	0.2	172
R1	20	0.29	29	29	76	457	40	360	0.5	184
R2	75	0.07	25	28	58	351	40	360	0.7	182
R3	41	0.07	28	29	72	432	40	360	0.5	189
Ref-R	21	0.29	36	28	86	514	40	360	0.6	172
V1	23	0.28	29	28	–	–	40	360	0.2	182
V2	27	0.07	26	26	–	–	40	360	0.3	186
V3	27	0.08	29	29	–	–	40	360	0.3	180
Ref-V	15	0.43	32	28	–	–	30	360	0.7	178

Annotation: measured for 2.0 g pellet; BT = burn time; BR = burn rate (10.0 g pellet); Y = yield; RH = relative humidity; T% = transfer rate; m_{HPLC} = dye content present in aerosol; IS = impact sensitivity; FS = friction sensitivity; ESD = electric discharge sensitivity; T_{onset} = onset temperature of decomposition.

Combining Higher Efficiency with Lower Costs: an Alternative Hexamine-Based White Smoke Signal

by

Teresa Küblböck and Thomas M. Klapötke



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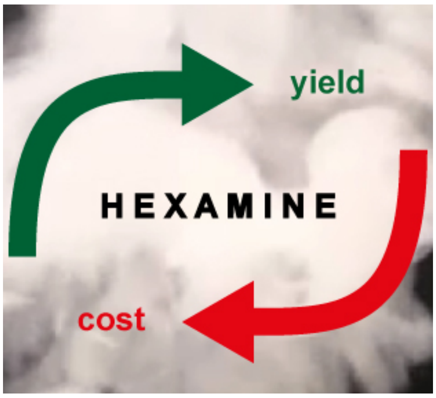

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Abstract The effect of applying hexamine as main fuel in terephthalic acid-based white smoke formulations is discussed. For this reason, a simple four ingredients mixture only consisting of terephthalic acid, hexamine, potassium chlorate and a magnesium carbonate derivative was introduced. We started from a minimum amount of dye and constantly increased the dye percentage in 5.0 wt% in the aerosol can be optimized to obtain the most persistent, thick white smoke cloud. Previous research on white smokes in our group indicated an overall higher smoke performance in terms of efficiency and advanced persistence by using 5-amino-1*H*-tetrazole as main fuel instead of sugar. From a costs point of view, hexamine would be favored, since it offers a low-cost alternative to 5-amino-1*H*-tetrazole.

9.1. Introduction

Smoke-generating pyrotechnics are commonly applied in the military sector. In this context, white smoke is used predominantly as obscurants for self-protection, while colored smoke is applied for both ground and ground-to-air signaling as well as marking.[1,2] Rarely, smoke signals find application in the civil sector as daylight firework, however, such events become more popular nowadays.[3] Today, the main consumer of white smoke still remains the military.[4] Historically, the AN-M8 hexachloroethane (HC) smoke grenade was used due to its high efficiency. In this case, the underlying smoke-generating mechanism is very different to colored smoke formulations: a typical HC mixture contains aluminum, zinc oxide and HC. During the combustion reaction, highly hygroscopic zinc (II) chloride is formed rapidly absorbing moisture from the air to generate a dense white smoke cloud.[1,5–7] As a result, smoke yields above 100 % can be reached under optimal conditions mainly depending on the humidity. However, Shinn indicated this kind of smoke as the worst for health and environment.[8] During the combustion, highly toxic polychlorinated organic compounds can arise, which are believed to be carcinogenic.[9,10] Therefore, due to toxicity issues the HC-based obscurants are no longer produced.[7] Up to now, the AN-M83 smoke grenade based on terephthalic acid (TA) served as an environmentally benign alternative. This mixture is very similar to the colored ones and follows the same sublimation-recondensation mechanism. However, the TA-based smoke cannot compete with historically used HC grenade in terms of thickness, smoke volume or optical properties making further research mandatory.[1,5,7]

In general, these kind of smoke signals can be referred to as cool-burning pyrotechnics reaching only temperatures in the range of the sublimation point of the applied dyes.[5,11] In contrast to this, HC-based smoke mixtures decompose at very high temperatures up to over 800 °C under luminous flame presence.[12] A cool-burning smoke mixture has the ability to gradually and slowly rise from the ground serving an effective screening and obscuration tool for military use.[5,11] If the resulting combustion temperature is in the optimal range, the dye is sublimate, leaves the compartment and recondensate in the surroundings. Additionally, the resulting dye particles are dispersed through the gaseous products of the proceeding redox reaction, creating a large dense smoke cloud.[1,5,13,14] The specific characterization of white and colored smoke signals include the color impression, quality and thickness of the emerging smoke cloud, the duration of smoke generation and the time it takes for the aerosol to sedimentate.[5,15] The produced aerosol not only consists of dye, but also other solid combustion products can arise.[16] The performance and in particular the yield of hygroscopic smoke mixtures is strongly dependent on the relative humidity, since at a higher humidity higher yields can be reached.[16] Therefore, it is mandatory to determine all smoke properties at the same ambient conditions to ensure reproducibility; however, minor changes in the humidity may have influence on the results.[16,17] The most important characteristic of white smoke is the optical performance with respect to their application as obscurant.[12,18,19] The mass-based figure of merit FM_m is a promising value to compare the efficiency of various obscurants to each other.[16,20]

Recent research on white smokes in our group has found that sugar can be fully exchanged by 5-amino-1*H*-tetrazole (5-AT) in the acquainted TA system resulting in an overall improvement of smoke quality and persistence.[18] Since 5-AT is a comparatively expansive substance, the effect of the much cheaper hexamine was investigated. Sabatini *et al.* stated earlier, that either 5-AT or hexamine could be used to deoxidize the combustion flame in chlorine-free red-burning flares and therefore, is usually applied as main fuel in pyrotechnic formulations.[21–25] The focus lies on novel smoke systems reducing the environmental impact, minimization of production time, production steps and most importantly multi-color signals. In addition, the efficiency of novel pyrotechnic compositions should at least be the same as or higher compared to the old formulations.[7,26] There are several promising approaches in the experimental stage in the literature: Shaw *et al.* discussed the use of boron carbide as pyrotechnic fuel in combination with potassium nitrate as a possible alternative to HC-based smoke.[25] In a further theoretical study, they compared the thermodynamics of this B_4C / KNO_3 composition with a boron phosphide (BP / KNO_3) system.[27] In this case, BP is expected to function as *in situ* phosphorus source, since the commonly applied red phosphorus suffers from the formation of toxic phosphine gas and phosphoric acid during combustion.[27,28] Another theoretical and experimental study is given by Koch *et al.* describing white smoke formulations based on phosphorus (V) nitride with various nitrate, chlorate and perchlorate oxidizers, which also surpass the FM_m of red phosphorus.[29]

The effect of hexamine as main fuel on the resulting smoke properties was investigated using a modified US Army white smoke signal. Therefore, TA served as white smoke dye.[1,7] Beneficially, TA is an important ingredient for the plastics industry and is available in high purity at a moderate price.[30] The oxidizer of choice was potassium chlorate, which seems to be the only oxidizing substance to be used in low temperature sublimation smoke due to its exothermic decomposition and relatively low melting point.[1,5] In combination with organic fuels, it generates the ideal temperature range to sublime the dye rather than combust it.[31] Hexamine was applied as the only fuel. The last component of the newly developed smoke mixtures was magnesium carbonate pentahydrate hydroxide (MCPH) as a smooth coolant.[32]

Table 9.1: Formulations **W9** to **W14** based on W6 with increased TA contents.

	TA/wt%	**Hexamine**/wt%	$\mathbf{KClO_3}$/wt%	**MCPH**/wt%
W9	35.0	26.0	32.5	6.5
W10	40.0	24.0	30.0	6.0
W11	45.0	22.0	27.5	5.5
W12	50.0	20.0	25.0	5.0
W13	55.0	18.0	22.5	4.5
W14	60.0	16.0	20.0	4.0

9.2. Results and Discussion

The white-smoking compositions consisted of only four ingredients: 30 % TA and the remaining 70 % of various ratios of potassium chlorate, hexamine and MCPH. In detail, this testing protocol was outlined by Domanico.[30] The different ratios of the underlying fuel mixtures are illustrated in Figure 9.1. Starting from the eight preliminary formulations **W1** to **W8**, only **W3**, **W4** and **W6** resulted in a thick, white smoke cloud. Surprisingly, only 30 % TA within the mixture was sufficient for a dense smoke generation.[6,8,10] However, **W3** and **W4** formed sparkles during the whole burn. The slightly higher percentage of hexamine in **W6** weakens this observation due to its deoxidizing effect on the combustion flame.[21] It seems to be advantageous to use lower contents of MCPH in order to ensure higher burning temperatures, since the sublimation point of TA is 402 °C.[33] For this reason, it is expected that the underlying pyrotechnic system in **W6** (40 % hexamine, 50 % $KClO_3$, 10 % MCPH) provided enough energy for sublimation, but on the same time avoiding the formation of sparkles.

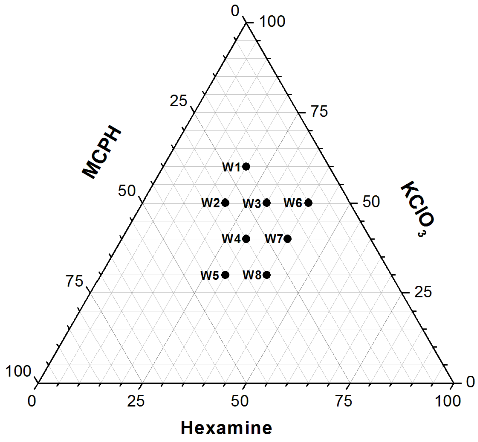


Figure 9.1: Triangle diagram of underlying fuel mixes of smoke formulations **W1** to **W8**. See ESI for an exact listing of weight percentages. An explanation is given by Kosanke in [34].

In analogy to the literature and – if applicable – to further optimize the smoke yield, the amount of TA was gradually increased from 30 % to 60 % in 5 % steps. The other components were each uniformly reduced, since the composition in W6 was the basis for the formulations **W9** to **W14** (Table 9.1). The best visual performance in terms of smoke thickness and burning behavior was observed in **W11** (45 % TA) and **W13** (55 % TA). It is noticeable, that an even higher amount of TA (60 %) in **W14** suffered from low smoke generation. Because of the relatively low content of other ingredients within this mixture, there are only few components left, which could promote the underlying redox reaction.

Table 9.2: Burn time, burn rate and yield factor of **W6**, **W11**, **W13**, **Ref-W1** and **Ref-W2**.

	BT/s	**BR**/g s^{-1}	**Y**/%	**RH**/%
W6	19	0.35	32	31
W11	38	0.26	35	31
W13	40	0.20	28	30
Ref-W1	28	–	27	66
Ref-W2	28	–	24	61

BT = burn time (2.0 g); BR = burn rate (10.0 g); Y = yield factor; RH = relative humidity.

For a more detailed characterization of smoke performance according to burning behavior, optical properties and yield, formulations **W6**, **W11** and **W13** were compared to literature-known references based on [18] (Table 9.2). The compositions of these white-smoking reference formulations are shown in the supporting information. In detail, **Ref-W1** applied a mixture of sucrose and 5-AT as fuel combination, while **Ref-W2** only contained 5-AT as main fuel. Thus, these formulations are suitable to investigate the effect of different fuels on the obscuration properties of white smokes. Moreover, both formulations contained stearic acid, which is commonly used as minor fuel and temperature regulator in pyrotechnics.[35] Another difference was the coolant. While **Ref-W1** also contained MCPH, the much stronger sodium bicarbonate was applied in **Ref-W2**.[32] **W6** has the highest burn rate of 0.35 g s^{-1}, followed by **W11** (0.26 g s^{-1}) and **W13** with 0.20 g s^{-1}. These values were also confirmed by the observed burn time: **W6** burned down very fast in 19 s, while **W11** and **W13** achieved almost similar time periods (38–40 s). As a result, it is possible to modify the burn rate and burn time by varying the TA content, while observing almost constant yields. For the references, no burn rates were given in the literature, however, it can be assumed by the burn times of 28 s that it would be in between **W6** and **W11**.

