

High-Nitrogen Fuels for Low-Smoke Pyrotechnics^[1]

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ABSTRACT

It has been demonstrated that the high-nitrogen compound, 3,6-dihydrazino-s-tetrazine (DHT), can be utilized as a pyrotechnic fuel requiring small amounts of metal salts for coloring the flame. In addition, DHT pyrotechnic formulations using non-metallic oxidants, specifically ammonium perchlorate and ammonium nitrate, produce little smoke when burned. In light of this application of high-nitrogen compounds, we have determined that two other high-nitrogen fuels, bis-(1(2)H-tetrazol-5-yl)-amine monohydrate (BTAw), 5,5'-bis-1H-tetrazole (BT) and their salts are likely candidates for low-smoke pyrotechnic fuels. The various characteristics of these fuels have been examined in some detail; these include impact sensitivity with and without oxidant ammonium perchlorate, spectra of colored flames, and thermal analyses of their hydrates and salts.

Keywords: high nitrogen fuel, low smoke, pyrotechnics, bis-(1(2)H-tetrazol-5-yl)-amine, 5,5'-bis-1H-tetrazole, 3,6-dihydrazino-s-tetrazine.

Introduction

Traditional pyrotechnic formulations are typically composed of carbonaceous fuels and metal salts. These salts are often used as both oxidant and flame colorant—for example, strontium nitrate. Such mixtures are known to burn with abundant smoke and often ash as well, which is attributed to partial combustion and the generation of non-gaseous products, particularly metal oxides. In addition, recent formulations have introduced chlorinated polymers for color enhancement, yet this has done

little to decrease the amount of noxious smoke. Here at the Los Alamos National Laboratory we have made progress in reducing smoke and the metal content in pyrotechnic formulations without sacrificing flame color. This work is an offshoot of our high-nitrogen synthesis program to synthesize high-nitrogen compounds for use as explosives and gas generants. It is our hope that this technology will alleviate the exposure of crew and audiences to potentially harmful smoke.

Previously, Chavez and Hiskey have reported^[2] that 3,6-dihydrazino-s-tetrazine (DHT) (Figure 1), when mixed with non-metallic oxidizers and 5 wt. % coloring agents, produces little smoke and ash when burned.^[3] These formulations needed no chlorinated polymeric binder since the preferred oxidant, ammonium perchlorate (AP), acted as both oxidizer and color enhancer. The authors were able to make strong compact stars by wetting the AP formulations with water, pressing them into shape and drying. Because of the hygroscopic nature of ammonium nitrate (AN), formulations containing AN were wetted with alcohol rather than water. These stars were protected from moisture by dipping in nitrocellulose lacquer. In addition, the authors have simplified the syn-

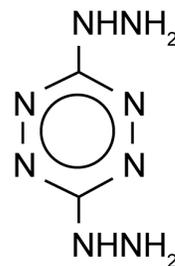


Figure 1. Structure of DHT.

thesis of DHT by bypassing the tedious hydrazinolysis of 3,6-diamino-*s*-tetrazine at elevated temperature.

Besides DHT, other high-nitrogen compounds have been studied for use as low-smoke pyrotechnic fuels. These compounds, bis-(1(2)*H*-tetrazol-5-yl)-amine monohydrate (BTAW) and 5,5'-bis-1*H*-tetrazole (BT) (Figure 2), are diprotic acids and can react with basic amines to form mono- and di-aminated salts, and with metal carbonates or hydroxides to form metal salts. Some of these salts are hydrates. By formulating these compounds with different ratios and compositions, it is now possible to achieve greater control and variability in burn rate and ignitability of high-nitrogen pyrotechnic formulations than with DHT alone.

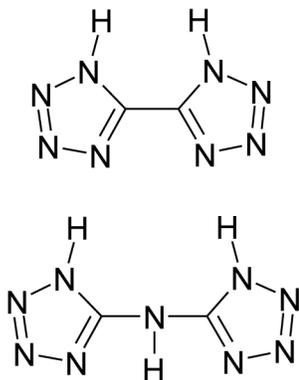
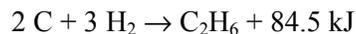


Figure 2. Structures of BT (top) and BTA (bottom). BTAW is the monohydrate of BTA.

Heats of Formation

A feature of these high-nitrogen fuels is their large positive heat of formation (ΔH_f), which is broadly described as the thermal change involved in the formation of one mole of fuel from its elements. Historically, because of the complexity of measuring absolute enthalpy, the elements have been assigned zero enthalpy of formation at standard temperature (25 °C) and pressure (1 atm). A compound having a negative heat of formation denotes that the reaction of its constitutive elements in the appropriate stoichiometric ratio is an exothermic reaction.

An example is the reaction of two moles of graphite (a form of pure carbon) with 3 moles of hydrogen gas to produce one mole of ethane gas, which would release 84.5 kJ of heat.



A compound with a positive heat of formation absorbs heat energy for its formation. The formation of one mole of DHT from its elements requires 535 kJ energy; thus its intrinsic chemical potential energy is comparably higher than that of ethane. However, it must be noted that the magnitude of a heat of formation *based on a mole of material* can be misleading.

A compound of large molecular weight can give the impression of having an unusually large heat of formation. This is because the heat of formation is dependent on the number and types of chemical bonds. Compounds with high molecular weights do, of course, have many bonds that contribute to the total heat of formation. The heat of formation of the hydrocarbon *n*-octane is -208 kJ/mol , which is more than twice that of ethane. This disparity could make one incorrectly believe that ethane has significantly more chemical potential energy than that of *n*-octane. For this reason it is usually best to compare the intrinsic enthalpies of different compounds by normalizing the heat of formation on a per mol·atom basis. Ethane has 8 atoms, so its normalized heat of formation is $-10.6 \text{ kJ/mol}\cdot\text{atom}$ (-84.5 kJ/mol divided by 8 atoms). The normalized heat of formation for *n*-Octane, with 26 atoms, is $-8.00 \text{ kJ/mol}\cdot\text{atom}$. Thus, it is seen that *n*-octane has an intrinsic enthalpy comparable to that of ethane gas.

In Table 1, the heats of formation of several traditional and high-nitrogen fuels are reported on a mole and mol·atom basis. Graphite and naphthalene have seemingly different heats of formation on a mole basis, but are similar when calculated on a per mol·atom basis. When compared on a mole basis, sucrose has a more negative heat of formation than that of potassium benzoate trihydrate. However, the benzoate salt has a more negative enthalpy than that of sucrose on a mol·atom basis. The large negative heat of formation of potassium benzoate is attributed to its being a salt and hydrated with three molecules of water.

Table 1. Heats of Formation, Heats of Reaction (balanced to CO₂ with AP as an Oxidizer), and Mol-Atom Normalized Values for Various Fuels.

Fuels	ΔH_f (kJ/mol)	ΔH_f (kJ/mol-atom)	ΔH_{rxn} (kJ/mol)	ΔH_{rxn} (kJ/mol-atom)
Graphite	0	0	-525	-58.4
Naphthalene	+60.2	+3.34	-6540	-57.4
Sucrose	-2220	-49.3	-6740	-47.8
K Benzoate·3H ₂ O	-1510	-62.9	-4020	-47.9
BTaw	+186	+10.9	-1940	-49.7
DHT	+536	+33.5	-2510	-57.0

Since pyrotechnic formulations are usually an intimate mixture of fuel and oxidizer, the heats of reaction of various fuels and AP have been calculated and are also included in Table 1. The calculations are based on one mole of fuel reacting with sufficient AP to oxidize all hydrogen to gaseous water and all carbon to carbon dioxide. Again, for the same reasons that the heats of formation were normalized, the heats of reaction were normalized on a mol-atom basis and are listed in Table 1. The number of atoms used in normalizing the heat of reaction is the total number of atoms in the fuel and AP adjusted stoichiometrically. These normalized heats of reaction are comparable, even for fuels with large disparity in heats of formation, such as graphite, naphthalene and DHT. So, from an enthalpic perspective, it appears unnecessary to resort to exotic compounds with large positive heats of formation for enhancing the energy content of fuel/oxidizer matrices.

Yet, these calculations were based on the assumption that a burning reaction reaches equilibrium efficiently (i.e., reacting to completion to produce water and carbon dioxide), which is hardly the case. Pyrotechnicians are perhaps familiar with the use of naphthalene as a fuel, if it could be called that. A mixture of naphthalene and potassium chlorate burns with dense carbonaceous smoke, which precludes any notion that such a reaction effectively reaches equilibrium condition. Burning sugars, or sugar-like fuels such as starches or cellulose, are not any better. Paradoxically, potassium benzoate trihydrate, which has a low heat of formation on a mol-atom basis, does burn comparatively cleanly with an oxidizer; how-

ever, it still produces much smoke. Most of this smoke is attributed to the formation of potassium compounds rather than soot-like combustion products. The high-nitrogen fuels, BTaw, BT, DHT and their derivatives, together with the appropriate amount of oxidizer *burn with little or no soot production*. This is attributed to the high nitrogen makeup of these formulations that allows them to burn with great efficiency and to reach equilibrium condition rapidly.

