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Research Article

M42 Primer Processing with Potassium and Copper Salt Formulations

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Abstract

There has been a significant effort to develop suitable replacements for many energetic formulations containing environmentally undesirable compounds, especially lead. The purpose of this work was to synthesize and characterize tetraazido(1,2-di(1*H*-tetrazol-1-yl)ethane)dicopper(II) (Cu-salt) and dipotassium di-nitraminobistetrazole (K-salt) with the intent to replace lead styphnate in the M42 primer, while maintaining other compounds in the formulation. The formulations were prepared using a manual dry mixing procedure. The prepared mixtures were manually hand-loaded and consolidated using a hydraulic press. The anvils were inserted and the primers were tested for proper performance function (primer sensitivity and pressure output). The developed process was used to manufacture a small set of primers (60 samples of each formulation) which were tested for primer sensitivity and pressure output characteristics. The sensitivity and pressure output data was then compared to commercial M42 primers currently used in grenade applications. The primers manufactured with formulation containing the lead syphnate replacement compounds demonstrated very good agreement with the required specifications (primer sensitivity and pressure output).

Keywords: Lead-Free Percussion Primers; Initiators; Ammunition

Introduction

In this application, a primer is an igniter that is used to initiate smokeless powder/delay compositions. Its composition is usually consisted of a lead based explosive, specifically lead styphnate, fuel, and oxidizer(s). Lead is known to be toxic to the environment and to human health. The use of lead in ammunition, pollutes training ranges and exposes manufacturers and users to serious health hazards. At times, the operator's exposure to lead is so high that many ranges or shoot houses have been shut down [1-4].

There have been many attempts to replace lead styphnate in percussion primers. Several different potential lead replacement mixtures include: i) metastable interstitial composites (MIC) [5], ii) red phosphorous [6], iii) DDNP based mixtures [7], iv) DBX-1 based mixtures [8-10], and v) KDNP based mixtures [11]. MIC and DBX-1 based mixtures are not only suitable for replacing lead but also provide opportunities for automation of the manufacturing process. Current primer manufacturing processes are manual, inherent with safety and health risks as well as increased manufacturing defects. Automation of the primer loading process eliminates occupational safety hazards related to worker's exposure to toxic and dangerous materials. MIC water-based processing and automated slurry loading have been developed and demonstrated [12-13]. The DBX-1 based mixtures have also shown great promise for processing and loading in slurry form, using a binary solvent of water and alcohol. The tested copper and potassium salt formulations, described in this text, were studied as a precursor to the DBX-1 based mixtures currently under development.

The potassium and copper salts were synthesized at Ludwig-Maximilians University of Munich (LMU), the formulations were developed at US Army Armament Research, Development and Engineering Center (ARDEC), and the primers were manufactured and tested at Innovative Materials and Processes, LLC (IMP). The work was performed collaboratively by ARDEC/IMP/LMU.

Materials and Methods

The methods used for characterization analysis of the Cu-salt and K-salt compounds, including Differential Thermal Analysis (DTA), Infrared (IR), Elemental Analysis (EA), Impact Sensitivity (IS), Friction Sensitivity (FS), Electro Static Discharge Sensitivity (ESD), Differential Scanning Calorimetry (DCS), Mass to Charge Ratio (m/z), and Raman, was performed using accepted procedures described in the AOP-7 document [14].

The M42 primers were manufactured at IMP using the following methods. The primer cups were manually loaded with the appropriate energetic formulation. The dry mix was loaded into the primer cups using a primer cup holder and a slide on cover attachment with a built in funnel. The dry loading setup is shown in Figure 1.

Figure 1. Dry loading setup for M42 primers.

Between 20.1 mg and 23.3 mg of the dry mixture was weighed out on a balance and loaded in dry powder form into M42 primer cups. The individually loaded cups were then flat pressed using a flat punch attachment in a pneumatic press (air-hydraulics, model: AP-1200) set to 241 kPa (1356 N). The pressed material heights, measured from the underside of the primer cup to the top of the pressed material, ranged from 1.079 mm to 1.219 mm.