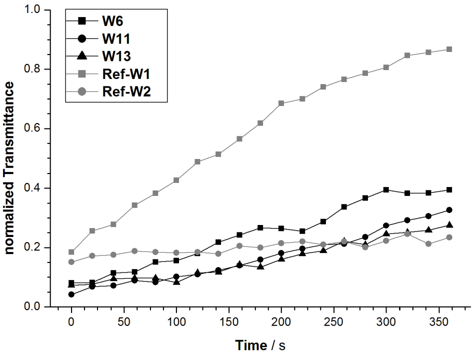


Figure 9.2: Normalized transmittance over time at 555 nm for **W6**, **W11**, **W13** and the references **Ref-W1** and **Ref-W2** for a time period of 6 min.

Unfortunately, the yield of the references **Ref-W1** and **Ref-W2** were determined at a humidity of 61–66 %, while the novel hexamine-based compositions were measured at 30–31 %. It is noticeable, that the yield of hexamine-based mixtures is significantly higher in comparison to the references considering the difference in humidity. **W6** with only 30 % TA content could provide a yield of 32 %. As expected, the increased amount of TA (45 %) in **W11** entailed an improvement of yield to 35 %. Nevertheless, the observed yield of formulation **W13** was reduced again to 28 %. The 5-AT-based reference **Ref-W2** led to a low yield of 24 %, while a fuel mixture of sugar and 5-AT

Table 9.3: Averaged transmittance over time and mass-based composition figure of merit FM_m of **W6**, **W11**, **W13**, **Ref-W1** and **Ref-W2**.

	T/%	$\mathbf{FM_m}$/m^2 g^{-1}	**RH**/%
W6	25	0.52	33
W11	17	0.66	34
W13	15	0.70	32
Ref-W1	59	0.20	27
Ref-W2	22	0.58	23

T = averaged transmittance (6 min, 555 nm); FM_m = mass-based figure of merit.

Table 9.4: Sensitivity data of **W6**, **W11**, **W13**, **Ref-W1** and **Ref-W2**.

	IS/J	**FS**/N	**ESD**/J	$\mathbf{T_{dec}}$/°C
W6	7	360	0.5	203
W11	10	360	0.6	203
W13	20	360	1.0	204
Ref-W1	35	360	1.0	164
Ref-W2	35	360	1.0	172

IS = impact; FS = friction; ESD = electrostatic discharge; T_{dec} = decomposition temperature.

in **Ref-W1** resulted in 27 %. Moreover, the characterization of optical properties of **W6**, **W11**, **W13** as well as **Ref-W1** and **Ref-W2** are summarized in Table 9.3. For discussion, the measurement carried out over a time period of 6 min for the transmittance at 555 nm is illustrated in Figure 9.2. The transmittance over time of **Ref-W1** changed drastically from 18 % to nearly 90 % in just 6 min. This means, that the smoke screen does not last long. In contrast, **Ref-W2** remained almost constant in the range of 15–23 % resulting in a well-dispersed, more persistent smoke cloud.[18]

Compared to the hexamine-based formulations, a similar trend to **Ref-W2** was observed. At the beginning of each measurement (0 s), the transmittance is in the range of 4–8 % for all three evaluated compositions. After 6 min of measurement, all three hexamine-based formulations were still in a range of 27–39 %, however, the transmittance increased slightly faster compared to **Ref-W2**. Finally, the transmittance over the whole time period of measurement was averaged for further comparison resulting in the values depicted in Table 9.3. Over the whole 6 min, **W13** achieved the lowest averaged transmittance of 15 %, while **W6** is slightly higher (25 %) and **W11** was in between. The averaged transmittance of **Ref-W1** performed the worst with 59 %, however, the 5-AT-based **Ref-W2** (22 %) is in the same range as **W6**.

As expected, the mass-based figure of merit FM_m of **Ref-W1** was even lower (0.20 m^2 g^{-1}) according to its yield and transmittance observed. The other formulations were all in a similar range of 0.52–0.70 m^2 g^{-1}. **Ref-W2** has a FM_m of 0.58 m^2 g^{-1} fitting in between **W6** and **W11**, while **W13** achieved the highest value of 0.70 m^2 g^{-1}. In conclusion, **W11** and **W13** resulted in similar efficiency.

Finally, an overview of the determined sensitivity data is given in Table 9.4. All tested white-colored smoke formulations were insensitive towards friction and electrostatic discharge. The reference mixtures were classified as less sensitive towards impact stimuli, while all hexamine-based compositions were moderate sensitive towards impact. Finally, the decomposition temperatures of hexamine-based smoke mixtures were in the range of 203–204 °C, while the decomposition temperatures of the references **Ref-W1** and **Ref-W2** were lower in the range of 164–172 °C. The slightly higher decomposition temperature of hexamine-based compositions could explain the higher yields observed, since more dye should be sublime. Although the mixtures should be handled with care and caution, since they are potentially sensitive energetic materials and can easily be ignited.[36]

9.3. Conclusion

Hexamine was investigated as alternative main fuel for white smoke compositions. Therefore, simple four ingredients mixtures were prepared consisting of only potassium chlorate, hexamine, TA and MCPH. As a consequence, three different white-smoking formulations were evaluated according to their burning behavior, yield as well as optical and energetic properties. For comparison, literature-known white-colored compositions based on 5-AT and a fuel mixture (sucrose / 5-AT) were considered. As a result, the newly developed hexamine-based formulations achieved always higher yields than the 5-AT- and sugar-based references. An explanation could be the significant higher decomposition temperature in the range of 203–204 °C, since it promotes the sublimation of TA rather than combustion. Further, the effect of increasing the TA content within a consistent mixture was studied. A slightly increase led to higher yields; a modification of burn time and burn rate is possible (**W6** and **W11**). However, an even higher TA percentage within the mixture (**W13**) worsens the yield, since the underlying redox reaction is suppressed.

The optical performance is one of the most important characteristic of white smoke. Therefore, the transmittance and mass-based figure of merit were determined to classify the optical properties. The transmittance of hexamine-based formulations was in the range of 4–8 % at the start of the measurement, which is significant lower compared to 5-AT. After 6 min of detection, the transmittance only increased to 15–17 % in comparison to the 5-AT (22 %) and sugar (59 %) mixture. For this reason, the hexamine-based formulations guarantee improved obscuration properties. All tested formulations were insensitive towards friction and ESD. However, the hexamine-based mixtures were slightly impact sensitive in comparison to the chosen references. Finally, the hexamine-based pyrotechnical compositions could serve as a low-cost alternative to 5-AT-based formulations due to the similar optical performance observed and at the same time higher yields.

9.4. Experimental Section

Chemicals. Hexamine (99 %, Acros Organics); 5-Amino-1*H*-tetrazole (98 %, abcr Chemicals); Terephthalic acid (98 %, Sigma-Aldrich); Sucrose (99 %, Sigma-Aldrich); Sodium bicarbonate (99 %, Sigma-Aldrich); Magnesium carbonate pentahydrate hydroxide (BioXtra, Sigma-Aldrich); Potassium chlorate (99 %, Grüssing GmbH); Stearic acid (95 %, Grüssing GmbH).

Sample Preparation. All pyrotechnic samples were prepared in 2.0 g scale using the same procedure in order to ensure the reproducibility. Therefore, the different ingredients were weighed into a sample glass according to their respective weight percentages in the formulations. After a rough initial mixing, each sample was transferred into a porcelain mortar and carefully ground to a homogeneous powder. The so-prepared compositions were pressed into a cylindrical shape with the aid of a tooling die using a hydraulic press with a dead load of 3.0 t for 3.0 s. All samples were burned within a smoke chamber (0.6 m × 0.6 m × 1.8 m). Each pellet was ignited using a resistance heating Kanthal® A1 wire (FeCrAl, 0.8 mm diameter, $2.9\,\Omega\,\mathrm{m}^{-1}$).[16,18]

Determination of Smoke Properties. The experimental setups for optical measurements, collecting the aerosol as well as the determination of burn rate and burn time were described previously (see ESI).[16,18] The transmittance mainly characterizes the ability of a smoke composition for visual obscuration, for this reason the peak photopic response of the human eye at 555 nm was chosen as fixed wavelengths for the evaluation of transmittance values.

Sensitivity Data. Impact and friction sensitivity were determined using a BAM Drophammer and a BAM Friction Tester (method 1 of 6). The sensitivities of the compositions are indicated according to the UN Recommendations on the Transport of Dangerous Goods (+): impact: insensitive >40 J, less sensitive ≥40 J, sensitive >4 J, very sensitive <4 J; friction: insensitive >360 N, less sensitive =360 N, sensitive 360 N > x > 80 N, very sensitive <80 N, extreme sensitive <10 N.[1] Thermal stability measurements: onset temperatures were measured with an OZM Research DTA 552-Ex Differential Thermal Analyzer at a heating rate of $5\,°\mathrm{C\,min}^{-1}$. Electrostatic discharge was measured with an OZM small-scale electrostatic spark X SPARK 10. ESD: sensitive <0.1 J, insensitive >0.1 J.

9.5. References

[1] T. Klapötke, *Chemistry of High-Energy Materials*, Boston: De Gruyter, Berlin, **2017**.

[2] H. Webster in *Inorganic red smoke compositions*, *Proceedings of the 8th International Pyrotechnics Seminar*, IPS, Steamboat Springs, CO, USA, **1982**.

[3] M. Russell, *The Chemistry of Fireworks*, The Royal Society of Chemistry, Cambridge, UK, **2009**.

[4] G. Lane, W. Smith, E. Jankowiak in *Novel Pyrotechnic Compositions for Screening Smoke*, *Proceedings of the 1st International Pyrotechnics Seminar*, IPS, Estes Park, CO, USA, **1968**.

[5] J. Conkling, C. Mocella, *Chemistry of Pyrotechnics: Basic Principles and Theory*, CRC Press, Boca Raton, **2010**.

[6] W. Muse, J. Anthony, J. Bergmann, D. Burnett, C. Crouse, B. Gaviola, S. Thomson, *Drug Chem. Toxicol.* **1997**, *20*, 293–302.

[7] J. Sabatini in *Advances Toward the Development of "Green" Pyrotechnics*, *Green Energetic Materials*, John Wiley & Sons Ltd, Inc., West Sussex, UK, **2014**.

[8] J. Shinn, *Smokes and Obscurants: A Guidebook of Environmental Assessment. Volume I. Method of Assessment and Appended Data*, DTIC Report, Acc. Num. ADA203810, **1987**.

[9] J. Conkling, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons Ltd, Inc., West Sussex, UK, **2000**.

[10] J. Eaton, R. Lopinto, W. Palmer, *Health Effects of Hexachloroethane (HC) Smoke*, DTIC Report, Acc. Num. ADA277838, **1994**.

[11] T. Klapötke, C. Sabate, J. Welch, *Dalton Trans.* **2008**, 6372–6380.

[12] H. Ellern, *Military and civilian pyrotechnics*, Chemical Pub. Co, New York City, NY, USA, **1968**.

[13] I. Rubin, M. Buchanan, J. Moneyhun, *Chemical characterization and toxicologic evaluation of airborne mixtures. Chemical characterization of combusted inventory red and violet smoke mixes*, U.S. Army Medical Research and Development Command, Fort Detrick, Maryland, USA, **1982**.

[14] Subcommittee on Military Smokes and Obscurants, National Research Council, *Toxicity of Military Smokes and Obscurants, Volume 3*, The National Academies Press, Washington, DC, USA, **1999**.

[15] *Engineering Design Handbook: Design of Ammunition for Pyrotechnic Effects*, Military Pyrotechnics Series, Part Four, Washington, DC, USA, **1974**.