Because these formulations burn cleanly, only small amounts of metal colorants are needed to color the flame. This double-bonus of sootless flames and low metal contents has made these formulations desirable in low-smoke pyrotechnic applications.

Sensitivity

The sensitivity of these high-nitrogen fuels, their salts and mixtures with AP were measured by impact analysis using a Type 12 machine. More details on the procedure can be obtained from a handbook compiled by Dobratz.^[4] An impact analysis is reported as a drop height (H_{50}), which is the height where a 2.5 kg weight—when dropped onto a 40 mg sample on sandpaper—has a 50% possibility of initiation. The maximum height that can be reached with the impact machine is 320 cm. For comparison, pentaerythrite tetranitrate (PETN) has a drop height of approximately 13 to 16 cm.^[4] The drop heights of the pure high-nitrogen fuels and their metal salts are listed in Table 2. Most of these fuels and salts are fairly insensitive ($H_{50} > 320$ cm), which makes them desir-

Table 2. Impact Sensitivities of High-Nitrogen Fuels and their Salts. Names and Formulas Are Given in the Synthesis Section.

Sample	H ₅₀ (cm)
DHT	65
BT	15
DA-BT	>320
DHA-BT	94
DHz-BT	>320
HA-BT	34
Hz-BT	112
DHT-BT2w	264
BTAw	>320
BTA (anhydrous)	26
DA-BTAw	>320
DHz-BTAw	>320
A-BTA	>320
Hz-BTA	>320
Sr-BT4w	>320
Ba-BT4w	>320
Cu-BT2w	23
Sr-BTA4w	>320
Ba-BTA	>320
Cu-BTA2w	269

able for storing and shipping. Pure AP oxidant, too, has a drop height greater than 320 cm. However, impact sensitivity does increase when these same fuels are mixed with AP. The H₅₀ values of a 34/66 weight ratio of dihydroxylammonium 5,5'-bis-1H-tetrazole (DHA-BT) and AP, a 50/50 ratio of BTAw/AP, and a

50/50 ratio of DHT/AP are 23, 27 and 33 cm respectively. Furthermore, the impact sensitivities of fuel and AP mixtures have been found to decrease with increasing atmospheric humidity. This is typical behavior of heterogeneous mixtures of fuel and inorganic oxidant, such as AP. Table 3 shows how similar DHT/AP formulations increase in impact sensitivity when the relative humidity (RH) is dropped from ca. 60 to 25% RH. Thus mixtures that are rather insensitive in a humid environment can become more sensitive with drier weather.

Stability

Because many of these materials are hydrated and amine salts, it was deemed worthwhile to perform thermogravimetric analysis (TGA) to determine at which temperatures loss of water, loss of amine and onset of decomposition are incurred.^[7] To simulate the effect of oven-drying, the TGA was performed at an extremely slow rate (0.1 °C/min). An example of a raw TGA spectrum is shown in Figure 3, which is a plot of a BTAw sample's weight versus temperature. Because numerous analyses had been performed and raw TGA spectra are unwieldy, the data were reworked and presented in a more utilizable format (see Figure 4). The shaded blocks in Figure 4 represent regions of different mass loss rates between 25 and 225 °C. These mass losses are due to decomposition and evaporation of organic amine and hydrated water. BTAw, for example, loses

Table 3. Impact Results of Various DHT-AP Formulations Demonstrate That Impact Sensitivity Is Highly Dependent on the Relative Humidity of the Atmosphere in Which the Analysis Is Performed. This Phenomenon Is Typical of Binary Compositions That Contain Fuel and Ammonium Perchlorate.

Composition (wt. %)				H ₅₀ (cm)	RH (%)
DHT	AP	Metal	Salt		
50.0	50.0	—	—	33	62
47.5	47.5	5.0	CuS	27	60
30.5	69.5	—	—	14	26
49.5	49.5	1.0	Li ₂ CO ₃	19	27
46.5	46.5	7.0	H ₃ BO ₃	22	20
47.5	47.5	5.0	SrCO ₃	19	28

hydrated water at a nominal rate (between 0.001 and 0.01%/min^[8]) in a temperature region from 74 to 94 °C. The rate increases above 0.01%/min at 94 °C, but later falls below 0.01%/min at 116 °C when the hydrated water has been depleted. Diammonium bis-(1(2)H-tetrazol-5-yl)-amine monohydrate (DA-BTAw), a substance having a more complex TGA profile than BTAw, loses water at ca. 55 °C, the first ammonia molecule at ca. 112 °C, the second ammonia molecule at ca. 165 °C, and finally begins decomposing at ca. 180 °C.

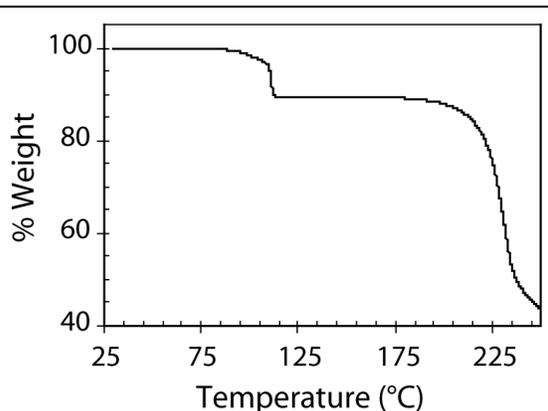


Figure 3. TGA analysis of BTAw at a rate of 0.1 °C/min. The loss of weight is recorded as a function of temperature. Hydrated water is first lost from 74 to 116 °C; decomposition begins at ca. 175 °C.

It must be noted that impact and friction sensitivities of a formulation can be greatly enhanced by the loss of hydrated water. For example, the drop height of BTAw is greater than 320 cm, but decreases to 26 cm when dried to its anhydrous form, BTA. Therefore, great care must be taken with mixtures con-

taining BTA, especially when mixed with an oxidizer. Fortunately it is fairly difficult to dry BTAw to BTA (ca. 112 °C for several hours) and BTA readily hydrates back to BTAw in air at 50% relative humidity. Drying is most useful with formulations containing the tetrahydrated strontium and barium salts of BT and BTA. Such mixtures have improved ignitability when some of the hydrated water from these salts is removed.

A simple test procedure was developed to determine at what humidity levels anhydrous salts convert back to their hydrated form. Four hygrometers were used for these controlled exposure tests. A saturated solution of potassium acetate at the bottom of a sealed chamber generates a 20% RH environment at room temperature. Likewise, saturated solutions of magnesium nitrate, sodium acetate and dibasic sodium phosphate (Na_2HPO_4) produce 52, 76 and 96% RH environments, respectively.^[9] Tared anhydrous samples were placed in the four hygrometers and their weights were measured a number of times over the course of several weeks. Samples that rehydrated weighed more, while those samples that remained anhydrous kept their original weight. The data are noted in the Synthesis section.

Ion exchanges between salts can be problematic for some of these formulations. Hydrazine and hydroxylammonium salts of BT or BTA can metathetically exchange with AP in a solution environment (such as water) to form stable ammonium derivatives of BT or BTA and the highly unstable *hydrazinium and hydroxylammonium perchlorates*. Therefore the risk of forming explosive salts precludes the use of hydrazine and hydroxylammonium salts for practical applications.