The pressed material within the primer cup was then wetted with 3 µL of isopropyl alcohol. The wetting of the surface allowed for the paper foil to be inserted using a flat hand press and slightly adhere to the surface of the wetted material. After the alcohol has evaporated from the surface of the pressed material, the anvils were inserted into the primer cups. M42 type anvils were inserted into each cup to a total primer height (cup + anvil) of 2.972 ± 0.025 mm.

The full primer production process is shown in step by step format in Figure 2.

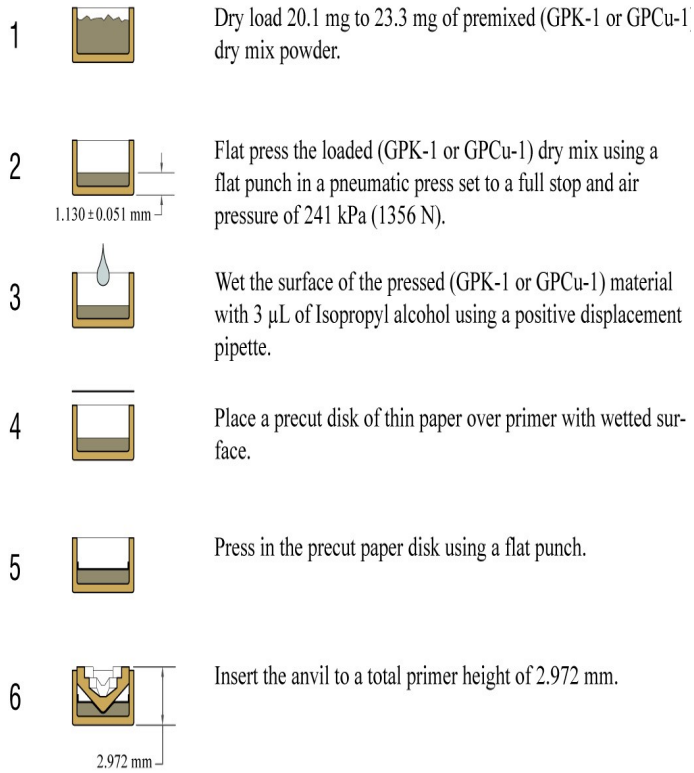

Figure 2. M42 primer processing, in step by step format.

The consolidated M42 primers were inserted into the test application (5.56 case stubs) using a pneumatic press set to 241 kPa (1356 N). The primer was inserted so that it bottomed out in the application primer pocket. The press stop was set to the maximum allowable insertion depth below flush, 0.152 mm in this case. All primers were inserted into the 5.56 test cases to 0.102 mm – 0.152 mm below case flush insertion depth.

Primer sensitivity testing was conducted using a ball drop device and the Neyer D-optimal testing method [15]. The Neyer method sensitivity testing provides output statistics of the average drop height (H_{avg}) and standard deviation (σ) from that height. A sample set of 30 to 50 primers is normally sufficient for Neyer sensitivity testing. The testing parameters included a 55 g drop ball and a 1.016 mm diameter firing pin. A photograph of the ball drop device is shown in Figure 3 (left).

Pressure output characterization was conducted using an IMP designed pressure cell device. The device utilizes a closed bomb pressure cell, a PCB piezoelectric pressure transducer (model #102A) and an oscilloscope to measure the pressure output. A primer was inserted into a 5.56 case stub and screwed into the pressure cell. The ball drop device was used to initiate the percussion primer using a 1.016 mm diameter firing pin at an all fire height, and the data was recorded using an oscilloscope. A photograph of the closed bomb pressure cell is shown in Figure 3 (right).