[16] J. Glück, T. Klapötke, M. Rusan, A. Shaw, *Propellants Explos. Pyrotech.* **2017**, *42*, 131–141.

[17] N. Sordoni, W. Heard, W. Rouse, *Pyrotechnical Smoke Analysis Volume 1*, Defense Technical Information Center, Fort Belvoir, VA, USA, **1993**.

[18] J. Glück, T. Klapötke, A. Shaw, *Cent. Eur. J. Energ. Mater.* **2017**, *14*, 489–500.

[19] U. S. Army Material Command, *Engineering Design Handbook: Theory and Application*, Military Pyrotechnics Series, Part One, Washington, DC, USA, **1967**.

[20] A. Shaw, G. Chen in *Advanced Boron Carbide-based Visual Obscurants*, *Proceedings of the 40th International Pyrotechnics Seminar*, IPS, Colorado Springs, CO, USA, **2014**.

[21] J. Sabatini, E. Koch, J. Poret, J. Moretti, S. Harbol, *Angew. Chem. Int. Ed.* **2015**, *54*, 10968–10970.

[22] J. Corbel, J. van Lingen, J. Zevenbergen, O. Gijzeman, A. Meijerink, *Angew. Chem. Int. Ed.* **2013**, *52*, 290–303.

[23] J. Glück, T. Klapötke, M. Rusan, J. Sabatini, J. Stierstorfer, *Angew. Chem. Int. Ed.* **2017**, *56*, 16507–16509.

[24] D. Juknelevicius, E. Karvinen, T. Klapötke, R. Kubilius, A. Ramanavicius, M. Rusan, *Chem. Eur. J.* **2015**, *21*, 15354–15359.

[25] A. Shaw, G. Diviacchi, E. Black, J. Moretti, R. Sadangi, H. Grau, R. Gilbert, *ACS Sustainable Chem. Eng.* **2015**, *3*, 1248–1254.

[26] Strategic Environmental Research and Development Program (SERDP), *Novel Pyrotechnics that Reduce Environmental Impact*, SON Number: WPSON-19-C4, FY 2019 Statement of Need, Alexandria, VA, USA, **2017**.

[27] A. Shaw, J. Brusnahan, J. Poret, L. Morris, *ACS Sustainable Chem. Eng.* **2016**, *4*, 2309–2315.

[28] M. Hemmilä, M. Hihkio, J. Kasanen, M. Turunen, M. Jarvela, S. Suhonen, A. Pasanen, H. Norppa, *Mutat. Res. Genet. Toxicol. Environ. Mutagen.* **2010**, *701*, 137–144.

[29] E. Koch, S. Cudziło, *Angew. Chem. Int. Ed.* **2016**, *55*, 15439–15442.

[30] J. Domanico in *Using a Standard Testing Protocol to Qualify Candidate Low Toxicity Colored Smoke Dyes*, *Proceedings of the 35th International Pyrotechnics Seminar*, IPS, Fort Collins, CO, USA, **2008**.

[31] A. Eslami, S. Hosseini, *J. Therm. Anal. Calorim.* **2010**, *104*, 671–678.

[32] C. Fish, G. Chen in *Characterization of Magnesium Carbonate for Use in Pyrotechnic Smoke Composition as a Thermal Regulator*, *Proceedings of the 35th International Pyrotechnics Seminar*, IPS, Fort Collins, CO, USA, **2008**.

[33] IFA, *GESTIS – Substance Database*, Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung, Sankt Augustin, Germany, **2018**.

[34] K. Kosanke, B. Kosanke, *Selected pyrotechnic publications of K. L. and B. J. Kosanke*, Journal of Pyrotechnics, Whitewater, CO, USA, **1995**.

[35] K. Kosanke, B. Kosanke, B. Sturman, T. Shimizu, M. Wilson, I. Maltitz, R. Hancox, N. Kubota, C. Jennings-White, D. Chapman, D. Dillehay, T. Smith, M. Podlesak, *Pyrotechnic Chemistry*, Journal of Pyrotechnics Inc., UK, **2004**.

[36] BAM Bundesanstalt für Materialforschung und -prüfung, *Empfehlungen für die Beförderung gefährlicher Güter - Handbuch über Prüfungen und Kriterien*, Bundesanstalt für Materialforschung und -prüfung, Berlin, **2015**.

9.6. Supporting Information

Smoke Generation of Hexamine-based Formulations

(a) **W6** with 30 % TA content.

(b) **W11** with 45 % TA content.

(c) **W13** with 55 % TA content.

Figure 9.3: White-colored smoke formulation: 1 s (left), 5 s (middle) and 10 s (right) after ignition.

Burn Rate

The smoke mixture (10.0 g) was pressed into a cardboard roll (1.6 mm wall thickness) with cylindrical shape (2.5 cm inner diameter, 4.0 cm height). The respective composition was pressed with a dead load of 3 t for 10.0 s. Each pellet was ignited using a resistance heating Kanthal® A1 wire (FeCrAl, 0.8 mm diameter, 2.9 Ω m^{-1}) and the whole burn was recorded with a digital video camera. The burn rate BR was determined by dividing the pellet mass m_p by the burn time BT according to:

$$BR = {}^{m_p}\!/_{BT}. \tag{9.1}$$

Figure of Merit

The mass-based composition figure of merit FM_m was calculated according to:

$$FM_m = {}^{-V \ln T}\!/_{m_p L}, \tag{9.2}$$

where V is the chamber volume, T the transmittance over time at 555 nm and L is the pathway of the light beam.

Aerosol and Yield Factor

The mass of produced aerosol m_a was calculated according to:

$$m_a = |\Delta m_{setup}| - |\Delta m_{bowl}|\,, \tag{9.3}$$

where Δm_{setup} is the mass difference of the whole setup before and after ignition and Δm_{bowl} is the mass difference of the bowl with the pellet before and after ignition. Using the mass of produced aerosol m_a led to the yield factor Y:

$$Y = {}^{m_a}\!/_{m_p} \times 100. \tag{9.4}$$

Table 9.5: Hexamine-based white-colored smoke formulations **W1** to **W14** (in wt%).

	TA	**Hexamine**	**$KClO_3$**	**MCPH**
W1	30.0	14.0	42.0	14.0
W2	30.0	14.0	35.0	21.0
W3	30.0	21.0	35.0	14.0
W4	30.0	21.0	28.0	21.0
W5	30.0	21.0	21.0	28.0
W6	30.0	28.0	35.0	7.0
W7	30.0	28.0	28.0	14.0
W8	30.0	28.0	21.0	21.0
W9	35.0	26.0	32.5	6.5
W10	40.0	24.0	30.0	6.0
W11	45.0	22.0	27.5	5.5
W12	50.0	20.0	25.0	5.0
W13	55.0	18.0	22.5	4.5
W14	60.0	16.0	20.0	4.0

TA = terephthalic acid; MCPH = magnesium carbonate pentahydrate hydroxide.

Table 9.6: White-colored reference smoke formulations **Ref-W1** and **Ref-W2** (in wt%).

	TA	**Sucrose**	**5-AT**	**$KClO_3$**	**MCPH**	**$NaHCO_3$**	**SA**	**PVA**
Ref-W1	41.6	13.8	14.8	22.8	3.0	–	3.0	1.0
Ref-W2	56.4	–	13.8	22.8	–	3.0	3.0	1.0

TA = terephthalic acid; 5-AT = 5-amino-1*H*-tetrazole; MCPH = magnesium carbonate pentahydrate hydroxide; SA = stearic acid. PVA = polyvinyl alcohol.

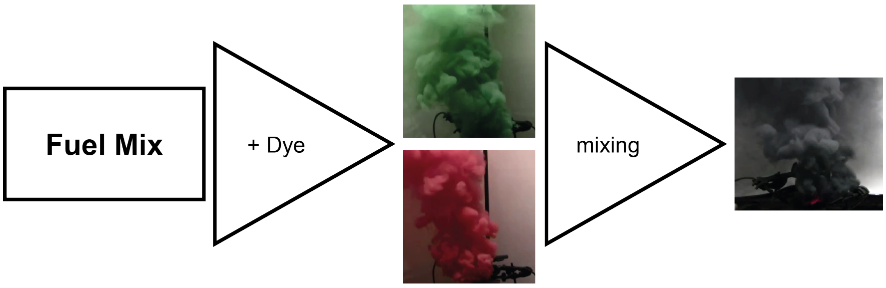
Table 9.7: Smoke properties of formulations **W6**, **W11**, **W13** and the references **Ref-W1** and **Ref-W2**.

	BT/s	**BR**/$g\,s^{-1}$	**Y**/%	**RH**/%	**T**/%	**m_a**/mg	**FM_m**/$m^2\,g^{-1}$	**RH**/%	**IS**/J	**FS**/N	**ESD**/J	**T_{onset}**/°C
W6	19	0.35	32	31	25	645	0.52	33	7	360	0.5	203
W11	38	0.26	35	31	17	693	0.66	34	10	360	0.6	203
W13	40	0.20	28	30	15	561	0.70	32	20	360	1.0	204
Ref-W1	28	–	27	66	59	–	0.20	27	35	360	1.0	164
Ref-W2	28	–	24	61	22	–	0.58	23	35	360	1.0	172

BT = burn time (2.0 g scale); BR = burn rate (10.0 g scale); Y = yield factor; RH =relative humidity; T = averaged transmittance over time at 555 nm; m_a = aerosol determination (2.0 g scale); FM_m = mass-based figure of merit; IS = impact sensitivity; FS = friction sensitivity; ESD = electrostatic discharge sensitivity; T_{onset} = onset temperature of decomposition.

Green is the new Black: An Environmentally Benign Black Smoke Fulfilling the Concept of Fuel Mixes

by
Teresa Küblböck and Thomas M. Klapötke



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New Trends in Research of Energetic Materials (NTREM), **2019**, *22*, 480–486

Abstract The concept of fuel mixes, which was established to generate multi-colored smoke signals with the colors red, violet, yellow and green, was extended by an additional black color impression. The underlying pyrotechnical system is based on commercially available potassium chlorate, 5-amino-1H-tetrazole and a magnesium carbonate derivative. In contrast to further naphthalene-based smoke mixtures, the black color was produced by mixing a green and red smoke dye (Solvent Green 3 / Disperse Red 9) as a much greener alternative. By using the same dyes as for red and green smoke, it was possible to apply a consistent pyrotechnical system with known performance. Standard methods of characterizing smokes according to their burning behavior, yield and energetic properties were used to estimate the effectiveness. The black-smoking compositions were compared to the already existing multi-colored smoke formulations.

10.1. Introduction

One of the most popular branches in the field of energetic materials is pyrotechnics because of their impressive and colorful effects. For the general public, the field of pyrotechnics consists mainly of light- and sound-generating compositions which are known from special events like New Year's Eve, amusement parks or openings.[1] Today, so-called daylight fireworks become more and more popular as alternative to the classical night fireworks, since the expected effect can be observed during daytime.[2] More accurate, these kinds of pyrotechnics are called smokes, which are more present in the military sector as tool for ground- and ground-to-air-signaling as well as marking unit flanks, target locations, drop zones and medical evacuation landing sites.[3–9] Nevertheless, the research on more environmentally benign pyrotechnics and especially on smokes is predominantly of military interest. The underlying pyrotechnical system for smoke generation which contains a dye, oxidizer, fuel and other additives remains the same for both applications.[10] In contrast to this, the only application area for black-colored smoke is in the Battlefield Effects Simulator to indicate through an emerging black smoke cloud that a target has been successfully disabled or killed.[11] Historically black smoke was generated by a mixture of naphthalene, potassium perchlorate and Laminac / Lupersol binder system (Table 10.1). This formulation does not fulfill today's awareness for more environmentally benign and greener pyrotechnical compositions.[8] Environment and health concerns arise from naphthalene which is believed to be carcinogenic as well as its resulting combustion products and soot.[12,13] Furthermore, potassium perchlorate is recommended of the Environmental Protection Agency (EPA) for regulation because it inhibits the iodine uptake in the thyroid gland.[14] The Laminac / Lupersol binder system contains toxic substances like methyl ethyl ketone peroxide or styrene monomer[15,16] For this reason, it is mandatory to find a suitable replacement.