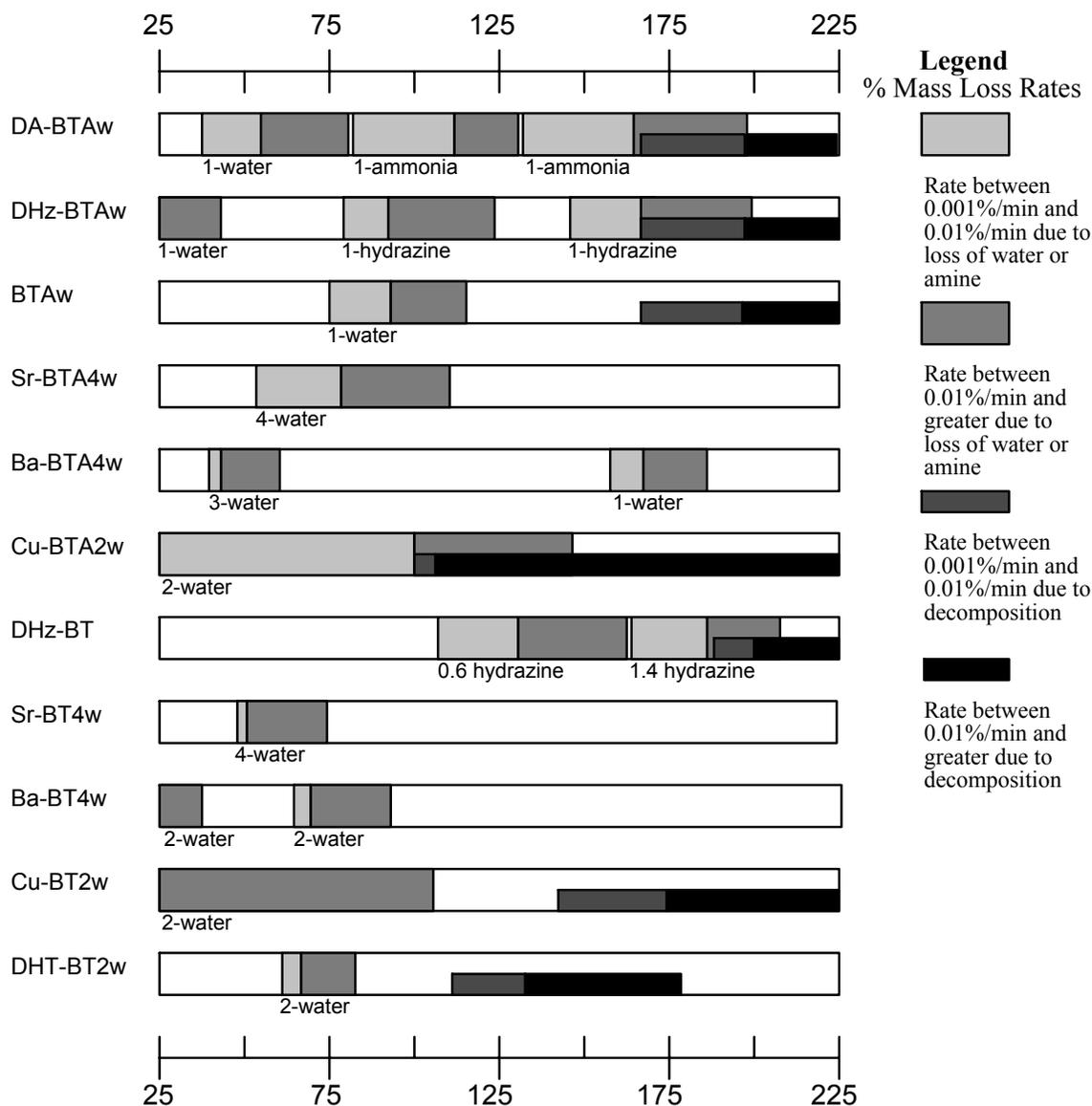


Figure 4. The thermal gravimetric analysis (TGA) data of various fuels and metal salts that undergo reversible decomposition (i.e., loss of hydrated water or organic amine) were reworked for clarity. Shaded blocks represent regions of different mass loss rates between 25 and 225°C. These analyses were performed at a slow rate (0.1 °C/min) to simulate the effect of oven-drying.

Synthesis

The synthetic procedures described below should only be attempted by those experienced with energetic material synthesis, equipped with proper laboratory facilities, and capable of properly disposing of the hazardous chemical waste. The materials used are toxic and flammable, most notably sodium azide, sodium cyanide and hydrazine. In addition, explosive metal

azides are easily formed from the metathetical exchange between sodium azide and metal salts. Some of these azides, such as silver, copper and lead azides, are extremely friction and heat sensitive. Hydrazine and its derivatives should be regarded as potential carcinogens and treated with care. All reagents were purchased from commercial sources except where noted. Elemental analyses were performed using a Perkin Elmer Series II CHNS/O Analyzer, Model 2400. Poor agreement between theoretical and meas-

ured results is a characteristic problem in the elemental analysis of high-nitrogen compounds. However all compounds were purified to the point that agreement of at least two elements was within 0.4%. All nuclear magnetic resonance (NMR) spectra were obtained on a JEOL GSX-270 spectrometer. Chemical shifts (δ) are reported relative to internal tetramethylsilane = 0 for ^{13}C NMR spectra.

The preparation of DHT was first reported in 1963,^[5] however, a more simplified procedure has been developed.^[3,6] The reported literature of BT, BTaw, their salts and hydrates is scanty and mostly located in obscure patents and government reports. The predominant interest in these compounds, as detailed by the uncovered literature, is their use as automobile air-bag gas generants and rocket propellant additives.

The syntheses of the numerous salts of BTaw and BT are similar, so a general method of synthesis is described here. The exact quantities and reagents are better detailed for each compound below that uses this general method. BTaw or BT, and one or two equivalents of organic amine or metal hydroxide are reacted in a sufficient amount of deionized water necessary for recrystallization. The resulting slurry mixture is stirred and heated to boiling, and—if necessary—filtered hot to remove insoluble impurities. The clear solution is cooled by an ice bath to approximately 10 °C with vigorous stirring to initiate precipitation. The salt is collected by filtration and air-dried.

5,5'-Bis-1*H*-tetrazole (BT)

The preparation of BT involves two steps, whereby manganese 5,5'-bis-1*H*-tetrazolate (Mn-BT) is generated as an intermediate followed by its conversion to the free acid when treated with a buffered solution of carbonic acid. The following preparation is a summarized adaptation of a method outlined by R. A. Henry.^[10]

To a 5-L flask, containing 2.4 L of water, 260 g sodium azide (4.00 mol) and 200 g sodium cyanide (4.08 mol) were added. While being stirred and cooled by an ice bath, 220 g of manganese dioxide (2.53 mol) were added.

Afterwards, a solution—comprised of 400 g concentrated sulfuric acid (4.08 mol), 320 g glacial acetic acid (5.33 mol) and 8 g copper(II) sulfate pentahydrate (26 mmol), previously dissolved in 1.0 L water—was added at a rate so that the reaction temperature was between 20 and 30 °C. After the addition, the mixture was brought to 90 °C over a one hour period and maintained between 90 and 95 °C for 3 hours. The reaction was cooled and the crude product, possibly containing some copper salts, was filtered and air-dried to yield 390 g of Mn-BT (102%).

To a slurry—composed of 200 g of Mn-BT (1.05 mol) and 1.6 L water—was added gradually 120 g of sodium carbonate (1.13 mol) over a 10 minute period. The mixture was boiled for 1.5 hours, filtered and the solids washed with 200 mL of boiling water. The filtrates were combined and neutralized with concentrated hydrochloric acid until CO_2 evolution stopped. An excess amount of concentrated HCl (140 mL) was added to ensure the precipitation of the di-acid, and not the less soluble acid-sodium salt. At this point any soluble copper salts were precipitated by either titrating with a 5% sodium sulfide solution^[11] or bubbling hydrogen sulfide gas. Thereafter the solution was reduced to 700 mL by boiling, cooled to 0 °C, and filtered to remove the crude product. Yields ranged from 97 to 107 g (65 to 75%). ^{13}C NMR (DMSO- d_6): δ 147.7.

The drop height of BT is 15 cm, which suggests that this material is too sensitive for use as a pyrotechnic fuel alone. The salts of BT, however, are much less sensitive and are readily applicable for low-smoke applications. It is strongly advised that when BT is freshly prepared and still contains moisture, that it be converted to the salt rather than air-dried and stored.

Diammonium 5,5'-Bis-1*H*-tetrazolate (DA-BT)

Using the general synthesis method, 10 g of BT (72 mmol) and 20 mL concentrated ammonium hydroxide were reacted in 300 mL water. DA-BT is one of the most stable high-nitrogen fuels; the onset of decomposition is ca. 280 °C. This salt is commercially available in bulk from

a US distributor at a cost of approximately US\$66 per kilogram.^[12]

Analysis for C₂H₈N₁₀:

Calculated: C, 13.95; H, 4.68; N, 81.36.

Found: C, 14.02; H, 4.94; N, 82.21.

Dihydrazinium 5,5'-Bis-1H-tetrazolate (DHZ-BT)

Using the general synthesis method, 15 g BT (0.11 mole) and 11 g hydrazine monohydrate (0.22 mole) were reacted in 100 mL of water. ¹³C NMR (DMSO-d₆): δ 154.4.

Analysis for C₂H₁₀N₁₂:

Calculated: C, 11.88; H, 4.99; N, 83.13.

Found: C, 11.93; H, 5.02; N, 83.27.

The filtrate of the above reaction, which contains a significant amount of soluble DHZ-BT, was treated with 30 mL of concentrated ammonium hydroxide to precipitate DA-BT. The recovered DA-BT can be recrystallized or converted to another salt. DHZ-BT loses approximately 0.6 hydrazine at ca. 130 °C, and loses the remaining hydrazine at ca. 195 °C. Star samples composed of this fuel melted and decomposed before catching fire. For this reason, DHZ-BT is perhaps one of the poorest performing fuels. However, stars formulated with copper salts burned with relative ease, which is attributed to the catalytic effect of copper salts on hydrazine. DHZ-BT might find use as an additive to adjust the ignitability or burn characteristics of pyrotechnic formulations.

