Blue Strobe Pyrotechnic Composition Based on Aminoguanidinium Nitrate

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

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

1 Introduction

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

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

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

In this work GN and aminoguanidinium nitrate (AGN) were employed as replacements for TMAN in blue strobe compositions containing AP, polyvinyl chloride (PVC) and basic copper carbonate, CuCO$_3$·Cu(OH)$_2$ (BCC). Due to better performance, AGN composition was studied in more detail.

2 Experimental Section

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

N.B., in previous work AGN was found to be extremely dangerous when mixed with copper bromate, Cu(BrO$_3$)$_2$ and copper iodate, Cu(IO$_3$)$_2$. The sensitivity to friction was extreme and small amounts of experimental mixtures self-ignited during storage. Also a side product of AGN reaction with BCC (black in color, obtain under acidic conditions) had self-ignited while being wet on a filter paper.

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

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

The strobe compositions were mixed using a mortar and pestle. Pellets of 2 g (13 mm in diameter, ~10 mm in height, \( \rho \approx 1.57 \text{ g cm}^{-3} \)) were pressed in one increment by a consolidation dead load of 2 tons. For extruding of 5 mm diameter rods the following procedure was followed: 2–4 g of composition was moistened with either MEK or Acetone to swell or dissolve the binder material (PVC or NC). Then a 5 mm ID plastic syringe with a cut end was used as a simple pump to press 10–25 mm long rods (~0.4 g each, \( \rho \approx 1.15 \text{ g cm}^{-3} \)). The syringe was filled with the moist strobe composition and while facing a hard surface the plunger was pressed down by hand to eject entrapped air and to consolidate the compositions as much as possible. Finally the compressed rod was extruded and left to dry overnight at room temperature.

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

### 3 Results and Discussion

#### 3.1 Aminoguanidinium Nitrate Blue Strobe

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

Hence AGN was suggested as a possible replacement that could surpass GN in its reactivity and have an advantage over TMAN being more easily available and cheaper option. A series of strobe compositions containing AP, GN, AGN, different copper sources (Cu, CuO, Cu₂O, BCC) were tested.

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

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

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

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

#### 3.2 Humidity Test

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

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

After exposure to RH 75% the first significant change in sample’s weight was registered. Moisture induces a reaction that releases gases, which causes the weight loss and the color change.
The color change was also registered in several sample compositions that were stored before pressing pellets. However, well dried compositions did not cause such reaction for up to 2 months of storage at room temperature. It must be noted that dry and acid-free AGN was used in our experiments (water solution shows pH of 7–8 on universal indicator paper). In our experience, compositions with non-acidic AGN have significantly greater shelf life.

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

<table>
<thead>
<tr>
<th>Compositions</th>
<th>A</th>
<th>B</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄ClO₄</td>
<td>30</td>
<td>25</td>
<td>55</td>
</tr>
<tr>
<td>GN</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AGN</td>
<td></td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>TMAN</td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>PVC</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>CuCO₃·Cu(OH)₂ (BCC)</td>
<td>15</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Cu powder (40–100 mesh)</td>
<td></td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Frequency, Hz</td>
<td></td>
<td>3.5 ± 2</td>
<td>8 ± 2</td>
</tr>
<tr>
<td>Linear burning rate</td>
<td>1.4</td>
<td>1.1</td>
<td>5.2*</td>
</tr>
<tr>
<td>Chemical stability (DTA), °C</td>
<td>247</td>
<td>179</td>
<td>245</td>
</tr>
<tr>
<td>Sensitivity tests</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Impact (J)</td>
<td>15</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>Friction (N)</td>
<td>&gt; 360</td>
<td>&gt; 360</td>
<td>&gt; 240</td>
</tr>
<tr>
<td>ESD (mJ)</td>
<td>42</td>
<td>33</td>
<td>51</td>
</tr>
</tbody>
</table>

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

Figure 1. Light intensity at 450 nm vs time.
When 3 g of acid-free AGN is dissolved in water and 1 g of finely ground BCC is added to the solution, the color of undissolved BCC changed first to light violet and then to purple. Bubbling is observed. After stirring the suspension and letting react overnight, 2,8 g of purple precipitate is formed, which is likely to be a Cu aminoguanidinium complex. When dried and ignited as loose powder, the complex material burns fiercely producing a green flame that comes from CuOH(g) emissions. The chemical stability this complex species is quite unclear, and as mentioned before, AGN and BCC reaction’s side product had self-ignited one time during drying. Therefore, long term stability tests at elevated temperatures are suggested before using in practice.