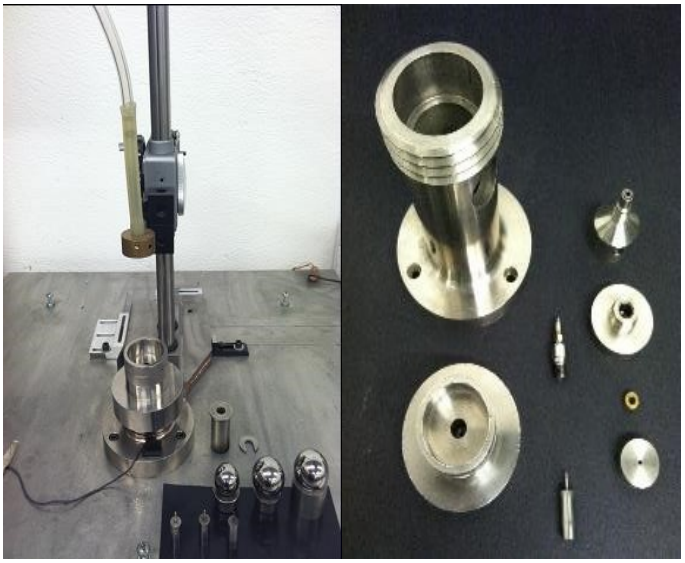

Figure 3. Photograph of the ball drop device (left) and the pressure cell device (right).

Results and Discussion

Two different compounds were considered for the replacement of lead styphnate in the formulation for the M42 percussion primers, namely tetraazido(1,2-di(1*H*-tetrazol-1-yl) ethane)dicopper(II) ($Cu_2(N_3)_4$(dte)), where dte = 1,2-di(1*H*-tetrazol-1-yl)ethane, and dipotassium dinitraminobistetrazole ($C_2K_2N_{12}O_4$ = K_2DNABT). The next section describes the synthesis procedures for both compounds, elemental analyses of final and intermediate compounds, as well as some physical properties of these compounds.

Synthesis of tetraazido(1,2-di(1*H*-tetrazol-1-yl)ethane)dicopper(II) (Cu-Salt)

The synthesis of this Cu-salt (see Figure 4) was done according to a previously described procedure in literature [16]. An aqueous solution (10 mL) containing sodium azide (0.4 mmol, 26 mg) and dte (0.1 mmol, 17 mg), in a tube, was layered by aqueous ethanol (50%, 5 mL), and an ethanol solution (10 mL) of $CuCl_2 \cdot 2\,H_2O$ (0.20 mmol, 34 mg) was carefully added. Slow diffusion at room temperature yielded crystals of [$Cu_2(N_3)_4$(dte)] in 10 days.

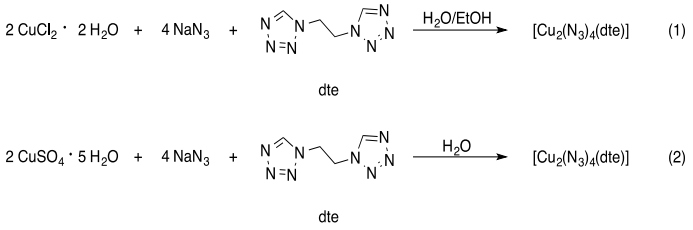

Figure 4. Schematics of reaction steps for the synthesis of $Cu_2(N_3)_4$(dte) (Cu-salt).

An aqueous solution of sodium azide (260 mg, 4 mmol) was added to a 70 °C warm solution of dte (166 mg, 1 mmol) and copper (II) sulfate pentahydrate (499 mg, 2.00 mmol) in water (15 mL). The complex started to precipitate immediately. The obtained brownish colored product was filtered off, washed with a small amount of water, and then air dried [17].

Yield: 0.39 g (0.85 mmol, 85 %). **DTA** (5 °C min^{-1}) onset: 197 °C (decomp.); IR (ATR, cm−1): $\tilde{V}$ = 3365 (w), 3319 (w), 3122 (m), 3018 (w), 2976 (w), 2953 (w), 2074 (m), 2044 (vs), 1809 (w), 1513 (m), 1499 (m), 1454 (m), 1449 (m), 1387 (w), 1339 (w), 1290 (s), 1274 (m), 1183 (s), 1135 (m), 1092 (s), 907 (s), 845 (w), 806 (w), 696 (s), 664 (s); **EA** calc. (%) for $C_4H_6Cu_2N_20$ (461.32 g mol^{-1}): C 10.41, H 1.31, N 60.72; found: C 11.01, H 1.32, N 59.45; IS: 1 J; FS: 5 N; ESD: 14 mJ (at grain size 100–500 µm).

Synthesis of dipotassium dinitraminobistetrazole (K-salt)

Compound 2 (see Figure 5) was obtained by a similar procedure, using btzb (1,2-ditetrazolylbutane) instead of btze.