Hydrazinium 5,5'-Bis-1H-tetrazolate (Hz-BT)

Using the general synthesis method, BT (8.0 g, 58 mmol) and hydrazine monohydrate (2.9 g, 58 mmol) were reacted in 50 mL of water. TGA shows that this monoamine salt is thermally stable to 175°C. ¹³C NMR (DMSO-d₆): δ 149.3.

Analysis for C₂H₆N₁₀:

Calculated: C, 14.12; H, 3.55; N, 82.33.

Found: C, 14.33; H, 3.67; N, 83.28.

Dihydroxylammonium 5,5'-Bis-1H-tetrazolate (DHA-BT)

Using the general synthesis method, BT (30 g, 0.22 mol) and 27 mL of 50% hydroxylamine solution (0.44 mol) were reacted in 1 L of water. The onset of decomposition is ca. 200 °C.

Analysis for C₂H₈N₁₀O₂:

Calculated: C, 11.77; H, 3.95; N, 68.61.

Found: C, 11.83; H, 4.21; N, 68.54.

Hydroxylammonium 5,5'-Bis-1H-tetrazolate (HA-BT)

Using the general synthesis method, BT (22.5 g, 0.16 mol) and 10 mL of 50% hydroxylamine solution (0.16 mol) were reacted in 90 mL of water. The onset of decomposition is ca. 196 °C.

Analysis for C₂H₅N₉O:

Calculated: C, 14.04; H, 2.94; N, 73.67.

Found: C, 14.00; H, 2.92; N, 73.86.

Barium 5,5'-Bis-1H-tetrazolate Tetrahydrate (Ba-BT4w)

Using the general synthesis method, BT (3.20 g, 23.2 mmol) and barium hydroxide octahydrate (7.40 g, 23.5 mmol) were neutralized in 200 mL water. Ba-BT4w loses its four hydrated water molecules in two stages. Two water molecules are readily lost when the barium salt is heated to ca. 40 °C, and the remaining two waters are lost when heated to ca. 90 °C. Anhydrous Ba-BT shows no indication of decomposition when heated above 300 °C. Because Ba-BT4w is partially efflorescent at room temperature, the hydrate was dried at 150 °C for several hours prior to elemental analysis. Anhydrous Ba-BT rapidly recovers one water at 20% RH over a period of three days. In the same time, the dry salt recovers two water molecules at 52 and 76% RH. At 96% RH, two waters are rapidly hydrated, and the remaining two waters are slowly recovered over a period of three weeks.

Analysis for C₂N₈Ba·4H₂O:

Calculated: C, 8.79; H, 0; N, 40.99.

Found: C, 8.79; H, 0.19; N, 40.80.

Strontium 5,5'-Bis-1*H*-tetrazolate Tetrahydrate (Sr-BT4w)

Using the general synthesis method, BT (1.37 g, 9.9 mmol) and strontium hydroxide octahydrate (2.66 g, 10 mmol) were neutralized in 50 mL water. Four molecules of hydrated water are lost when Sr-BT4w is heated to ca. 75 °C. Similar to the barium salt, this material appears to be thermally stable above 300 °C. Anhydrous Sr-BT recovers approximately one half water over three weeks at 20% RH. At 52% RH and above, the dry salt recovers approximately three water molecules within three days, while the fourth water is hydrated slowly over a period of four weeks.

Analysis for $C_2N_8Sr \cdot 4H_2O$:

Calculated: C, 8.12; H, 2.73; N, 37.89.

Found: C, 8.07; H, 2.60; N, 38.13.

Copper(II) 5,5'-Bis-1*H*-tetrazolate Dihydrate (Cu-BT2w)

To a warmed solution composed of BT (1.38 g, 10 mmol) and 50 mL water was added a solution of copper(II) sulfate pentahydrate (2.5 g, 10 mmol) and 20 mL water. The bright blue solid was filtered and air-dried. Cu-BT2w loses one molecule of water readily below 80 °C, and loses its second water from 80 to 110 °C. The copper salt is fairly stable having an onset of decomposition from ca. 140 to 145 °C.

Analysis for $C_2N_8Cu \cdot 2H_2O$:

Calculated: C, 10.19; H, 1.71; N, 47.55.

Found: C, 10.12; H, 1.86; N, 46.04.

3,6-Dihydrazino-*s*-tetrazinium 5,5'-Bis-1*H*-tetrazolate Dihydrate (DHT-BT2w)

To 13.8 g of BT (0.10 mol) in 200 mL of water was added 14.2 g DHT. The slurry was stirred for 48 hours, whereupon the original red color of DHT changed to a bright orange. The product was collected by filtration and air-dried. The two hydrated waters are rapidly lost at ca. 75 °C. Anhydrous DHT-BT remains non-hydrated at 76% RH, but recovers the two water molecules at 96% RH over a period of several weeks.

Analysis for $C_4H_8N_{16} \cdot 2H_2O$:

Calculated: C, 15.19; H, 3.82; N, 70.87.

Found: C, 15.28; H, 3.84; N, 71.59.

Bis-(1(2)*H*-tetrazol-5-yl)-amine Monohydrate (BTaw)

The syntheses of BTaw and its hydrated, acid sodium salt were first described by Norris and Henry.^[13] In one method cyanoguanyl azide is treated with azide in the presence of a trialkylammonium salt as an acid catalyst; in the second, sodium dicyanoamide is reacted with azide and trialkylammonium salt catalyst. These preparations have the drawback of utilizing a commercially expensive catalyst that converts to an odorous free-based trialkylamine as a by-product. Highsmith et al. have improved the synthetic method in their detailed US patent; for convenience, an extracted excerpt (Example 27) of the highest yielding method is included as note 14. It should be noted that the patent authors have not characterized nor inferred the synthesized amine as the monohydrate. The effect of drying the product in vacuo at 60 °C for three days, as specified by Example 27, is *insufficient* for converting the monohydrate to the anhydrous form. This might have been an oversight since their reported method of characterizing the amine was by ¹³C NMR only, an analytical technique that cannot detect hydrated water. Using the patented synthesis method, the authors estimate the bulk cost of BTaw to be between US\$50 and \$100 per kilogram. ¹³C NMR (DMSO-*d*₆): δ 153.4.

The purification of BTaw, which was easily done by recrystallization from water, was critical for proper burning and flame coloration of our pyrotechnic formulations. To 4 L of boiling water were added 85g of crude BTaw. The solution was filtered hot and cooled slowly with stirring. The material was collected by filtration and air-dried. As shown in Figures 3 and 4, hydrated water is lost very slowly at ca. 80 °C but increases in rate when heated to ca. 110 °C. Anhydrous BTA remains non-hydrated at 20% RH and becomes 70% hydrated after one week at 52% RH. The onset of decomposition of BTA is approximately 170 °C. The impact sensitivity of pure BTaw is greater than 320 cm but drops to 26 cm when converted to

the anhydrous form, BTA. Thus for reasons of safety it is not desirable to dry BTaw to the anhydrous form for use as a pyrotechnic fuel. In addition, given that a 50/50 wt. % mixture of BTaw and AP has an impact sensitivity of 27 cm, it is very likely that such a mixture—if dried to remove the hydrated water—would exhibit much greater sensitivity. Our typical BTaw pyrotechnic formulations consisted of 50/50 wt. % fuel to AP, to which some metal salt colorant was added. More details on these and other formulations are in the Flame Color section.

Diammonium Bis-(1(2)*H*-tetrazol-5-yl)-amine Monohydrate (DA-BTaw)

Using the general synthesis method, BTaw (5.8 g, 34 mmol) and concentrated ammonium hydroxide solution (5.7 g, 0.10 mol) were neutralized in 30 mL water. ^{13}C NMR (DMSO- d_6): δ 158.9.

Analysis for $\text{C}_2\text{H}_9\text{N}_{11}\cdot\text{H}_2\text{O}$:

Calculated: C, 11.71; H, 5.40; N, 75.09.

Found: C, 11.99; H, 5.54; N, 75.26.

DA-BTaw is one the most soluble high-nitrogen salts, which makes its use as a pyrotechnic fuel impractical. Synthesis and purification of this material usually resulted in poor yield due to attrition, and again, there was more loss of the fuel through leaching when DA-BTaw formulations were wetted with water and processed into stars.

Ammonium Bis-(1(2)*H*-tetrazol-5-yl)-amine (A-BTA)

Using the general synthesis method, BTaw (17.1 g, 0.10 mol) and concentrated ammonium hydroxide (5.8 g, 0.10 mol) were neutralized in 500 mL of water. This mono-ammonium salt has a very low bulk density, having the appearance of cotton. This ammonium derivative of BTA is much less soluble in water than DA-BTaw. ^{13}C NMR (DMSO- d_6): δ 156.2.