Chen *et al.* outlined the possibility of mixing a black color impression according to the subtractive color model (Figure 10.1), which can further be applied like an ordinary colored smoke formulation.[11] The subtractive color

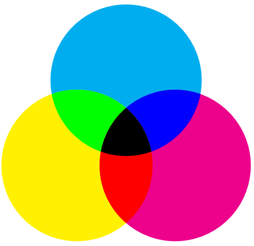

Figure 10.1: Subtractive color model.

model contains three primary colors. A combination of two primary colors results in a secondary color, while a mixture of either all three primary or two secondary colors creates the tertiary color. For instance a red color is obtained, because the material absorbs all other colors in the visible spectrum except for red. Using a smoke dye causes the absorption of a certain part of the visible spectrum, depending on the respective color.[17] This physical background can be exploited to generate several color impressions, even if no single, specific dye is available. As a result, it is possible to generate a black color by mixing green, red or blue dye. This could be favored, since the same dyes and compositions can be applied as for common smokes.

For decades, the M18 colored smoke grenades were in-use because of their efficiency and high performance. However, the underlying pyrotechnical system does not meet today's environmental and health requirements, since it applies a mixture of an anthraquinone dye, sulfur, potassium chlorate, sodium bicarbonate and optional kerosene as well as tricalcium phosphate.[18,19] As a consequence, the main combustion product would be hazardous SO_2.[8] The problematic sulfur-containing formulations were replaced by a combination of sugar and potassium chlorate in modern smoke signals.[20,21] The smoke generation is caused by a sublimation / recondensation process. The oxidizer / fuel pair provides enough energy to sublimate the dye, which can further recondensate to obtain the desired colored smoke cloud. Additionally, the resulting dye particles would be dispersed through the gaseous reaction products.[1,4,19,22] However, up to now it was not possible to find a suitable and greener alternative for potassium chlorate as oxidizer because of its exothermic decomposition and comparatively low melting point.[1,4,20] The most important characteristics of colored smoke formulations are the burn time, burn rate and yield factor Y, which are necessary to qualify the smoking and burning behavior as well as the efficiency. For this reason, the yield factor gives information about how many dye particles and other solid combustion products are present in the emerging smoke cloud.[23]

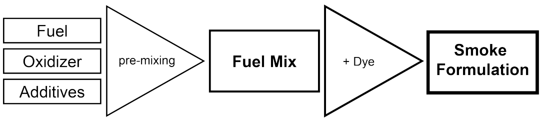

Figure 10.2: Schematic illustration of the concept of fuel mixes based on [24].

In 2017, the Strategic Environmental Research and Development Program (SERDP) presented a Statement of Need with the topic "*Novel Pyrotechnics that Reduce the Environmental Impact*" in which they emphasize the demand and requirements of so-called future pyrotechnics. One of the discussed topics was the investigation of special multi-color approaches to produce a variety of different colors with the same pyrotechnical system.[25] To face this issue in the field of smokes, the author's introduced the concept of fuel mixes which offers the possibility of multi-color smoke signals for the first time.[24] A schematic illustration of the concept is given in Figure 10.2. In detail, all

Table 10.1: Black smoke formulation of the M26 Target Kill Simulator (in wt%).[11]

	Naphthalene	**$KClO_4$**	**Binder**
Black M26	35.0	26.0	32.5

Table 10.2: Black-colored smoke formulations **B1**, **B2**, **B3** and **Ref-B** based on fuel mixes FM1, FM2, FM3 and sugar-based reference Ref-FM as stated in [24] (in wt%).

	DR9	**SG3**	**Sucrose**	**5-AT**	**$KClO_3$**	**MCPH**
B1	10	20	–	35	21	14
B2	10	20	–	35	14	21
B3	10	20	–	42	14	14
Ref-B	10	20	28	–	28	14

components of the fuel mix consisting of fuel, oxidizer and further additives would be premixed and subsequently combined with a dye to obtain a smoke formulation. It is possible to produce a variety of color impressions with the same underlying pyrotechnical system. The benefits of this concept are obvious: producers save time, since the simple quick-mixing of a fuel mix and dye produces every color impression with known quality. Further, the required space for storing drops significantly, since less energetic material is needed.[24] The concept of fuel mixes was proofed by the author's for red (Disperse Red 9), violet (Violet Smoke Dye Mix), yellow (Solvent Yellow 33) and green (Solvent Green 3) dye. It is obvious to transfer this working system to other colors.

10.2. Results and Discussion

The concept of fuel mixes was the basis for the presented study of black smoke. More precisely, the formulations consisting of 30 % dye and the remaining 70 % is the respective fuel mix. These fuel mixes are limited to three ingredients: 5-amino-1*H*-tetrazole (5-AT) as fuel, potassium chlorate as oxidizing agent and magnesium carbonate pentahydrate hydroxide (MCPH) as coolant (Table 10.2).[24] The main combustion product of the fuel 5-AT would be N_2 guaranteeing the optimal dispersion of the dye particle.[26]

Since the pyrotechnical system was already given by the 5-AT-based fuel mixes (Table 10.2), the challenge was to generate a black color impression with other colored dyes. In a first step, all three secondary colors were mixed with equal parts: green (Solvent Green 3), red (Disperse Red 9) and blue. The blue dye was copper (II) phthalocyanine (CuPh) which is also applied as food additive and printing ink.[27] However, it was not possible to obtain a black color when applying the blue dye, since only a blue to dark blue color could be observed. The solution was a mixture of Solvent Green 3 (SG3) and Disperse Red 9 (DR9) dye (2:1) resulting in a saturated black color impression. Other ratios ranging from pink to a dark green. In Table 10.2 the composition of the final black smoke formulations are summarized.

Table 10.3: Properties and sensitivites of black-colored smoke formulations based on fuel mixes FM1, FM2, FM3 and Ref-FM according to burn time (BT), burn rate (BR), yield *Y*, relative humidity (RH), impact sensitivity (IS), friction sensitivity (FS), electrostatic discharge (ESD) and onset temperature of decomposition (T_{dec}).

	based on	**BT**/s	**BR**/$g\,s^{-1}$	**Y**/%	**RH**/%	**IS**/J	**FS**/N	**ESD**/J	$\mathbf{T_{dec}}$/°C
B1	FM1	20	0.26	43	77	40	360	0.5	185
B2	FM2	38	0.10	36	73	40	360	0.4	195
B3	FM3	38	0.13	36	72	40	360	0.4	187
Ref-B	Ref-FM	10	0.41	44	76	35	360	0.7	168

Table 10.4: Properties and sensitivites of multi-colored smoke formulations (red, violet, green, yellow) based on fuel mixes FM1, FM2, FM3 and Ref-FM to burn time (BT), burn rate (BR), yield *Y*, relative humidity (RH), impact sensitivity (IS), friction sensitivity (FS), electrostatic discharge (ESD) and onset temperature of decomposition (T_{dec}) as summarized in [24].

based on	**BT**/s	**BR**/$g\,s^{-1}$	**Y**/%	**RH**/%	**IS**/J	**FS**/N	**ESD**/J	$\mathbf{T_{dec}}$/°C
FM1	15–23	0.28–0.34	29–36	26–33	40	360	0.2–1.0	182–192
FM2	26–75	0.07–0.10	21–26	23–34	40	360	0.2–0.7	182–198
FM3	29–41	0.07–0.12	28–31	29–33	40	360	0.3–0.5	180–194
Ref-FM	13–21	0.29–0.43	32–36	28–29	40	360	0.2–0.7	172–178

As outlined in the introduction, these black-smoking mixtures were determined with standard methods according to their burn time (BT), burn rate (BR) as well as yield factor *Y* and further compared to the characterization of 5-AT-based colored smoke formulations. The investigation of properties and behavior of black smoke compositions is the first of its kind, since the information in the literature is unexpected limited. The results are shown in Table 10.3 for black smoke and in Table 10.4 for colored smoke (red, violet, green, yellow).[24]

In general, a similar trend as for colored smoke formulations was observed: FM1- and Ref-FM-based compositions resulted in a rapid, strong smoke generation. The opposite behavior is obtained by FM2- and FM3-based mixtures with a weaker smoke generation over a longer time period.[24] As a result, the burn time of **B1** and **Ref-B** was in the range of 10–20 s, while **B2** and **B3** burned significantly longer (38 s). In comparison to colored smoke formulations (Table 10.4) based on the same fuel mixes, similar time ranges were observed (FM1 / Ref-FM: 13–23 s, FM2 / FM3: 26–75 s). As it was expected, the burn rates were higher for **B1** and **Ref-B** (0.26–0.41 $g\,s^{-1}$) in contrast to **B2** and **B3** (0.10–0.13 $g\,s^{-1}$). Therefore, it is a similar result as for colored smoke formulations (FM1 / Ref-FM: 0.28–0.43 $g\,s^{-1}$, FM2 / FM3: 0.07–0.12 $g\,s^{-1}$).

The yield factor *Y* gives information about the smoke's efficiency. It is dependent on the relative humidity, since at higher humidity, higher yields can be observed.[23,24] For black smoke formulations, the yield was significantly higher (36–44 %) than for the other colored compositions, which can be explained with the high


(a) 1 s after ignition.


(b) 5 s after ignition.


(c) 10 s after ignition.

Figure 10.3: Smoke generation of **B1**.

level of humidity. In detail, **B1** and the reference (43–44 %) are superior to **B2** and **B3** (36 %). However, the overall trend of the black-smoking pyrotechnics is the same as for other colored smoke formulations. In Figure 10.3 the smoke generation of **B1** is illustrated over a time period of 10 s. To classify the energetic properties, all formulations were examined with standard methods according to their impact and friction sensitivity, electrostatic discharge as well as thermal behavior. In detail, it is mandatory to determine the sensitivities of possible energetic material to ensure safe handling, preparing and storing. Therefore, the results are shown in Table 10.3 for black smoke and in Table 10.4 for colored smoke (red, violet, green, yellow).[24]

All black-colored smoke formulations were insensitive towards impact and friction with the sugar-based reference as exception (IS: 35 J). These values are confirmed by the classification of the other colored smoke mixtures. Further, all black and colored compositions were insensitive towards electrostatic discharge. The onset temperature of decomposition is slightly higher for 5-AT-based formulations (185–195 °C) in contrast to the reference. However, all determined decomposition temperatures were in the same range as for colored smoke formulations. The exception is **Ref-B** (168 °C), which is significantly lower than the other sugar-based references (172–178 °C). Finally, these mixtures should be handled with care, since they can easily be ignited.[28]

10.3. Conclusion

The concept of fuel mixes was expanded by a further black color impression. Therefore, the fuel mix consisting of 5-AT, potassium chlorate and MCPH was combined with red and green smoke dye in a suitable ratio (1:2). Former naphthalene-based black smoke can now be exchanged by dyes, which are also commonly being used for other smoke color impressions. Moreover, the same underlying pyrotechnical system entails known performance and quality. Further, the energetic, thermal and burning properties were determined according to standard procedures. The results of these tests were reproducible with all values of colored smoke formulations based on the same fuel mixes. The modification of burning behavior was also possible by applying different fuel mixes. As a consequence, the expansion to black color is a proof of concept for the so-called concept of fuel mixes. To sum up, it is possible to generate a black-colored smoke based on the concept of fuel mixes with the smoke dyes Disperse Red 9 and Solvent Green 3 with consistent quality. Therefore, it is much safer, easier and healthier than former approaches for smoke generation.