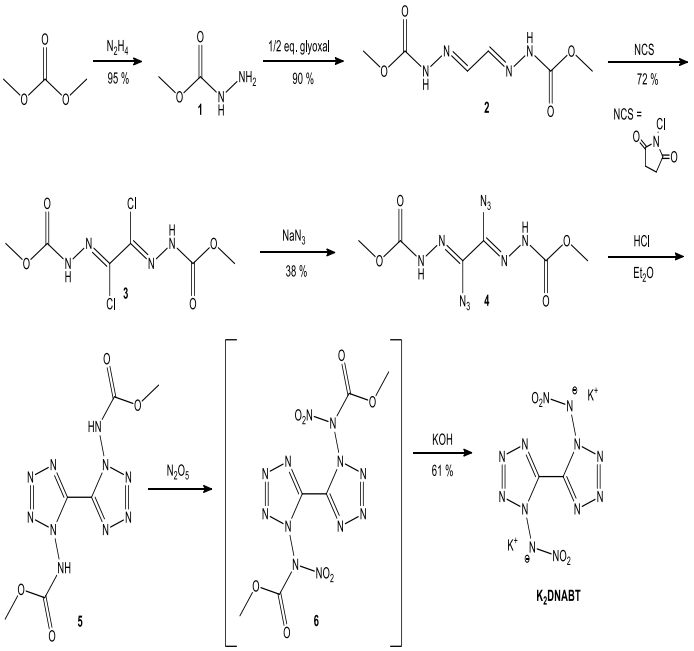

Figure 5. Schematics of reaction steps for the synthesis of K_2DNABT (K-salt).

Dichlorodimethoxycarbonylglyoxal bishydrazone (Compound 3)

10.1 g (50 mmol) of Compound 2 were suspended in 300 mL DMF and 20 g (150 mmol) NCS were added. The mixture was stirred overnight at room temperature and filtered, washed with water, ethanol, and ether. The dry product weighed 9.79 g.

Diazidodimethoxycarbonylglyoxal bishydrazone (Compound 4)

960 mg (3.452 mmol) of Compound 3 were suspended in 10 mL DMF and cooled to 0–5 °C. 650 mg (10 mmol) of sodium azide were added and the mixture was stirred overnight at room temperature. The mixture was diluted with 30 mL of ice-water and filtered, washed with water, ethanol, and ether yielding 387 mg (38 %) of Compound 4.

Dimethoxycarbonyl diaminobistetrazole (Compound 5)

1 g of Compound 4 was suspended in 50 mL of diethyl ether. The suspension was cooled with an ice bath and saturated at 5°C with gaseous HCl. The flask was sealed and stirred at room temperature for 3 days. The solvent was removed and the solid recrystallized from methanol yielding Compound 5 as colourless plates.

Dipotassium dinitraminobistetrazole (Compound 7)

1 g (3.52 mmol) of Compound 5 was suspended in 50 mL dry acetonitrile and cooled to −5 °C. 1.5 g (13.9 mmol) N2O5 were added and the mixture was stirred at this temperature. After all starting material was dissolved (1–2 h) the solution was stirred for additional 30 min. Then, 14 mL of 2 M KOH were added and the mixture was stirred vigorously at an ice bath temperature. Additional KOH solution was added until the pH of the aqueous phase stabilized constantly at 12 or above. The precipitated solid was filtered and suspended in 20 mL of water, stirred for 5 minutes and filtered again yielding 720 mg (61 %) of finely powdered colourless Compound 7.

EA ($C_2K_2N_{12}O_4$, 334.30): C 7.19, N 50.28%; found: C 7.62, N 47.95%;

IR (KBr, cm^{-1}): $\tilde{V}$ = 3450 (m), 1635 (w), 1440 (s), 1382 (w), 1360 (w), 1300 (vs), 1256 (m), 1163 (w), 1124 (w), 1031 (w), 998 (w), 872 (w), 773 (w), 729 (w); **Raman** (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{V}$ = 1610 (100), 1455 (9), 1270 (12), 1251 (19), 1142 (6), 1084 (14), 1016 (34), 992 (4), 889 (2), 750 (2), 732 (3), 512 (7), 301 (4); **DSC** (5 °C min^{-1}): 200 (dec); m/z (FAB^-): 257 ($C_2HN_{12}O_4^-$); **IS**: 1 J; **FS**: <5 N; **ESD**: 3 mJ.