Analysis for $\text{C}_2\text{H}_6\text{N}_{10}$:

Calculated: C, 14.12; H, 3.55; N, 82.33.

Found: C, 14.27; H, 3.61; N, 82.58.

Dihydrazinium Bis-(1(2)*H*-tetrazol-5-yl)-amine Monohydrate (DHZ-BTaw)

Using the general synthesis method, BTaw (17.1 g, 0.10 mol) and hydrazine monohydrate (10.5 g, 0.21 mol) were neutralized in 175 mL water. DHZ-BTaw is efflorescent at room temperature depending on the level of humidity and length of exposure to dry air. The anhydrous form of this salt recovers one water molecule at 20% RH over several days.

Analysis for $\text{C}_2\text{H}_{11}\text{N}_{13}\cdot\text{H}_2\text{O}$:

Calculated: C, 10.21; H, 5.57; N, 77.41.

Found: C, 10.19; H, 5.88; N, 76.61.

Hydrazinium Bis-(1(2)*H*-tetrazol-5-yl)-amine (Hz-BTA)

Using the general synthesis method, BTaw (8.0 g, 47 mmol) and hydrazine monohydrate (2.4 g, 47 mmol) were reacted in 125 mL water.

Analysis for $\text{C}_2\text{H}_7\text{N}_{11}$:

Calculated: C, 12.97; H, 3.81; N, 83.22.

Found: C, 13.16; H, 3.96; N, 83.52.

Strontium Bis-(1(2)*H*-tetrazol-5-yl)-amine Tetrahydrate (Sr-BTA4w)

Using the general synthesis method, BTaw (6.3 g, 37 mmol) and strontium hydroxide octahydrate (10 g, 38 mmol) were neutralized in 400 mL water. The anhydrous form of Sr-BTA recovers about two water molecules after one month at 20% RH. Over the same period, all four waters are recovered at 52% RH.

Analysis for $\text{C}_2\text{HN}_9\text{Sr}\cdot 4\text{H}_2\text{O}$:

Calculated: C, 7.73; H, 2.92; N, 40.56.

Found: C, 7.77; H, 2.75; N, 40.85.

Barium Bis-(1(2)*H*-tetrazol-5-yl)-amine Tetrahydrate (Ba-BTA4w)

Using the general synthesis method, BTaw (2.6 g, 15 mmol) and barium hydroxide octahydrate (5.0 g, 16 mmol) were neutralized in 300 mL water. The tetrahydrated salt readily loses three waters at ca. 60 °C, but the removal of its fourth (last) water requires prolonged heating at ca. 175 °C. The monohydrate of Ba-BTA does not recover any water at 20% RH,

but hydrates the remaining three molecules of water at 52% RH over a period of one month.

Analysis for $C_2HN_9Ba \cdot 4H_2O$:

Calculated: C, 6.66; H, 2.52; N, 34.97.

Found: C, 6.72; H, 2.28; N, 35.30.

Copper(II) Bis-(1(2)*H*-tetrazol-5-yl)-amine Dihydrate (Cu-BTA2w)

To a boiling solution of BTaw (1.0 g, 5.9 mmol, in 50 mL water) was added a solution of copper(II) sulfate pentahydrate (1.5 g, 6.0 mmol in 20 mL water). The green precipitate was filtered and air-dried.

Analysis for $C_2HN_9Cu \cdot 2H_2O$:

Calculated: C, 9.58; H, 2.01; N, 50.29.

Found: C, 9.65; H, 1.96; N, 49.84.

3,6-Dihydrazino-*s*-tetrazine (DHT)

The various synthetic methods of DHT have been discussed in previous publications.^[3,5,6] DHT formulations containing copper salts have been found to be unsuitable for long term storage, especially in humid environments. Stars composed of such formulations swelled into dark porous masses approximately twice their original size when stored for several months. In addition, the burn rate of DHT is increased by the addition of copper salts. For these reasons, the authors have relied on BTaw and BT as the choice fuel-base for all formulations containing copper colorant. Iron(III) oxide was found to profoundly increase the burn-rate of DHT, and the authors strongly advise not to use it in DHT-based formulations.

Flame Color

Colored flames are obtained by the introduction of metallic salts into a fuel/oxidizer matrix. The excitation of gaseous metal monochlorides is the chief source of the emission spectra for copper, strontium and barium flames.^[15] In many traditional pyrotechnic formulations, chlorine sources such as PVC or Parlon[®] are used to enhance the formation of the monochlorides. In order to achieve the cleanest burn with the least amount of smoke, these high-nitrogen formulations have AP as

both oxidizer and chlorine donor. It is possible to substitute some of the AP with AN without serious loss in color-performance, but for sake of simplicity, singly recrystallized AP^[16] was used exclusively.

The flame colors of various star compositions were measured using an Ocean Optics S2000 Series Fiber Optic Spectrophotometer coupled to a SAD500 interface. The diffraction grating was type 2 (200–850 nm) and the entrance slit was 25 microns wide. The instrument wavelength response was calibrated with an LS-1 tungsten halogen light source obtained from Ocean Optics. Although Ocean Optics gives the color temperature of the light source as 3100 K, Meyerriecks^[17] believes the true filament temperature to be closer to 3030 to 3035 K. The authors chose 3035 K as the filament temperature and calculated the appropriate emittance data as a function of wavelength using Planck's formula.

With these emittance values and the spectral data of the tungsten halogen lamp, wavelength dependent correction coefficients were calculated and incorporated into a spreadsheet. The spreadsheet was used to tabulate spectral data, correct instrument response, integrate and calculate a color coordinate using C.I.E. 1931 tristimulus coefficients. This was done by multiplying the emittance with each of the three tristimulus coefficients (in 5 nm increments) to give three subsequent curves. These curves were numerically integrated to give three areas, represented as **X**, **Y**, and **Z**. The *x* and *y* color coordinates were obtained by normalizing the areas.

$$x = X / (X+Y+Z) \text{ and } y = Y / (X+Y+Z)$$

Fortner and Meyer^[18] provide a comprehensive discussion about the C.I.E. color system and its history. This method is a reasonable attempt to characterize visually observed color in a 2-D coordinate system.

Some of these formulations were burned as a powdered mix while other times they were burned as stars. Stars were made by wetting the formulation with deionized water, pressing them into shape and air-drying. No discernible spectral difference could be found between powder and star samples. The samples were

Table 4. Color Coordinate Values (C.I.E. 1931) of Various DHT Formulations.

Composition (wt. %)				Color	x	y
DHT	AP	Metal	Salt			
47.5	47.5	5.0	Sr-BT4w	Red	0.697	0.291
47.5	47.5	5.0	Cu-BTA2w	Blue	0.206	0.144
46.5	46.5	7.0	BaF ₂	Green	0.226	0.648
47.0	47.0	6.0	Boric Acid	Green	0.357	0.489
48.3	48.3	3.4	CaCO ₃	Red-Orange	0.650	0.347
49.5	49.5	1.0	Li ₂ CO ₃	Pumpkin	0.534	0.398

burned on a porcelain plate, and the position of the fiber optic lens relative to the burning sample was adjusted to obtain the greatest response by the spectrophotometer. A number of burns were recorded, and those that gave reasonably similar values were averaged. Reproducibility was generally good with an estimated variability of ± 0.01 in the color coordinates.

Tables 4, 5 and 6 list various high-nitrogen pyrotechnic formulations together with their measured coordinate color values. In addition to the above color data, three pyrotechnic formulations describing the primary colors—red, blue and green—were prepared from traditional ingredients and analyzed spectrophotometrically. Their formulations and respective color coordinates are given in Table 7. These formulations were selected from a large collection of traditional formulations and tested for best color purity. In spite of this, and because of the enormous quantity of published pyrotechnic formulations, the authors do not suggest that these have the best color purity of all formulations. Nevertheless, they are useful for comparing traditional and high-nitrogen flame colors.

To illustrate the enhanced color purity of the high-nitrogen flame, Figure 5 is a graph of the color coordinates taken from Tables 4 through 7 of the 1931 C.I.E. Chromaticity Diagram. The triangle in the center of the diagram is constructed from the three color coordinates obtained from Table 7. This triangular area represents the approximate region of possible colors when different ratios of the primary colors, green (barium), blue (copper) and red (strontium) are mixed in a traditional-style formulation and burned. In theory, these colors are limited to the ingredients listed in Table 7. All of the high-nitrogen color coordinates representing formulations containing 5 to 7 wt. % of barium, copper or strontium colorants fall outside of the triangle. (The few points within the triangle are formulations that do not contain barium, copper or strontium.) This demonstrates that color purity of pyrotechnic flames can be improved by the use of high-nitrogen fuels.