10.4. Experimental Section

Chemicals. Sucrose (99 %, Sigma-Aldrich); Magnesium carbonate pentahydrate hydroxide (BioXtra, Sigma-Aldrich); 5-Amino-1*H*-tetrazole (98 %, abcr Chemicals); Potassium chlorate (99 %, Grüssing GmbH); Solvent Green 3 (Nation Ford Chemical); Disperse Red 9 (Nation Ford Chemical).

Sample Preparation. All pyrotechnic samples were prepared in 2.0 g scale. Therefore, the different ingredients were weighed into a sample glass according to their respective weight percentages in the formulations. After a rough initial mixing, each sample was transferred into a porcelain mortar and carefully ground to a homogeneous powder. The so-prepared compositions were pressed into a cylindrical shape with the aid of a tooling die using a hydraulic press with a dead load of 3.0 t for approximately 3.0 s. All samples were burned within a smoke chamber (0.6 m × 0.6 m × 1.8 m). Each pellet was ignited using a resistance heating Kanthal® A1 wire (FeCrAl, 0.8 mm diameter, $2.9\,\Omega\,\mathrm{m}^{-1}$).[23,24,29]

Determination of Smoke Properties. The experimental setups for collecting the aerosol as well as the determination of burn rate and burn time were described previously.[23,24,29]

Sensitivity Data. Impact and friction sensitivity were determined using a BAM Drophammer and a BAM Friction Tester (method 1 of 6). The sensitivities of the compositions are indicated according to the UN Recommendations on the Transport of Dangerous Goods (+): impact: insensitive $>$40 J, less sensitive $\geq$40 J, sensitive $>$4 J, very sensitive $<$4 J; friction: insensitive $>$360 N, less sensitive $=$360 N, sensitive $360\,\mathrm{N} > x > 80\,\mathrm{N}$, very sensitive $<$80 N, extreme sensitive $<$10 N.[4] Thermal stability measurements: onset temperatures were measured with an OZM Research DTA 552-Ex Differential Thermal Analyzer at a heating rate of $5\,°\mathrm{C\,min}^{-1}$. Electrostatic discharge was measured with an OZM small-scale electrostatic spark X SPARK 10. ESD: sensitive $<$0.1 J, insensitive $>$0.1 J.

10.5. References

[1] J. Conkling, C. Mocella, *Chemistry of Pyrotechnics: Basic Principles and Theory*, CRC Press, Boca Raton, **2010**.

[2] UK Firework Review, `http://www.firework-review.org.uk/daytime-fireworks/` (visited on January 22, 2018).

[3] C. Sterling, *Military Communications: From Ancient Times to the 21st Century*, ABC-CLIO, Santa Barbara, CA, USA, **2008**.

[4] T. Klapötke, *Chemistry of High-Energy Materials*, Boston: De Gruyter, Berlin, **2017**.

[5] H. Webster in *Inorganic red smoke compositions*, *Proceedings of the 8th International Pyrotechnics Seminar*, IPS, Steamboat Springs, CO, USA, **1982**.

[6] G. Diviacchi in *Evaluation of Low Toxicity Colored Smoke Dyes*, *Proceedings of the 35th International Pyrotechnics Seminar*, IPS, Fort Collins, CO, USA, **2008**.

[7] J. Domanico in *Using a Standard Testing Protocol to Qualify Candidate Low Toxicity Colored Smoke Dyes*, *Proceedings of the 35th International Pyrotechnics Seminar*, IPS, Fort Collins, CO, USA, **2008**.

[8] J. Sabatini in *Advances Toward the Development of "Green" Pyrotechnics*, *Green Energetic Materials*, John Wiley & Sons Ltd, Inc., West Sussex, UK, **2014**.

[9] H. Ellern, *Military and civilian pyrotechnics*, Chemical Pub. Co, New York City, NY, USA, **1968**.

[10] *Engineering Design Handbook: Design of Ammunition for Pyrotechnic Effects*, Military Pyrotechnics Series, Part Four, Washington, DC, USA, **1974**.

[11] G. Chen, S. Showalter, G. Raibeck, J. Wejsa, *Environmentally Benign Battlefield Effects Black Smoke Simulator*, **2006**.

[12] D. Liscinsky, Z. Yu, B. True, J. Peck, A. Jennings, H. Wong, J. Franklin, S. Herndon, R. Miake-Lye, *Environ. Sci. Technol.* **2013**, *47*, 4875–4881.

[13] Y. Pashin, L. Bakhitova, *Environ. Health Perspect.* **1979**, *30*, 185–189.

[14] K. Sellers, K. Weeks, W. Alsop, S. Clough, M. Hoyt, B. Pugh, J. Robb, *Perchlorate: Environmental Problems and Solutions*, CRC Press, Boca Raton, FL, USA, **2006**.

[15] G. Lakshminarayanan, G. Chen, R. Ames, W. Lee, J. Wejsa, *Mitigation Of Critical Single Point Failure (SPF) Material – Laminac 4116 Binder Replacement Program For Parachute And Cluster Stars Illuminant Compositions For Hand Held Signals*, Army Armament Research, Development and Engineering Center (ARDEC), Picatinny Arsenal, NJ, USA, **2006**.

[16] J. Sabatini, C. Freeman, J. Poret, A. Nagori, G. Chen, *Propellants Explos. Pyrotech.* **2011**, *36*, 145–150.

[17] N. Ibraheem, M. Hasan, R. Khan, P. Mishra, *ARPN Journal of Science and Technology* **2012**, *2*, 265–275.

[18] D. Lundy, J. Eaton, *Occupational Health Hazards Posed by Inventory US Army Smoke / Obscurant Munitions*, US Army Medical Research Detachment, Wright-Patterson Air Force Base, for Walter Reed Army Institute of Research, Washington, DC, USA, **1994**.

[19] I. Rubin, M. Buchanan, J. Moneyhun, *Chemical characterization and toxicologic evaluation of airborne mixtures. Chemical characterization of combusted inventory red and violet smoke mixes*, U.S. Army Medical Research and Development Command, Fort Detrick, Maryland, USA, **1982**.

[20] A. Eslami, S. Hosseini, *J. Therm. Anal. Calorim.* **2010**, *104*, 671–678.

[21] C. Fish, G. Chen in *Characterization of Magnesium Carbonate for Use in Pyrotechnic Smoke Composition as a Thermal Regulator*, *Proceedings of the 35th International Pyrotechnics Seminar*, IPS, Fort Collins, CO, USA, **2008**.

[22] Subcommittee on Military Smokes and Obscurants, National Research Council, *Toxicity of Military Smokes and Obscurants, Volume 3*, The National Academies Press, Washington, DC, USA, **1999**.

[23] J. Glück, T. Klapötke, M. Rusan, A. Shaw, *Propellants Explos. Pyrotech.* **2017**, *42*, 131–141.

[24] J. Glück, T. Klapötke, T. Küblböck, *New J. Chem.* **2018**, *42*, 10670–10675.

[25] Strategic Environmental Research and Development Program (SERDP), *Novel Pyrotechnics that Reduce Environmental Impact*, SON Number: WPSON-19-C4, FY 2019 Statement of Need, Alexandria, VA, USA, **2017**.

[26] A. Lesnikovich, O. Ivashkevich, S. Levchik, A. Balabanovich, P. Gaponik, A. Kulak, *Thermochim. Acta* **2002**, *388*, 233–251.

[27] W. Herbst, K. Hunger, *Industrielle Organische Pigmente: Herstellung, Eigenschaften, Anwendung*, Wiley-VCH Verlag, Weinheim, Germany, **2009**.

[28] BAM Bundesanstalt für Materialforschung und -prüfung, *Empfehlungen für die Beförderung gefährlicher Güter - Handbuch über Prüfungen und Kriterien*, Bundesanstalt für Materialforschung und -prüfung, Berlin, **2015**.

[29] J. Glück, T. Klapötke, A. Shaw, *Cent. Eur. J. Energ. Mater.* **2017**, *14*, 489–500.

Guanidinium 5,5'-Azotetrazolate: A Colorful Chameleon for Halogen-free Smoke Signals

by

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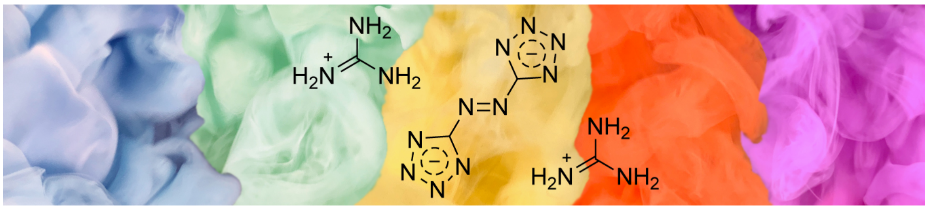

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Abstract A progressive halogen-free multicolored smoke system to obtain white, red, violet, yellow, green, and blue smoke color is presented. The nitrogen-rich salt guanidinium 5,5'-azotetrazolate (GZT), which is usually applied as a gas generator or propellant ingredient, was combined with different smoke dyes (Solvent Red 1, Solvent Violet 47, Solvent Green 3, Solvent Yellow 33). These two-component smoke mixtures offer a convenient and safe multicolor approach without the need for potassium chlorate or any other hazardous material. The common smoke characteristics with respect to burn time / burn rate, yield factor, transfer rate, as well as energetic properties were determined and compared with classic chlorate-based formulations currently used. To the best of our knowledge, nothing comparable is known in the literature and a completely new research area in modern pyrotechnics is opened.

11.1. Introduction

The application of colored smoke as daylight fireworks as well as for color effects during photography shootings or fashion shows has become very popular in the last few years.[1,2] Colored smoke is now known and accessible to a much broader target group than before, and it is more important than ever to ensure safe handling and reduce health concerns during their use by untrained people. Moreover, there is an increasing priority regarding issues such as sustainability and environmental effects.[3] However, to date research efforts have only been driven from a military point of view. In this context, they are commonly applied as reliable non-electronic communication tools for either ground-to-ground or ground-to-air signaling.[4–6] In 2017, the Strategic Environmental Research and Development Program (SERDP) reported the need for so-called "next generation pyrotechnics" that reduce the environmental and health effects.[3] The field of smoke-producing pyrotechnics offers a wide variety of research possibilities.

The first colored smoke signals consisted of an organic dye, sulfur, potassium chlorate, sodium bicarbonate, and optional amounts of kerosene or tricalcium phosphate.[7,8] Sulfur in combination with potassium chlorate offers a low ignition and combustion temperature; therefore, it is the perfect candidate for low-temperature smoke.[4,9] The color impression can easily be obtained by a simple sublimation recondensation mechanism.[4,9–12] In detail, the pyrotechnic mixture provides the energy to sublime the dye, which can subsequently recondense as small particles.[4,11,12] Maintaining the lower combustion temperatures is mandatory, otherwise the organic dye would be burned rather than sublimed.[11,13] Finally, the gaseous combustion products disperse the emerging dye particles, which results in a dense colored smoke cloud.[12]

A big step forward was the substitution of sulfur by alternative fuels.[9,14,15] During the combustion of sulfur-based smoke mixtures, hazardous SO_2 is formed that causes a burning sensation in the lungs when inhaled.[9] Fortunately, sugar-based fuels such as sucrose or lactose act in a comparable manner to sulfur when paired with potassium chlorate.[9,16,17]Sugar is considered a less toxic alternative, since the resulting combustion products are limited to mainly harmless water and carbon dioxide[9,18]

Another big challenge in today's research is the elimination of halogens and halogen-containing molecules.[3,9] In the case of smoke signals, potassium chlorate still seems to be the only suitable oxidizing agent to ensure the optimal temperature range for necessary dye sublimation.[11,19,20] Several serious issues arise from the use of potassium chlorate: It is highly reactive and tends to undergo spontaneous ignition, particularly in combination with combustible low-melting fuels.[11,19,20] Furthermore, as a consequence of its water solubility and persistence, it can cause problems to aquatic life as it is toxic.[21] The combustion products, in particular, are an underestimated risk in pyrotechnics. Chlorates in combination with organic materials are known to form toxic and carcinogenic chlorinated organic compounds such as polychlorinated dibenzo-*p*-dioxins (PCDD) or dibenzofurans (PCDF). These gaseous side products can be inhaled very easily during combustion.[22–26] Nevertheless, because of the lack of sufficient alternatives, potassium chlorate is still commonly used as the oxidizer in smoke-producing mixtures.