Formulations

The standard M42 primer formulation (PA-101 composition) consists of lead styphnate, barium nitrate, antimony sulfide, aluminum, tetrazene, and binder. Two formulations were developed to replace only the lead styphnate component, one was using potassium salt complex and the other formulation was using copper salt complex as the replacement material. Both formulations were tested for primer sensitivity and pressure output performance in the M42 primer configuration.

Testing

The GPK-1 (K-salt based) energetic mixture (Lot: RDD13K054-102) and GPCu-1 (Cu-salt based) energetic mixture (Lot: RDD13K054-103) was dry loaded into M42 primer cups. A set of 60 M42 primer cups was loaded with K-salt and Cu-salt dry mix formulations. The individually loaded cups were then flat pressed using a flat punch attachment in a pneumatic press. The pressed material heights were measured from the underside of the primer cup to the top of the pressed material. The variation in pressing heights is directly related to the variation of material loading weights. The relationship between the material charge weights and final pressed heights can be observed in Figure 6, for K-salt based primers, and in Figure 7, for Cu-salt based primers.

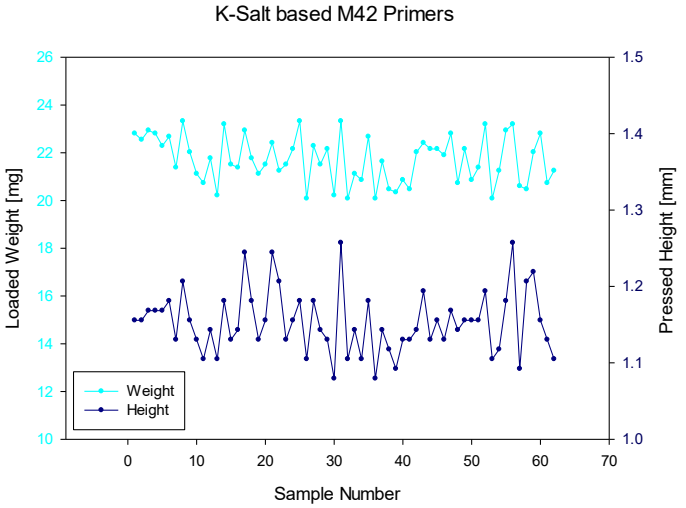

Figure 6. Charge weight and pressing height data for K-salt based M42 primers.

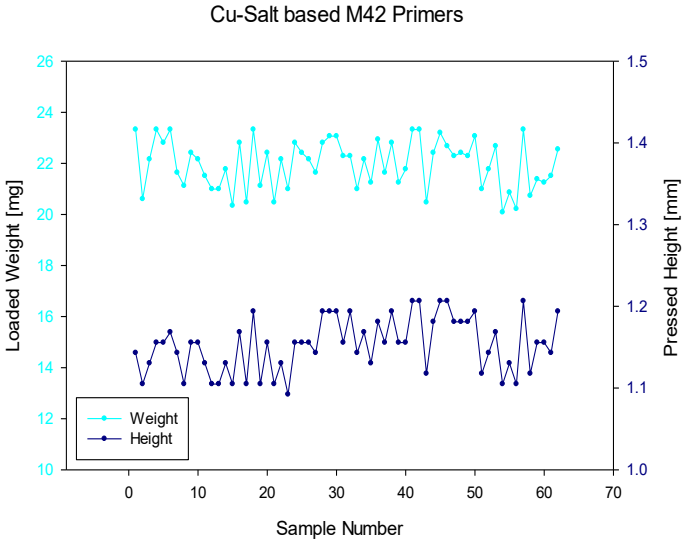

Figure 7. Charge weight and pressing height data for Cu-Salt based M42 primers.

The manufactured K-salt and Cu-salt based M42 primers were tested for primer sensitivity and pressure output characteristics.