Table 5. Color Coordinate Values (C.I.E. 1931) of the Various BT-Based Formulations.

Composition (wt. %)						
DHT-BT2w	AP	Metal	Salt	Color	x	y
47.5	47.5	5.0	Sr-BTA4w	Red	0.702	0.290
47.5	47.5	5.0	Cu-BTA2w	Blue	0.187	0.123
46.5	46.5	7.0	Ba-BT4w	Green	0.212	0.675
DHA-BT						
DHA-BT	AP	Metal	Salt(s)	Color	x	y
47.5	47.5	5.0	Sr-BT4w	Red	0.707	0.291
47.5	47.5	5.0	Cu-BTA2w	Blue	0.189	0.136
46.5	46.5	7.0	BaF ₂	Green	0.230	0.650
43.5	52.0	2.7	Cu-BTA2w	Purple	0.352	0.179
		+1.8	Sr-BT4w			
43.5	52.0	1.8	Cu-BTA2w	Red-Purple	0.446	0.214
		+2.7	Sr-BT4w			
43.0	52.0	2.1	Cu-BTA2w	Pink	0.524	0.289
		+2.9	CaCO ₃			
42.3	50.7	0.2	Cu-BTA2w	Blue-Green	0.209	0.588
		+6.8	Ba-BT4w			
HA-BT						
HA-BT	AP	Metal	Salt	Color	x	y
47.5	47.5	5.0	Sr-BT4w	Red	0.703	0.291
47.5	47.5	5.0	Cu-BTA2w	Blue	0.193	0.129
46.5	46.5	7.0	Ba-BT4w	Green	0.204	0.684
DHZ-BT						
DHz-BT	AP	Metal	Salt	Color	x	y
42.5	52.5	5.0	Sr-BTA4w	Red	0.673	0.303
42.5	52.5	5.0	Cu-BTA2w	Blue	0.221	0.165
42.0	51.0	7.0	Ba-BTA4w	Green	0.265	0.636
Hz-BT						
Hz-BT	AP	Metal	Salt(s)	Color	x	y
40.0	55.0	5.0	Sr-BTA4w	Red	0.700	0.290
40.0	55.0	5.0	Cu-BTA2w	Blue	0.197	0.131
39.0	54.0	7.0	Ba-BT4w	Green	0.186	0.714
41.2	51.4	0.3	Cu-BTA2w	Blue-Green	0.219	0.587
		+7.1	Ba-BT4w			
DA-BT						
DA-BT	AP	Metal	Salt	Color	x	y
42.5	52.5	5.0	Sr-BTA4w	Red	0.696	0.291
42.5	52.5	5.0	Cu-BTA2w	Blue	0.182	0.116
51.0	42.0	7.0	Ba-BTA4w	Green	0.227	0.674

The greatest improvement in color purity is that of barium green. Traditional color flames have color coordinate values that center about $x = 0.4$ and $y = 0.5$, which make it nearly impossible to generate blue-green flames with mixtures of barium and copper salts. Such traditional compositions generate white light, or pale blue-green at best. High-nitrogen green flames, on the other hand, are considerably more pure and have color values shifted away from the central portion of the chromaticity diagram (white light region). For this reason, formulations containing mixtures of copper and barium give aesthetically pleasing shades of blue-green. High-nitrogen formulations with boric acid col-

orant do not give a deep green color that can be obtained with barium salts, but the much less toxic nature of boric acid makes it suitable for indoor applications. The color purity of DHT/ boric acid composition is nearly the same as the best traditional barium formulation. Coloring high-nitrogen flames with very low concentrations (ca. 1%) of lithium salts create interesting shades of pumpkin-orange, whereas calcium carbonate gives an intense red-orange color. Formulations with copper and calcium salts generate a wide variety of intense pink, purplish pink and purple flames. Strontium and copper salts give bright and pure shades of purple and red-purple flames.

Table 6. Color Coordinate Values (C.I.E. 1931) of the Various BTA-Based Formulations.

Composition (wt. %)						
BTAw	AP	Metal	Salt(s)	Color	x	y
47.5	47.5	5.0	Sr-BT4w	Red*	0.700	0.289
47.5	47.5	5.0	Cu-BTA2w	Blue*	0.177	0.108
47.5	47.5	5.0	Ba-BT4w	Green*	0.196	0.700
46.5	46.5	6.7	Ba-BT4w	Blue-Green	0.185	0.471
		+0.3	Cu-BTA2w			
47.5	47.5	3.1	Sr-BTA4w	Purple	0.368	0.197
		+2.1	Cu-BTA2w			
DHZ-BTAw						
DHz-BTAw	AP	Metal	Salt	Color	x	y
38.0	57.0	5.0	Sr-BT4w	Red	0.685	0.302
38.0	57.0	5.0	Cu-BTA2w	Blue	0.199	0.127
37.0	56.0	7.0	Ba-BT4w	Green	0.348	0.573
Hz-BTA						
Hz-BTA	AP	Metal	Salt	Color	x	y
40.0	55.0	5.0	Sr-BT4w	Red	0.693	0.298
40.0	55.0	5.0	Cu-BTA2w	Blue	0.200	0.126
39.0	54.0	7.0	Ba-BT4w	Green	0.337	0.581
DA-BTA						
DA-BTA	AP	Metal	Salt	Color	x	y
38.0	57.0	5.0	Sr-BT4w	Red	0.695	0.294
38.0	57.0	5.0	Cu-BTA2w	Blue	0.188	0.121
37.0	56.0	7.0	Ba-BT4w	Green	0.311	0.613
A-BTA						
A-BTA	AP	Metal	Salt	Color	x	y
40.0	55.0	5.0	Sr-BT4w	Red	0.700	0.294
40.0	55.0	5.0	Cu-BTA2w	Blue	0.185	0.121
39.0	54.0	7.0	Ba-BT4w	Green	0.204	0.685

*The spectrum of this formulation is shown in Figure 6.

Table 7. Color Coordinate Values (C.I.E. 1931) of the Red, Blue and Green Formulations Using Traditional Ingredients. These Formulations Were Found To Burn with Best Color Purity.

Composition (wt. %)	Color	x	y
60% Strontium nitrate	Red	0.653	0.315
20% Magnalium alloy			
10% Polyvinyl chloride			
10% Red gum			
61% Potassium perchlorate	Blue	0.218	0.185
17% Cupric oxide			
10% Polyvinyl chloride			
6% Hexamine			
3% Red gum			
3% Dextrin			
56% Barium nitrate	Green	0.366	0.522
18% Polyvinyl chloride			
10% Magnalium alloy			
6% Potassium perchlorate			
5% Red gum			
5% Hexamine			

In Figure 6, the spectra of the three traditional formulations representing the primary colors (Table 7) are shown together with selected spectra of high-nitrogen flames. The most apparent difference is that traditional blue and green spectra have poorer baselines. The extra light output over most of the visible spectral region is akin to “washing out” the blue or green light with white light. Because strontium monochloride emits light efficiently, the baselines of both traditional and high-nitrogen red spectra are comparatively better. In the traditional red spectrum, however, there is a broad peak of significant intensity at ca. 606 nm (red-orange). This emission, which is attributed to SrOH, slightly degrades the red color purity. Additional sources of color degradation come from sodium (589 nm) and potassium impurities, which are ubiquitous in traditional ingredients. Fortunately this is less of a problem with high-nitrogen formulations due to their inherent purity.