In 2015, the very first chlorine-free red flare was investigated by Sabatini *et al.*[27] Their strategy was to add molecules such as hexamine or 5-amino-1*H*-tetrazole instead of unwanted potassium perchlorate to a common flare formulation. They concluded that these nitrogen-rich fuels have a deoxidizing effect on the flame and thus result in a lower combustion temperature.[27] This concept was successfully transferred to smoke-generating pyrotechnics by Glück *et al.* for both colored and white smoke formulations.[28–30] It was possible to replace sugar by hexamine and 5-amino-1*H*-tetrazole as the main fuel, which led to an overall more persistent and thick smoke cloud.[28–31] Another positive side effect is the release of a high volume of gaseous products such as N_2, which further disperse the dye particles.[32–34] Nevertheless, until now it was not possible to eliminate potassium chlorate in smoke, not even through the use of nitrogen-rich molecules.[4,5,7,9,11,28–31]

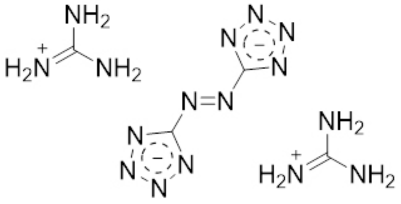


Figure 11.1: Guanidinium 5,5'-azotetrazolate (GZT).

The next logical step is to find a suitable nitrogen-rich molecule for smoke signals, which – in the best case – can be applied without any potassium chlorate or other halogen sources. An extensive literature research revealed an interesting molecule with an overall nitrogen content of 78.9 %: guanidinium 5,5'-azotetrazolate (GZT, Figure 11.1).[35,36] GZT is a bright yellow powder and burns with white smoke.[32,37] As a consequence of its beneficial properties – ranging from high thermal stability, insensitivity towards external stimuli, to desirable low combustion temperatures – it is expected to be an ideal candidate for application in clean propulsion systems, new gas-generators, and low signature propellants.[32,34–39] GZT derives its power from a high heat of formation in combination with the release of a large gas volume, which is mainly cool and inert because of the formation of N_2.[32,34–37,39] As a consequence of its beneficial properties, GZT was also considered as a gas-generating compound in smoke signals.

Table 11.1: Selected properties as well as sensitivities of GZT and GZT-based smokes in comparison with chlorate-based references.[29] The exact composition of formulations, the theoretical background as well as experimental setup is described in ESI.

	BT/s	**BR**/mm s^{-1}	$\mathbf{m_a}$/mg	**Y**/%	$\mathbf{m_d}$/mg	**T%**/%	$\mathbf{T_{onset}}$/°C
GZT	19	11.8	654	32	–	–	239
W3	26	6.9	582	29	–	–	215
Y3	26	5.3	783	38	164	55	239
R3	25	5.6	745	36	169	56	239
V3	29	5.6	779	38	–	–	237
B3	24	6.8	726	35	–	–	239
G3	19	7.3	715	35	–	–	238
Ref-W	38	–	693	35	–	–	203
Ref-Y	13	–	670	33	435	73	178
Ref-R	21	–	729	36	514	86	172
Ref-V	15	–	652	32	–	–	178
Ref-G	19	–	642	32	–	–	172

BT = burn time (2.0 g scale); BR = linear burn rate (5.0–6.0 g scale); m_a = mass of produced aerosol (2.0 g scale); Y = yield factor; m_d = dye content present in produced aerosol; T% = transfer rate; T_{dec} = temperature of decomposition.

11.2. Results and Discussion

First, the energetic properties of GZT were reviewed (Table 11.1, see also Table 11.10 in the Supporting Information). GZT burned with the generation of moderately strong white smoke and a burn time of 19 s, which correlated with the burn rate (11.8 mm s^{-1}). The impact sensitivity was confirmed to be 35 J, and it was not sensitive towards friction and electrostatic discharge.[32] GZT decomposed at 239 °C. The nonsensitive energetic properties in combination with the high decomposition temperature are advantageous for modern pyrotechnics, since they guarantee safe preparation, storage, and handling.

The newly developed smoke formulations should combine acceptable smoke performance, an economical manufacturing process, as well as safe application (also by untrained people).[3] For this reason, the smoke system must be as simple and efficient as possible. As a starting point, GZT was quick-mixed with various proportions of dye (5–35 %) to develop two-component smoke. The combustion of GZT was assumed to provide enough heat for dye sublimation, and the white smoke generated should switch its color impression. All GZT-based smoke mixtures were characterized according to their burning behavior (burn time: *BT*, burn rate: *BR*), smoke quality (mass of aerosol m_a, yield factor *Y*, mass of dye present in the aerosol m_d, transfer rate *T%*) as well as energetic properties and then further compared with classic chlorate- / sugar-based smokes. The reference formulations consisted of different dyes (terephthalic acid, Disperse Red 9, Violet Dye Mix, Solvent Yellow 33, Solvent Green 3), potassium chlorate, sucrose or hexamine, and magnesium carbonate hydroxide pentahydrate (see Table 11.3 and Table 11.9).

It is obvious to expect GZT to be a white smoke generator (Figure 11.2a). For this reason, we determined the mass of aerosol formed during combustion (654 mg) as well as the yield factor (32 %). These results are very similar to the white hexamine / chlorate reference (693 mg, 35 %). GZT has the advantage of its superior impact sensitivity (35 J instead of 10 J); however, for application, the spectral properties must also be considered in detail. In common less-toxic white smoke signals the dye of choice is terephthalic acid (TA), since it is easily accessible at moderate prices and has acceptable properties.[4,9,40] To improve the performance of GZT alone, terephthalic acid was added stepwise (see Table 11.2 and Table 11.3). We found that the upper limit is 15 % TA content; above that, it was no longer possible to ignite the GZT / TA mixture. The sublimation temperature of TA is 402 °C and, therefore, slightly higher than anthraquinone or quinoline dyes (approximately 300–350 °C).[21] As a result, the sublimation of TA might consume too much energy from the system, since smoke properties dropped significantly to 582 mg aerosol and 29 % yield. For this reason, the combination of GZT and TA was excluded from further investigation.

Environmentally benign multicolored smoke signals are a current research topic, because the variety of application areas as well as the demand is rising.[1–6] Therefore, GZT was simply mixed with various dyes to obtain red (Solvent Red 1), violet (Solvent Violet 47), yellow (Solvent Yellow 33), blue (Solvent Green 3), and green (Solvent Yellow 33 + Solvent Green 3) color impressions. The same procedure as for white smoke was applied, whereby the dyes were added stepwise to GZT (see Tables 11.4 to 11.8). Since GZT burns with white smoke, it is advantageous to have as much dye content as possible, otherwise, the color impression might be lacking. As was observed for TA, the upper limit for colored dyes was also 15 % for constant igniting and burning behavior. Initial tests with these two-component dye / GZT mixtures showed the generation of strong and thick smoke (Figure 11.2). The expected color impression is slightly lighter because of the presence of GZT; however, it is still clearly recognizable. The new smoke system was set to 15 % dye in combination with 85 % GZT for all colors. It is noteworthy that the dye content of the GZT system is half as much as for reference formulations, which needs to be considered during characterization and comparison. In contrast to the simple two-component GZT system, the references were based on sucrose and potassium chlorate (see Table 11.9).

The burn times of colored smokes were in the range of 24–29 s, with **G3** as the only exception (19 s). In contrast, the underlying redox reaction of sucrose / chlorate mixtures is much more violent and results in faster smoke generation and shorter burn times (13–21 s). The yield factor of pure GZT was 32 %, which could be further increased by the addition of dye (35–38 %). The yield factor as well as the mass of aerosol m_a is in a similar range as the reference formulations. These results indicated that the dye particles have been dispersed by GZT. To determine whether the organic dyes were transformed or destroyed during combustion,[4–6] HPLC analysis was performed to quantify the exact amount of dye present in the aerosol.[29,30] The resulting transfer rate $T\%$ is a measure of the effectiveness of smoke mixtures in dispersing the dye rather than combusting it. In

(a) White. **(b)** Yellow. **(c)** Red. **(d)** Violet. **(e)** Blue. **(f)** Green.

Figure 11.2: Burning of GZT-based smoke formulations.

comparison to red and yellow reference formulations (73–86 %), the two-component GZT system reached a transfer rate of up to 55–56 %. This means, that about 55 % of the dye particles in the pellet are sublimed and present in the generated smoke cloud. It should be noted that only half of the dye content was used in the GZT system than in the reference mixtures (15 % instead of 30 %). Therefore, we suggest that the probability of sublimation might be influenced by the significantly different particle content. Nonetheless, these novel and simple nitrogen-rich smokes already showed a promising trend to reach similar smoke performance as in the currently used formulations.

A special highlight is the overall nonsensitive energetic properties of GZT in combination with a high decomposition temperature (239 °C). The addition of dye resulted in formulations that are not sensitive to impact, friction, or electrostatic discharge. The decomposition temperatures of all the colored smoke mixtures were in the same range as that of GZT. In comparison, the use of the sugar / chlorate mixture is very questionable, since it is known to undergo spontaneous reactions as well as being unpredictable.[4,11,20,41–43] This creates high risks during production and storage.[11] The elimination of the controversial potassium chlorate results in a much safer way of generating smoke. This is also advantageous for untrained people, since they can use pyrotechnics without exposing themselves to the danger of unexpected reactions.

As potassium chlorate and sugar are essential materials in the global industry, they are available in adequate quantities at reasonable prices.[44–46] In contrast, the nitrogen-rich salt GZT is more complex to produce and, therefore, more expensive. However, common in-use smokes consist not only of oxidizer and fuel, but a coolant and other additives are also required. It should be considered that GZT can be applied as a single compound, which greatly simplifies the manufacturing process, purchasing, and storage as well as the previously discussed safety issues.

11.3. Conclusion

Herein we have discussed halogen-free two-component smoke mixtures based on the nitrogen-rich salt guanidinium 5,5'-azotetrazolate, which was combined with various dyes. The examined system consisted of 15 % dye and 85 % GZT. First, GZT was evaluated in terms of its energetic properties and its applicability to generate white smoke. The colored system was based on using various organic dyes: Solvent Red 1, Solvent Violet 47, Solvent Yellow 33 as well as Solvent Green 3. These simple two-component smoke systems were able to generate thick colored smoke clouds without the need for any potassium chlorate. A similar yield factor and mass of aerosol was observed as for commonly used sucrose / chlorate mixtures. Only the transfer rates were slightly lower than for the references.

Guanidinium 5,5'-azotetrazolate is only one representative of the group of nitrogen-rich gas-generating compounds. There might be other possible candidates, which could further improve the effectiveness of smoke mixtures. For these future compounds, the dye content should be increased to ensure unique and brilliant color impressions. One of the most challenging tasks in pyrotechnics is the toxicity of combustion products. Potassium chlorate in combination with organic material leads to carcinogenic polychlorinated compounds, which can now be prevented by using nitrogen-rich smokes. However, the toxicity of these combustion products should also be further evaluated to satisfy health aspects.

11.4. Experimental Section

Caution! The described pyrotechnical mixtures might initiate during preparing, handling or manipulating! They are potential explosives, which are sensitive to environmental stimuli such as impact, friction, heat, and electrostatic discharge. Please handle these materials with care! Precautionary measures are mandatory and protective equipment like safety glasses, face shields, leather coats, Kevlar® gloves, and ear protectors is highly recommended.