During the primer sensitivity testing of the K-salt based M42 primers, it was observed that the primer cup would suffer a firing pin perforation and punch-out on majority of the fired primers. All except 2 out of the 13 primers which fired during the experiment suffered this punch-out casualty. A photograph of the perforated and punched-out primer cups is shown in Figure 8. The 2 remaining primers which fired but did not punch-out the primer cup suffered noticeable flow-back deformation. A photograph of the primer cups with flow-back is shown in Figure 9. The primer cup punch-out caused the firing pin and the drop ball to be ejected back out at the operator and equipment. The testing was halted due to safety concerns of the operator and testing equipment caused by the effects of the primer cup punch-out. The results determined by the Neyer test, up to the stop point of the experiment (25 samples), for the K-salt based formulation were as follows: average drop height (H_{avg}) = 14.55 cm and standard deviation (σ) = 1.37 cm.

Figure 8. Photograph of perforated and punched-out primer cups from Neyer D-optimal sensitivity testing of K-salt based M42 primers.

Figure 9. Photograph of flow-backed primer cup bottoms from Neyer D-optimal sensitivity testing of K-salt based M42 primers.

The Neyer primer sensitivity test was also initiated for the Cu-salt based M42 primers, but was halted immediately when similar primer cup punch-out was encountered. No data was gathered from this test.

Pressure output was tested on the Cu-salt based primers to determine if excessive pressure was the cause of the primer cup punch-out. Only 4 samples were tested for pressure output before the experiment was halted due to the continued primer cup punch-out. For the Cu-salt based M42 primers, the results from the pressure output tests were as follows for each sample: 22.8 MPa, 23.1 MPa, 23.9 MPa, and 20.1 MPa. It was determined that the pressure output was within an acceptable range and not significantly high enough to cause a primer cup failure.

At an earlier time, primer sensitivity and pressure output characterization was performed on a sample set of 30 commercial Olin M42 primers (Lot: WCC09F002-029), which are currently used in the M67 grenade application. The sensitivity results determined by the Neyer test on a sample set of 30 were as follows: H_{avg} = 12.14 cm and standard deviation (σ) = 1.27 cm. The results from the pressure output tests were as follows for the six samples: 23.5 MPa, 20.2 MPa, 12.0 MPa, 20.1 MPa, 20.3 MPa and 14.6 MPa.

Conclusions

A slight separation of constituents was observed during the weighing and loading steps, especially in the K-salt based formulation. This separation could be a cause of an increased particle size variation in the dry mix observed in the formulation. During the processing of the K-salt and Cu-salt based M42 primers, a slight amount of material dusting was observed. The nature of dusting was caused by dry loading and pressing of powders in the absence of a binder additive.

During characterization of the primer sensitivity and pressure output of the K-salt and Cu-salt M42 primers, it was observed that the primer cups would punch-out when initiated. This effect was observed on the majority of the primers which fired. The pressure output did not appear to be significantly higher than the commercial Olin M42 primers, which would lead to the conclusion that the primer cup punch-out was not an effect of over pressurization. Further investigation into the failure of the primer integrity is required to provide a full understanding.

Because of the continual primer cup failure due to punch-out, testing was halted due to personnel safety and testing equipment concerns. The data gathered for 25 samples of K-salt based M42 primers yielded a Neyer sensitivity of H_{avg} = 14.55 cm and standard deviation (σ) = 1.37 cm. Based on the data collected, the sensitivity performance of K-salt based primers was within the required specification. The upper sensitivity limit of $H_{avg} - 2\sigma > 5.1$ cm was met with the value of 11.8 cm and the lower sensitivity limit of $H_{avg} + 5\sigma < 30.5$ cm was met with the value of 21.4 cm. No pressure data for the K-salt based M42 primers was collected. The pressure output data collected for 4 samples of Cu-salt based M42 primers yielded a P_{avg} output of 22.5 MPa with a standard deviation of 1.6 MPa. The pressure

output characteristics clearly show that the dry loaded primers have a slightly higher maximum pressure output than the currently used commercial Olin M42 primers (P_{avg} of 18.1 MPa with standard deviation of 4.7 MPa). For grenade applications, lower maximum output pressures are desired to prevent any possible damage to the delay fuse during primer ignition.

Due to the observed higher energy output of the K-salt and Cu-salt, these materials may be suited better as lead azide replacement candidates. Other suitable substitutes for the lead styphnate component, in the M42 primer formulation, could include DBX-1. MIC primers have also shown good performance in the M42 primer configuration.

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