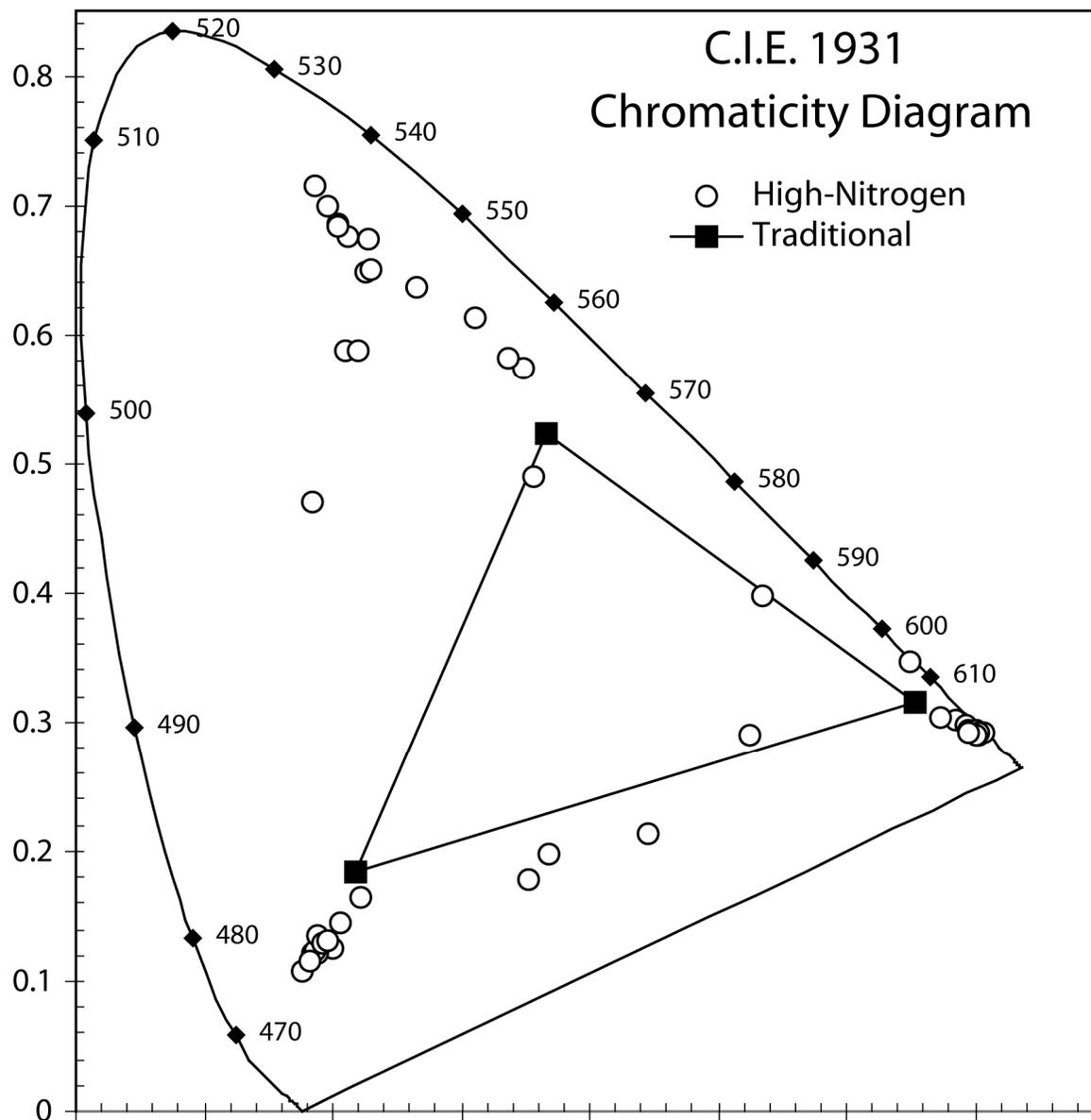


Figure 5. Color coordinates taken from Tables 4 through 7 are shown on a C.I.E. 1931 Chromaticity Diagram. The central triangular region approximately represents the possible colors that can be obtained using traditional fuels and barium, copper and strontium metal colorants (see Table 7).

Red, Blue and Green Spectra

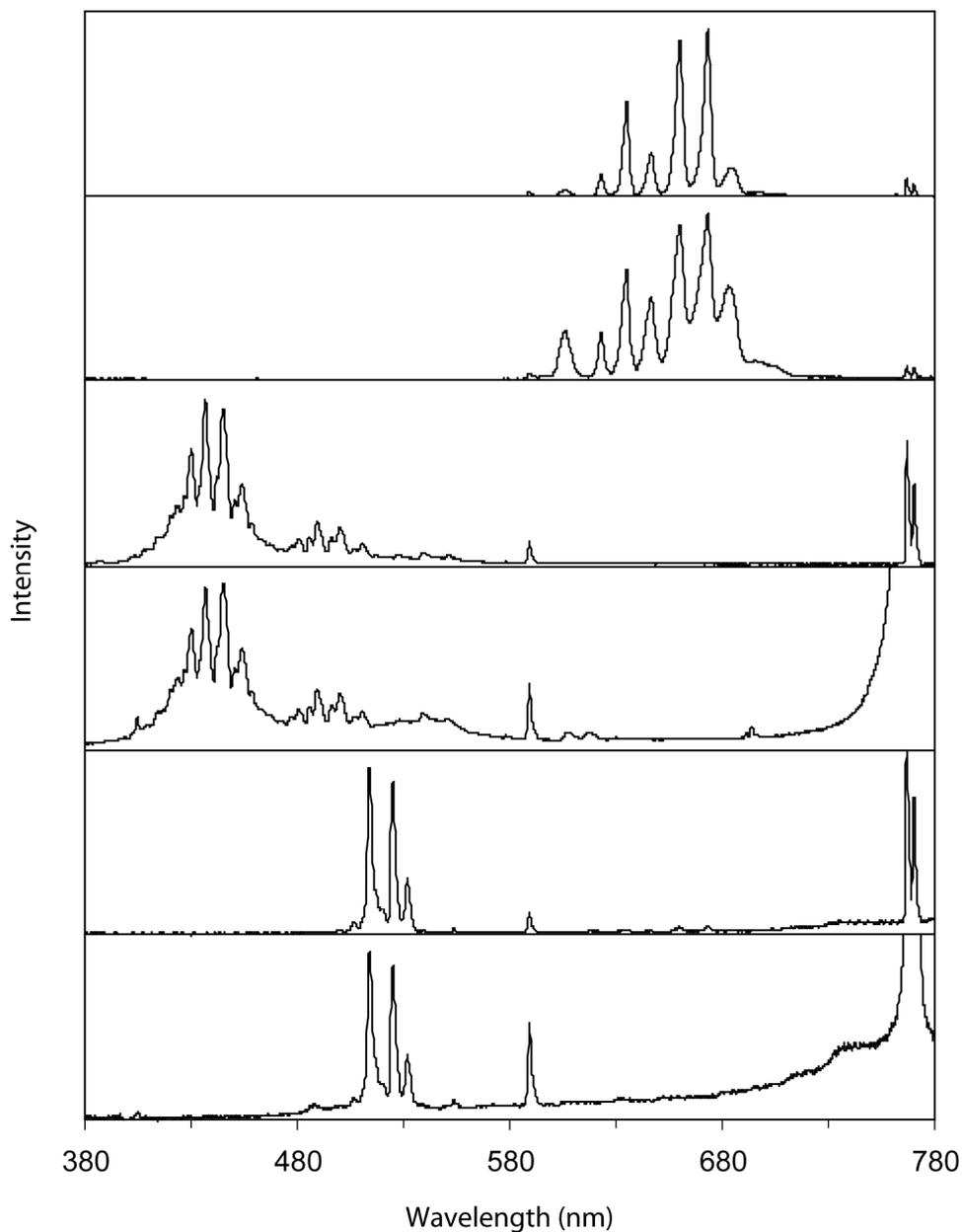


Figure 6. Cleaner baselines and reduced ancillary emissions from impurities are the typical differences between the spectra of traditional (see Table 7) and high-nitrogen flames. The spectra are from top down: high-nitrogen strontium red; traditional strontium red; high-nitrogen copper blue; traditional copper blue; high-nitrogen barium green and traditional barium green. The formulations of the high-nitrogen spectra are the first three in Table 6. The peak at 589 nm is due to sodium impurity. The traditional blue and green formulations generated strong potassium emissions (ca. 760 nm) that were clipped by the spectrophotometer. The calculated color coordinate values for these spectra were not corrected because the tristimulus values are approximately zero in this clipped region.

Table 8. Three Primary Color Series Were Formulated and Photometrically Analyzed To Demonstrate the Effect of Metal Salt Concentration on Flame Color Purity. The Formulations Are in Wt. % and the Color Coordinates Are Based on the C.I.E. 1931 System.