Chemicals. Sucrose ($\geq$99 %), terephthalic acid (98 %), Solvent Red 1 (reagent grade) and magnesium carbonate hydroxide pentahydrate (BioXtra) were purchased from Sigma-Aldrich. 5-Amino-1*H*-tetrazole (98 %) was purchased from abcr chemicals. Potassium chlorate (99 %) was purchased from Grüssing GmbH. Disperse Red 9, Solvent Green 3, Solvent Yellow 33, Solvent Violet 47 and Violet Mix Smoke Dye were purchased from Nation Ford Chemical. Guanidinium 5,5'-azotetrazolate was donated by Explosia.

Sample Preparation. All pyrotechnic samples were prepared in 2.0 g scale using the same procedure in order to ensure the reproducibility. Therefore, the different ingredients were weighed into a sample glass according to their respective weight percentages in the formulations. Each sample was transferred into a porcelain mortar and carefully ground to a homogeneous powder. After grinding, the binder solutions were added followed by a curing step. The so-prepared compositions were ground again and then, pressed into a cylindrical shape with the aid of a tooling die using a hydraulic press with a dead load of 2.0 t for 3.0 s. Each pellet was ignited using a resistance heating Kanthal® A1 wire (FeCrAl, 0.8 mm diameter, $2.9\,\Omega\,\mathrm{m}^{-1}$). For each evaluated composition, three pellets were tested, and the results were averaged.

Figure 11.3: Cardboard roll for determination of burn rate.

Burn Rate. The smoke mixture (5.0–6.0 g) was pressed into a cardboard roll (2.7 mm wall thickness) with cylindrical shape (1.0 cm inner diameter, 9.0 cm height) sealed on one side. Each pellet was ignited using a resistance heating Kanthal® A1 wire (FeCrAl, 0.8 mm diameter, 2.9 Ω m^{-1}) and the whole burn was recorded with a digital video camera. The compositions were tested four times and the results were averaged. The mass burn rate BR was determined by dividing the pellet mass m_p by the burn time BT according to:

$$\mathrm{BR} = {}^{m_p}/_{\mathrm{BT}}, \tag{11.1}$$

while the linear burn rate was calculated by dividing the pellet length l_p the burn time:

$$\mathrm{BR} = {}^{l_p}/_{\mathrm{BT}}. \tag{11.2}$$

Aerosol and Yield Factor.[30] The mass of produced aerosol m_a was calculated with:

$$m_a = |\Delta m_{\mathrm{setup}}| - |\Delta m_{\mathrm{bowl}}|, \tag{11.3}$$

where $\Delta m_{\mathrm{setup}}$ is mass difference of the whole setup before and after ignition and Δm_{bowl} is the mass difference of the bowl with pellet before and after ignition. Using the mass of produced aerosol m_a led to the yield factor Y:

$$Y = {}^{m_a}/_{m_p} \times 100. \tag{11.4}$$

HPLC Strategy.[29,30] After ignition, the arising aerosol not only consists of recondensed dye, but also of other unknown combustion products. Therefore, it is necessary to investigate the collected aerosol with respect to its exact dye content by HPLC. The transfer rate $T\%$ is defined as quotient between dye content present in produced aerosol m_d divided by amount of dye in the pellet m_{pd}:

$$T\% = {}^{m_d}/_{m_{pd}} \times 100. \tag{11.5}$$

For dye quantification a Shimadzu Prominence® HPLC with LC-20AD pump module and SPD-M20A Diode Array Detector and LabSolutions v5.86 software was used. The analytical column was a Phenomenex Kinetex® (2.6 µm Biphenyl, 100 Å, 150 mm × 4.6 mm).

Mobile phase: B = water, C = acetonitrile
Gradient: 0 min (50 % B, 50 % C), 5 min (10 % B, 90 % C), 9 min (10 % B, 90 % C), 14 min (50 % B, 50 % C)
Time: 15 min
Flow rate: 0.5 mL min^{-1}
Injection volume: 1 µL
Oven temperature: 40 °C
Sample temperature: 15 °C

Sensitivity Data.[47,48] The impact and friction sensitivities were determined using a BAM Drophammer and a BAM Friction Tester. The sensitivities of the compositions are indicated according to the UN Recommendations on the Transport of Dangerous Goods (+). Impact: insensitive >40 J, less sensitive ≥40 J, sensitive >4 J, very sensitive <4 J; friction: insensitive >360 N, less sensitive =360 N, sensitive 360 N > x > 80 N, very sensitive <80 N, extreme sensitive <10 N. Electrostatic discharge was measured with an OZM small-scale electrostatic spark X SPARK 10. ESD: sensitive <0.1 J, insensitive >0.1 J. The thermal stability was carried out using an OZM Research DTA 552 Ex Differential Thermal Analyzer with a heating rate of 5 °C min^{-1}.

11.5. References

[1] Everything You Need To Know About Smoke Photography, `https://www.format.com/magazine/resources/photography/smoke-bomb-photography-guide` (visited on March 13, 2020).

[2] UK Firework Review, `http://www.firework-review.org.uk/daytime-fireworks/` (visited on January 22, 2018).

[3] Strategic Environmental Research and Development Program (SERDP), *Novel Pyrotechnics that Reduce Environmental Impact*, SON Number: WPSON-19-C4, FY 2019 Statement of Need, Alexandria, VA, USA, **2017**.

[4] T. Klapötke, *Chemistry of High-Energy Materials*, Boston: De Gruyter, Berlin, **2017**.

[5] C. Sterling, *Military Communications: From Ancient Times to the 21st Century*, ABC-CLIO, Santa Barbara, CA, USA, **2008**.

[6] H. Webster in *Inorganic red smoke compositions*, *Proceedings of the 8th International Pyrotechnics Seminar*, IPS, Steamboat Springs, CO, USA, **1982**.

[7] D. Lundy, J. Eaton, *Occupational Health Hazards Posed by Inventory US Army Smoke / Obscurant Munitions*, US Army Medical Research Detachment, Wright-Patterson Air Force Base, for Walter Reed Army Institute of Research, Washington, DC, USA, **1994**.

[8] Subcommittee on Military Smokes and Obscurants, National Research Council, *Toxicity of Military Smokes and Obscurants, Volume 3*, The National Academies Press, Washington, DC, USA, **1999**.

[9] J. Sabatini in *Advances Toward the Development of "Green" Pyrotechnics*, *Green Energetic Materials*, John Wiley & Sons Ltd, Inc., West Sussex, UK, **2014**.

[10] W. Muse, J. Anthony, J. Bergmann, D. Burnett, C. Crouse, B. Gaviola, S. Thomson, *Drug Chem. Toxicol.* **1997**, *20*, 293–302.

[11] J. Conkling, C. Mocella, *Chemistry of Pyrotechnics: Basic Principles and Theory*, CRC Press, Boca Raton, **2010**.

[12] S. Kaye, *Encyclopaedia of Explosives and Related Items*, US Army Armament Research and Development Command, Large Calibre Weapon Systems Laboratory, Dover, NJ, USA, **1978**.

[13] K. Kosanke, B. Kosanke, B. Sturman, T. Shimizu, M. Wilson, I. Maltitz, R. Hancox, N. Kubota, C. Jennings-White, D. Chapman, D. Dillehay, T. Smith, M. Podlesak, *Pyrotechnic Chemistry*, Journal of Pyrotechnics Inc., UK, **2004**.

[14] J. Moretti, J. Sabatini, A. Shaw, G. Chen, R. Gilbert, K. Oyler, *ACS Sustainable Chem. Eng.* **2013**, *1*, 673–678.

[15] J. Moretti, J. Sabatini, A. Shaw, R. Gilbert, *ACS Sustainable Chem. Eng.* **2014**, *2*, 1325–1330.

[16] G. Chen, S. Showalter, G. Raibeck, J. Wejsa, *Environmentally Benign Battlefield Effects Black Smoke Simulator*, **2006**.

[17] G. Raibeck, G. Chen in *Assessment of Organic Fuels for Use in Environmentally Benign Colored Smoke Formulations*, *Proceedings of the 35th International Pyrotechnics Seminar*, IPS, Fort Collins, CO, USA, **2008**.

[18] Headquarters, *Field Manual 21-60, Visual Signals*, Department of the Army, US Government Printing Office, Washington, DC, USA, **1987**.

[19] A. Eslami, S. Hosseini, *J. Therm. Anal. Calorim.* **2010**, *104*, 671–678.

[20] T. Shimizu, *Fireworks: The Art, Science, and Technique*, Pyrotechnica Publications, Austin, Texas, USA, **1996**.

[21] IFA, *GESTIS – Substance Database*, Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung, Sankt Augustin, Germany, **2018**.

[22] P. Brandhuber, S. Clark, K. Morley, *J. Am. Water Works Assn.* **2009**, *101*, 63–73.

[23] Environmental Protection Agency, Contaminant Candidate List 3, `https://www.epa.gov/ccl/contaminant-candidate-list-3-ccl-3` (visited on July 1, 2019).

[24] P. Dyke, P. Coleman, *Organohalogen Compd.* **1995**, *24*, 213–216.

[25] O. Fleischer, H. Wichmann, W. Lorenz, *Chemosphere* **1999**, *39*, 925–932.

[26] L. Wackett, M. Sadowsky, L. Newman, H. Hur, S. Li, *Nature* **1994**, *368*, 627–629.

[27] J. Sabatini, E. Koch, J. Poret, J. Moretti, S. Harbol, *Angew. Chem. Int. Ed.* **2015**, *54*, 10968–10970.

[28] J. Glück, T. Klapötke, A. Shaw, *Cent. Eur. J. Energ. Mater.* **2017**, *14*, 489–500.

[29] J. Glück, T. Klapötke, T. Küblböck, *New J. Chem.* **2018**, *42*, 10670–10675.

[30] J. Glück, T. Klapötke, M. Rusan, A. Shaw, *Propellants Explos. Pyrotech.* **2017**, *42*, 131–141.

[31] T. Küblböck, T. Klapötke, *Propellants Explos. Pyrotech.* **2018**, *43*, 1184–1189.

[32] M. Hiskey, N. Goldman, J. Stine, *J. Energ. Mater.* **1998**, *16*, 119–127.

[33] S. Levchik, O. Ivashkevich, A. Balabanovich, A. Lesnikovich, P. Gaponik, L. Costa, *Thermochim. Acta* **1992**, *207*, 115–130.

[34] S. Cheng, K. Cheng, M. Liu, Y. Hong, C. Chen, *J. Mol. Model.* **2013**, *19*, 3705–3717.

[35] G. Steinhauser, T. Klapötke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3330–3347.

[36] G. Steinhauser, T. Klapötke, *Angew. Chem.* **2008**, *120*, 3376–3394.

[37] A. Hammerl, M. Hiskey, G. Holl, T. Klapötke, K. Polborn, J. Stierstorfer, J. Weigand, *Chem. Mater.* **2005**, *17*, 3784–3793.

[38] T. An, F. Zhao, Q. Wang, D. Sheng, Q. Pan, H. Feng, J. Yi, Y. Wang, *J. Anal. Appl. Pyrolysis* **2013**, *104*, 405–411.

[39] H. Schmid, N. Eisenreich, *Propellants Explos. Pyrotech.* **2000**, *25*, 230–235.

[40] J. Domanico in *Using a Standard Testing Protocol to Qualify Candidate Low Toxicity Colored Smoke Dyes*, *Proceedings of the 35th International Pyrotechnics Seminar*, IPS, Fort Collins, CO, USA, **2008**.

[41] H. Ellern, *Military and civilian pyrotechnics*, Chemical Pub. Co, New York City, NY, USA, **1968**.

[42] M. Russell, *The Chemistry of Fireworks*, The Royal Society of Chemistry, Cambridge, UK, **2009**.

[43] U. S. Army Material Command, *Engineering Design Handbook: Safety, Procedures and Glossary*, Military Pyrotechnics Series, Part Two, Washington, DC, USA, **1966**.