3.3 Differential Thermal Analysis (DTA)

DTA measurement was performed for composition B and certain compositions with AGN. It was found that BCC catalyzes the decomposition of AGN and significantly changes the DTA curve of AGN (Figure 4). The B curve is very similar to AGN/BCC with the same decomposition point at 179°C, meaning that AP and PVC do not participate in this process. Sometimes during the incremental heating of the DTA sample, the test composition B (and very similar ones) showed a high-order deflagration (likely at 238°C) that were powerful enough to rupture the mini glass test tube of the DTA instrument. The sample weight was ~40 mg.

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

<table>
<thead>
<tr>
<th>Salt</th>
<th>Relative humidity at 25°C, %</th>
<th>K₂CO₃</th>
<th>NaBr</th>
<th>NaCl</th>
<th>KNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>43</td>
<td>57,6</td>
<td>75,3</td>
<td>93,6</td>
</tr>
<tr>
<td>Pellets</td>
<td>Weight change</td>
<td>0</td>
<td>0,0004</td>
<td>-0,0005</td>
<td>-0,0246</td>
</tr>
<tr>
<td></td>
<td>Color change/cracks</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>yes*</td>
</tr>
<tr>
<td>Powder</td>
<td>Weight change</td>
<td>0,001</td>
<td>-0,002</td>
<td>-0,0115</td>
<td>-0,0375</td>
</tr>
<tr>
<td></td>
<td>Color change</td>
<td>no</td>
<td>greyish violet (lite)</td>
<td>greyish violet</td>
<td>deep purple**</td>
</tr>
</tbody>
</table>

* In 6 h purple spots appear. ** In 3 h turns grey-violet, in 6 h purple, after three days – deep purple.
3.4 Origin of the Bright Blue Flash

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

During the smolder phase gases are generated from the reaction surface (Figure 5). Around 50% of the smolder reaction time small blue-glowing lines of gases appear at the reaction surface as well as micro blue flashes (Figure 6A). As the glowing gases eject from the burning surface, sometimes, especially few milliseconds before the flash reaction, a significantly brighter flame spot appear (Figure 6A, fifth frame) that travels upwards with the flow of gases. Perhaps this is a region of higher temperature or a piece of molten reactive composition being ejected from the pellet’s surface, that has a delayed ignition and burns to produce a significantly bright blue flash/spot, that is associated to the same brightness and color of the flash reaction (Figure 6A).

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

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

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

Interestingly, being thin and fragile as the scaffold is, it did not fall apart due the stoobe reaction that would make one expect to have a certain pressure fluctuation at the surface that is accompanied by the popping sound observed every time when testing compressed and uncompressed B composition. For example, a classical white strobe composition based on AP/MgAl/BaSO₄ [8] burns to produce flashes that are more similar to a small portions of flash powder deflagrating. This produces pressure fluctuations, that can

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

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

Figure 7. The ash scaffold is formed due to a strong heat loss to the surrounding atmosphere during the combustion of 5 mm rod (comp. B). Partially red glowing ash scaffold in the last frame is observed.
be seen when such composition is compact into a cardboard casing, that eventually burns off and the remaining’s of the paper casing are blown away by the pressure waves of the flashes. However, in the case of rod, the ash scaffold remained still, indicating that there are no significant pressure fluctuations at the burning surface, what supports the second assumption.

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

4 Conclusions

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

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

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

5 Abbreviations

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

Acknowledgements

The DAAD (one-year grant) program is acknowledged for a scholarship (D.J.). The authors are very grateful to Per Alenfelt from Hansson Pyrotech AB, Kaj Fredriksson from Sweden and Rutger Webb from Clearspark B.V. for many inspiring discussions related to the experimental work presented herein. Also Marcel Holler and Marcus Lommel for helping with the high speed camera experiments, Stefan Huber for the sensitivity measurements and Maximilian Wurzenberger for various discussions and the help with the DTA measurements.

References

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