Red				
DHT	AP	Sr-BT4w	x	y
47.5	47.5	5.0	0.697	0.291
48.0	48.0	4.0	0.699	0.292
48.5	48.5	3.0	0.687	0.295
49.0	49.0	2.0	0.685	0.290
49.5	49.5	1.0	0.649	0.318
49.75	49.75	0.5	0.597	0.356
Blue				
BTAw	AP	Cu-BT2w	x	y
46.25	46.25	7.5	0.179	0.115
47.5	47.5	5.0	0.177	0.108
48.5	48.5	3.0	0.182	0.113
49.1	49.1	1.8	0.193	0.128
49.5	49.5	1.0	0.215	0.157
Green				
BTAw	AP	Ba-BT4w	x	y
25.0	50.0	25.0	0.204	0.693
32.5	50.0	17.5	0.171	0.731
37.5	50.0	12.5	0.182	0.705
45.0	50.0	5.0	0.196	0.700
47.5	50.0	2.5	0.228	0.662

The effect of varying the concentration of metal salt on flame color purity was measured for red, blue and green high-nitrogen flames. The experimental color coordinates for the three color series are found in Table 8. Figure 7 gives detailed placement of these coordinates on the C.I.E. 1931 Chromaticity Diagram. For red colored flames, the transition where the color rapidly deteriorates with decreasing amount of Sr-BT4w is approximately 2 wt. %. Although formulations within the 2 to 5 wt. % metal colorant range have similar color values (i.e., the same color purity), a 5 wt. % strontium formulation has a more intense color than that of the 2 wt. % formulation. For the blue series, formulations composed of 3 to 7.5 wt. % Cu-BT2w gave similar color values, and only with 1.8 wt. % copper salt did the color degrade only slightly. Statically burned copper-based blue stars had unaesthetic orange flame tips. However, the orange flame-tips disappear when the burning

stars are propelled through the air or burned in a nitrogen atmosphere. It is believed that the blue-emitting species, CuCl, is converted by atmospheric oxygen to CuO (orange-emitting) in the outer envelope of the flame. Burning a star in nitrogen atmosphere precludes the formation of CuO, and it may be that when a burning star is moving through the air, the flame envelope is too cool for CuO emission. Flame-tip chemistry is briefly discussed in a pyrotechnic treatise.^[19] The green series—five formulations of varying Ba-BT4w concentrations—shows that a fairly concentrated amount of barium salt (ca. 17.5 wt. %) is needed for the best possible color purity. However, a formulation composed of 25 wt. % Ba-BT4w has a color purity no better than that obtained from 5 wt. % Ba-BT4w. This degradation in color purity with formulations greater than 17.5 wt. % is attributed to the incandescence of solid barium products.

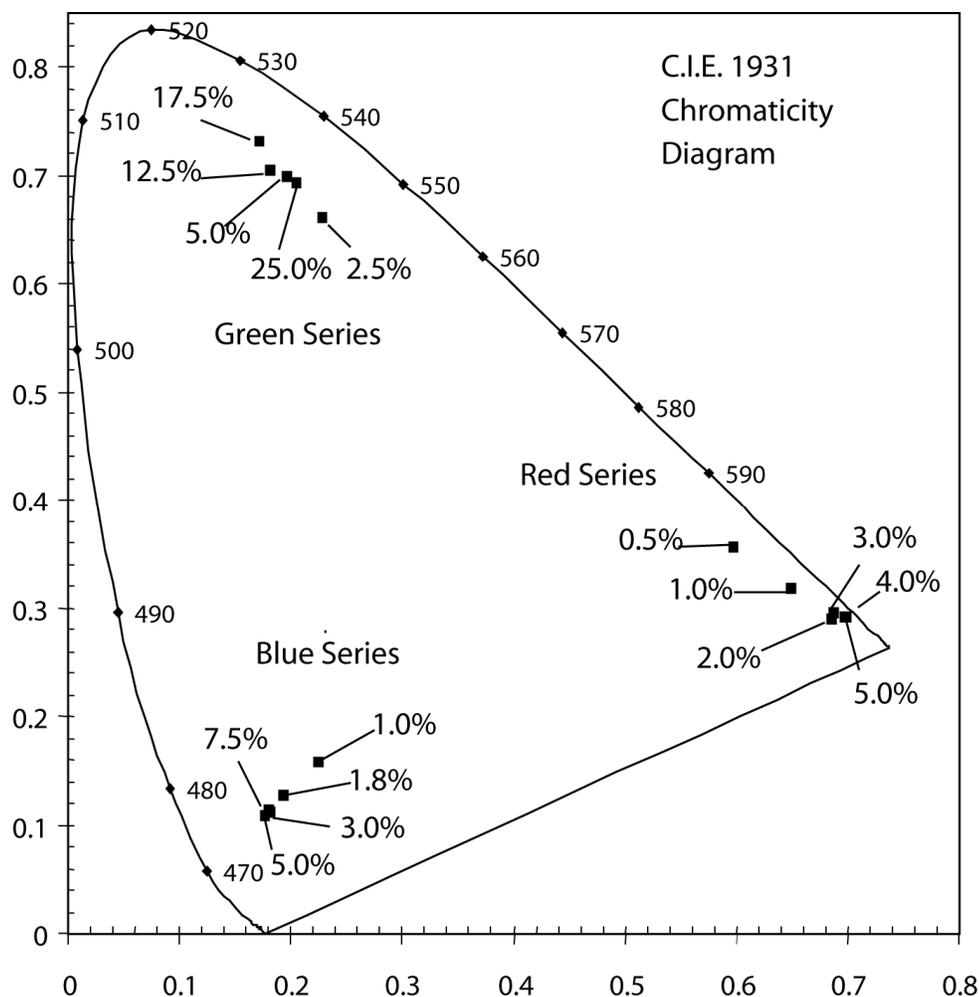


Figure 7. The same high-nitrogen color series taken from Table 8 are represented on a C.I.E. 1931 Chromaticity Diagram. These results demonstrate that color purity can still be maintained with unprecedented low levels of metal salts.

Conclusion

A number of high-nitrogen fuels and salts were synthesized and investigated for their utility in low-smoke applications. It was found that mixtures of high-nitrogen fuels and oxidant ammonium perchlorate require only 1 to 7 wt. % metal colorants to achieve exceptionally pure flame colors. This level of metal content is considerably less than that found in traditional pyrotechnic formulations. The spectral data of a large variety of burning high-nitrogen formulations were gathered and converted into useful C.I.E. 1931 color coordinates. These results are reported together with those of several tradi-

tional pyrotechnic formulations. In addition, impact sensitivity testing was performed to provide baseline hazards of these high-nitrogen pyrotechnic ingredients, and thermogravimetric analysis was conducted to provide stability data.

Notes and References

- 1) Patent Pending.
- 2) Also known as Hz₂Tz.
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- 4) B. M. Dobratz, *LANL Explosives Handbook. Properties of Chemical Explosives and Explosives Simulants*, National Technical Information Service, UCRL-52997, 1981.
- 5) H. J. Marcus and A. Remanick, *J. Org. Chem.*, Vol. 28, 1963, p 2372; US Patent 3,244,702, April 5, 1966.
- 6) D. E. Chavez and M. A. Hiskey, *J. Heterocyclic Chem.*, Vol. 35, 1998, p 1329.
- 7) TGA analyses were performed using a High Resolution Modulated TGA 2950 manufactured by TA Instruments.
- 8) The unit, %/min, or mass percent per minute, is used in this paper to describe mass loss rate.
- 9) N. A. Lange, *Lange's Handbook of Chemistry*, 7th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1949, p 1432.
- 10) Adapted from a synthesis method described by R. A. Henry, Code 38505, Chemistry Division, Naval Weapons Center, China Lake, CA 93555 USA.
- 11) A large excess of sodium sulfide should be avoided since under acidic conditions colloidal sulfur can be formed and contaminate the product.
- 12) Summit Pharmaceuticals Corp., 400 Kelby Street, Fort Lee, NJ 07024 USA. Phone: (201) 585-9004, Fax: (201) 585-9653.
- 13) W. P. Norris and R. A. Henry, *J. Org. Chem.*, Vol. 29, 1964, p 650.
- 14) T. K. Highsmith, R. M. Hajik, R. B. Wardle, G. K. Lund and R. J. Blau, Methods for Synthesizing and Processing bis-(1(2(H)-tetrazol-5-yl)-amine, US Patent 5,468,866, Nov. 21, 1995; "Example 27. In a 22 liter flask equipped with a mechanical stirrer, nitrogen inlets, reflux condensers, and thermometer was placed 1848 g of boric acid and 840 g of sodium dicyanoamide in 4.6 liters of distilled water. To this solution was added 1296 g of sodium azide in 4.0 liters of distilled water. The reaction mixture was then refluxed 48 hours at which time a sample was taken, evaporated in a stream of nitrogen, and analyzed by ¹³C NMR. The hot solution was then pumped into a 5°C solution of 2.4 liters of water and 2.4 liters of concentrated HCl. The acidification was not allowed to exceed 15°C by the addition of ice as necessary to the acid solution. This was done in order to obtain small, amorphous particles. The precipitated BTA was collected by filtration. The solid was then washed by suspension in distilled water, stirring vigorously and subsequently refiltered. This process was repeated until the washings obtained had a pH of 3. The filtercake was then dried in vacuo at 60°C for several days. The product was obtained (1222 g) as a white buff solid which was pure by ¹³C NMR."
- 15) A. A. Shidlovskiy, *Principles of Pyrotechnics*, Mashinostroyeniye Press, Moscow, 1964, pp 182–186; T. Shimizu, *Fireworks. The Art, Science and Technique*, Pyrotechnica Publications, Austin, TX, 1981, pp 57–61; J. A. Conkling, *Chemistry of Pyrotechnics*, Marcel Dekker, New York, 1985, pp 150–163.
- 16) Singly recrystallized AP was made by dissolving 45 g commercial AP in 100 g boiling water, filtering hot, and cooling to 5°C to initiate precipitation. The crystalline solid was filtered and dried.
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