[44] Glam Research, *Global Potassium Chlorate Market (EM-102754)*, Glam Research, New Sangvi, India, **2019**.

[45] Glam Research, *Global White Sugar Market (EM-114276)*, Glam Research, New Sangvi, India, **2019**.

[46] Glam Research, *Global Milk sugar Market (EM-233962)*, Glam Research, New Sangvi, India, **2020**.

[47] BAM Bundesanstalt für Materialforschung und -prüfung, *Empfehlungen für die Beförderung gefährlicher Güter - Handbuch über Prüfungen und Kriterien*, Bundesanstalt für Materialforschung und -prüfung, Berlin, **2015**.

[48] Committee of Experts on the Transport of Dangerous Goods, *UN Recommendations on the Transport of Dangerous Goods*, United Nations Economic and Social Council, New York City, NY, USA, **2019**.

11.6. Supporting Information

Table 11.2: White-colored smoke formulations **GZT** and **W1**–**W7** (in wt%).

	Terephthalic Acid	GZT
GZT	0	100
W1	5	95
W2	10	90
W3	15	85
W4	20	80
W5	25	75
W6	30	70
W7	35	65

Table 11.3: White hexamine-based reference smoke formulations (in wt%).[31]

	Terephthalic Acid	$KClO_3$	Hexamine	MCHP
Ref-W	45	27.5	22	5.5

Table 11.4: Yellow-colored smoke formulations **Y1**–**Y7** (in wt%).

	Solvent Yellow 33	GZT
Y1	5	95
Y2	10	90
Y3	15	85
Y4	20	80
Y5	25	75
Y6	30	70
Y7	35	65

Table 11.5: Red-colored smoke formulations **R1**–**R7** (in wt%).

	Solvent Red 1	**GZT**
R1	5	95
R2	10	90
R3	15	85
R4	20	80
R5	25	75
R6	30	70
R7	35	65

Table 11.6: Violet-colored smoke formulations **V1**–**V7** (in wt%).

	Solvent Violet 47	**GZT**
V1	5	95
V2	10	90
V3	15	85
V4	20	80
V5	25	75
V6	30	70
V7	35	65

Table 11.7: Blue-colored smoke formulations **B1**–**B7** (in wt%).

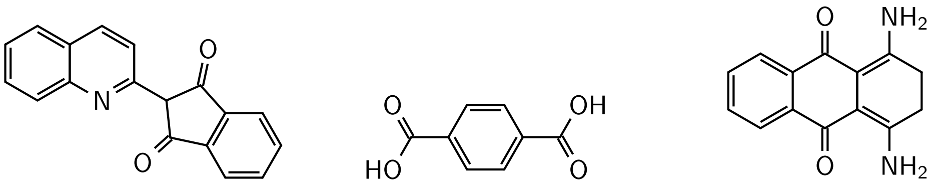
	Solvent Green 3	**GZT**
B1	5	95
B2	10	90
B3	15	85
B4	20	80
B5	25	75
B6	30	70
B7	35	65

Table 11.8: Green-colored smoke formulations **G1**–**G7** (in wt%).

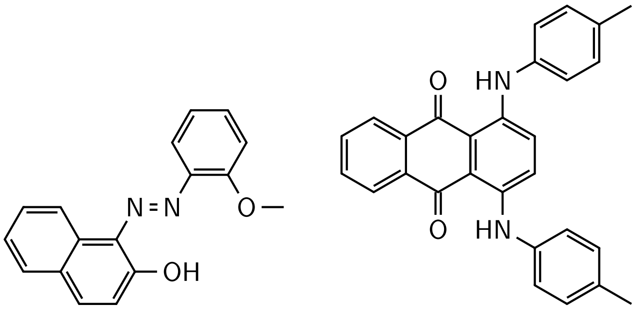
	Solvent Green 3	**Solvent Yellow 33**	**GZT**
G1	3.3	1.7	95
G2	6.7	3.3	90
G3	10	5	85
G4	13.3	6.7	80
G5	16.7	8.3	75
G6	20	10	70
G7	23.3	11.7	65

Table 11.9: Multi-colored sugar-based reference smoke formulations fulfilling the concept of fuel mixes (in wt%).[29]

	SY 33	**SG 3**	**DR 9**	**VDM**	**$KClO_3$**	**Sucrose**	**MCHP**
Ref-Y	30	–	–	–	28	28	14
Ref-R	–	–	30	–	28	28	14
Ref-V	–	–	–	30	28	28	14
Ref-G	10	20	–	–	28	28	14



(a) Solvent Yellow 33. **(b)** Terephthalic Acid. **(c)** Solvent Violet 47.



(d) Solvent Red 1. **(e)** Solvent Green 3.

Figure 11.4: List of applied dyes in presented study.[8]

Table 11.10: Properties as well as sensitivities of GZT and GZT-based smokes in comparison with chlorate- / sugar-based references.[29]

	BT/s	**BR**/mm s^{-1}	**BR**/g s^{-1}	$\mathbf{m_a}$/mg	**Y**/%	**RH**/%	$\mathbf{m_d}$/mg	**T%**/%	**IS**/J	**FS**/N	**ESD**/J	$\mathbf{T_{dec}}$/°C
GZT	19	11.8	0.07	654	32	58	–	–	35	360	1.0	239.2
W3	26	6.9	0.04	582	29	61	–	–	40	360	1.0	214.9
Y3	26	5.3	0.03	783	38	63	164	55	40	360	1.0	238.5
R3	25	5.6	0.03	745	36	58	169	56	40	360	1.0	238.8
V3	29	5.6	0.04	779	38	58	–	–	40	360	1.0	236.5
B3	24	6.8	0.04	726	35	62	–	–	40	360	1.0	239.1
G3	19	7.3	0.04	715	35	61	–	–	40	360	1.0	237.6
Ref-W	38	–	0.26	693	35	31	–	–	10	360	0.6	203
Ref-Y	13	–	0.43	670	33	29	435	73	40	360	0.3	178
Ref-R	21	–	0.41	729	36	28	514	86	40	360	0.6	172
Ref-V	15	–	0.29	652	32	28	–	–	30	360	0.7	178
Ref-G	19	–	0.43	642	32	28	–	–	30	360	0.2	172

BT = burn time (2.0 g scale); BR = linear / mass burn rate (5.0–6.0 g scale); m_a = mass of produced aerosol (2.0 g scale); Y = yield factor; RH = relative humidity during yield determination; m_d = dye content present in produced aerosol; T% = transfer rate; IS = impact sensitivity FS = friction sensitivity; ESD = electrostatic discharge sensitivity; T_{dec} = temperature of decomposition.

Part V.

Appendix

A. List of Publications

A.1. Publications

1. Johann Glück, Teresa Küblböck, Thomas M. Klapötke, Development of a Sustainable Perchlorate-Free Yellow Pyrotechnical Strobe Formulation, *ACS Sustainable Chemistry & Engineering* **2018**, *6*, 4400–4404 (doi:10.1021/acssuschemeng.8b00105).
2. Teresa Küblböck, Johann Glück, Thomas M. Klapötke, 5-Amino-1*H*-tetrazole-based multi-coloured smoke signals applying the concept of fuel mixes, *New Journal of Chemistry* **2018**, *42*, 10 670–10 675 (doi:10.1039/c8nj01786g).
3. Teresa Küblböck, Thomas M. Klapötke, Combining Higher Efficiency with Lower Costs: an Alternative Hexamine-Based White Smoke Signal, *Propellants, Explosives, Pyrotechnics* **2018**, *43*, 1184–1189 (doi:10.1002/prep.201800245).
4. Teresa Küblböck, Johann Glück, Thomas M. Klapötke, The Flame Emission of Indium from a Pyrotechnical View, *Zeitschrift für anorganische und allgemeine Chemie* **2019**, *645*, 1–6 (doi:10.1002/zaac.201900185).
5. Teresa Küblböck, Johann Glück, Thomas M. Klapötke, Fine-Tuning: Advances in Chlorine-Free Blue-Light-Generating Pyrotechnics, *European Journal of Inorganic Chemistry* **2020**, *4*, 349–355 (doi:10.1002/ejic.201901097).
6. Teresa Küblböck, Gaspard Angé, Greta Bikelytė, Jiřina Pokorná, Radovan Skácel, Thomas M. Klapötke, Guanidinium 5,5'-Azotetrazolate: A Colorful Chameleon for Halogen-free Smoke Signals, *Angewandte Chemie, International Edition* **2020** (doi:10.1002/anie.202007489).
7. Teresa Küblböck, Gaspard Angé, Greta Bikelytė, Jiřina Pokorná, Radovan Skácel, Thomas M. Klapötke, Guanidin 5,5'-Azotetrazolat: Ein farbenfrohes Chamäleon für halogenfreie Rauchsignale, *Angewandte Chemie* **2020** (doi:10.1002/ange.202007489).

A.2. Conference Publications and Presentations

Conference Publications

1. Teresa Küblböck, Johann Glück, Thomas M. Klapötke, Multi-colored smoke signals applying the concept of fuel mixes, *Proceedings of the 21st International Seminar: New Trends in Research of Energetic Materials (NTREM)* **2018**, University of Pardubice, Pardubice, Czech Republic.

2. Teresa Küblböck, Thomas M. Klapötke, Green is the new Black: An Environmentally Benign Black Smoke Fulfilling the Concept of Fuel Mixes, *Proceedings of the 22nd International Seminar: New Trends in Research of Energetic Materials (NTREM)* **2019**, University of Pardubice, Pardubice, Czech Republic.

3. Teresa Küblböck, Johann Glück, Thomas M. Klapötke, Investigation of indium in pyrotechnical compositions, *Proceedings of the 23rd International Seminar: New Trends in Research of Energetic Materials (NTREM)* **2020**, University of Pardubice, Pardubice, Czech Republic.

Conference Presentations

1. Teresa Küblböck, Multi-colored smoke signals applying the concept of fuel mixes, *21st International Seminar: New Trends in Research of Energetic Materials (NTREM)* **2018**, University of Pardubice, Pardubice, Czech Republic.

2. Teresa Küblböck, Johann Glück, Multi-colored smoke signals applying the concept of fuel mixes, *43rd International Pyrotechnic Seminar (IPSUSA)* **2018**, IPSUSA Seminars, Fort Collins, USA.

Conference Poster Presentations

1. Teresa Küblböck, Thomas M. Klapötke, Green is the new Black: An Environmentally Benign Black Smoke Fulfilling the Concept of Fuel Mixes, *22nd International Seminar: New Trends in Research of Energetic Materials (NTREM)* **2019**, University of Pardubice, Pardubice, Czech Republic.

2. Teresa Küblböck, Johann Glück, Thomas M. Klapötke, Investigation of indium in pyrotechnical compositions, *Proceedings of the 23rd International Seminar: New Trends in Research of Energetic Materials (NTREM)* **2020**, University of Pardubice, Pardubice, Czech Republic.

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Johann Glück, Thomas M. Klapötke, Teresa Küblböck, Development of a Sustainable Perchlorate-Free Yellow Pyrotechnical Strobe Formulation, *ACS Sustainable Chemistry & Engineering* **2018**, *6*, 4400–4404 (doi:10.1021/acssuschemeng.8b00105). Reprinted with permission. © **2018** American Chemical Society.

Johann Glück, Thomas M. Klapötke, Teresa Küblböck, 5-Amino-1*H*-tetrazole-based multi-coloured smoke signals applying the concept of fuel mixes, *New Journal of Chemistry* **2018**, *42*, 10 670–10 675 (doi:10.1039/c8nj01786g). Reproduced with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.

Teresa Küblböck, Thomas M. Klapötke, Combining Higher Efficiency with Lower Costs: an Alternative Hexamine-Based White Smoke Signal, *Propellants, Explosives, Pyrotechnics* **2018**, *43*, 1184–1189 (doi:10.1002/prep.201800245). © **2018** Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.