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Energetic Nanocomposite Lead-Free Electric Primers

Kelvin T. Higa*
U.S. Naval Air Warfare Center, China Lake, California 93555

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To address environmental concerns on airborne lead from small- and medium-caliber ammunition, the military and ammunition manufacturers have been actively developing lead-free percussion electric primers. Airborne lead endangers the health of military personnel, hampers training, and lead cleanup of indoor and outdoor ranges is high. Although commercial lead-free primers are available, they do not meet the military all-up round action time requirements of 4 ms at 160 to −65°F. Our current objective is to develop lead-free electric primers for medium caliber ammunition based on energetic nanocomposites with gas generating additives. The action time is controlled by the nature of the nanocomposite, mixing conditions, gas additive, and the quantity of gas generating additive. Ignition and ignition reliability are greatly improved by the addition of 2 wt% binder and 2 wt% carbon. Lead-free electric primers composed of 76% Al/MoO_3 nanocomposite, 20% 3, 6-bis (1H-1, 2, 3, 4-tetrazol-5-ylamino)-tetrazine, 2% Kel-F, and 2% carbon have been successfully fired at ambient and low temperatures meeting the military specifications. Aging of the energetic nanocomposite negatively impacts primer performance and aging of the nanocomposite ingredients have been investigated. The nanoaluminum powder passivation layer thickness is an important factor affecting the aging in air. Climax's nanooxidizer, MoO_3, is both photosensitive and hydroscopic in air. However, heat treatment methods have been developed that eliminate the aging behavior of the oxidizer.

I. Introduction

THE military and ammunition manufacturers must address airborne lead emissions from primers and projectiles to meet EPA regulations. Lead emissions impact military training, range contamination, range cleanup, and the health of military personnel. About 80% of the airborne lead in conventional ammunition originates from reaction of hot gas with the lead bullet [1] and 20% from the primer. Total metal jacketed bullets reduce the lead airborne emission but they fragment on impact and continue to be a source of lead contamination in indoor and outdoor ranges. The ammunition industry has also developed lead-free primer formulations based on diazodinitrophenol [2–4], dinitrobenzofuroxan [5,6], and cupric azide [7], however, they do not meet the military shelf-life standard of 20 years and do not meet the all-up round action time of 4 ms for the temperature range of 160 to −65°F. The use of energetic nanocomposites is currently under investigation as a lead-free primer alternative that will be suitable for both commercial and military applications. The idea was first described in a patent by Dixon et al. [8], "Lead-Free Percussion Primer Mixes Based on Metastable Interstitial Composite (MIC) Technology" in 1998. A number of different energetic nanocomposites are viable with heats of reaction (Table 1, [9]) that are higher than the standard M52A3B1 primer.

However, primers based on pure energetic nanocomposites were found to have unacceptable all-up round action times (AUR-ATs) in excess of 40 ms. The M52A3B1 primer is composed of approximately 44% lead styphnate, 40% barium nitrate, 13% calcium silicide, 1% acacia gum, 1% acetylene black, and 1% styphnic acid and releases approximately 1.5 kJ/g of energy and 12.1 mol of gas per kilogram of primer. Energetic nanocomposites release more energy but are deficient in gas generation (1.4–5.4 mol of gas per kilogram of nanocomposite). The incorporation of a gas additive in a nanocomposite primer was first reported by Doris [10] and AUR-ATs of less than 4 ms were achieved for small caliber ammunition.

The focus of this paper will be on the development of a lead-free electric primer for medium caliber ammunition and the identification of critical factors impacting performance, material preparation, reliability, aging, and material safety properties. Aging studies of nanophase Al powders have been reported [11–13], as well as the effect of aging on Al powder reactivity [14]. However, the effect of the thickness of original oxide passivation layer on the aging properties has not been reported. The conventional M52A3B1 primer is used as our baseline for performance and safety properties.

II. Experimental

All nanoaluminum powder starting materials were obtained from Technanogy (50 nm) or NanoTechnologies (80 nm) and stored under argon in a VAC-Atmospheres glove box. Energetic nanocomposites, sometimes called metastable interstitial composites (MIC), were obtained from Technanogy, the U.S. Naval Surface Warfare Center–Indian Head (NSWC-IH), or prepared inhouse. Nanomolybdenum trioxide, MoO_3 (41 nm), was obtained from Climax Engineered Materials and stored under argon. Bismuth trioxide, Bi_2O_3, was obtained from Sigma-Aldrich (320 nm), Skylighter, Inc. (2.5 μm), and Nanophase Technologies Corporation (50 nm). Nanocarbon (50 nm) made from acetylene was obtained from Chevron Phillips. Three, 6-bis (1H-1, 2, 3, 4-tetrazol-5-ylamino)-1, 2, 4, 5-tetrazine (BTATz) was prepared by literature methods [15].

Safety equipment and handling precaution: Energetic nanocomposites in general should be handled with extreme care. The properties are often as sensitive as or even more sensitive than primary explosives such as lead azide and lead styphnate. These materials exhibit high electrostatic discharge (ESD), impact and friction sensitivities. These composites have ESD sensitivities as low as 2 μJ, impact sensitivities below 5 cm with a 2.5 kg weight, and Allegheny Ballistic Laboratory (ABL) friction sensitivities that are less than 0.05 N. Extreme caution should be used when working with these materials. Suitable safety equipment includes safety glasses, lab coat, proper grounding of personnel and equipment, antistatic bags/conductive vials, grounding wrist straps and tester, conductive gloves, and hearing protection.

A. Material Characterization

Aluminum and Climax's nano-MoO_3 powders were stored in aluminum bags and plastic bottles in Al bags, respectively, under an argon atmosphere in a Vacuum Atmospheres Company HE-43 glove box, except for aging studies. Thermogravimetric analysis (TGA) on

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*Weapons Division, 1900 North Knox Road.

Al powders were conducted using a TA Instruments Hi-Res TGA 2950 thermogravimetric analyzer with a DuPont 2100 thermal analyst controller. TGAs of Al powders and baselines were performed using alumina pans in air. The heating profile for the aluminum powders was heating at 20°C/ min to 350°C, 3°C/ min to 700°C, 20°C/ min to 850°C, and hold for 4 h at 850°C. Brunauer, Emmett, and Teller (BET) surface area measurements were performed on a Quantachrome Autosorb-1 automated gas sorption system. Specific surface area in meters squared per gram is determined by adsorption of nitrogen molecules on the sample surface at liquid nitrogen temperature. The bulb is about half-filled with the sample, degassed by heating under vacuum, then weighed to determine the weight of dried powder analyzed. The surface area analysis is fully automated and seven data points (different pressures of nitrogen) were used in the analyses (7-point BET). X-ray powder diffractions were collected on a Scintag PAD-V using Cu K_α radiation. Samples were dispersed on zero background quartz slides coated with a thin film of Vaseline.

B. Energetic Nanocomposite Preparation

Ultrasonic Bath:

NSWC-IH presonicated the starting material (1 g in 25 ml of hexane) for 15 min. The 50 nm Al (0.45 g) and MoO_3 (0.55 g) of the presonicated powders were mixed in 25 ml of hexane, sonicated for 60 min, and then isolated.

GE 100 Watt Ultrasonic Processor:

In a typical preparation, 20 ml of hexane was added to 0.45 g of 50 nm Al and 0.55 g of MoO_3 (41 nm) in a 25 ml glass vial. The horn was centered in the vial with the tip of the horn about 2–5 mm above the bottom of the vial. The sample was sonicated at 100% amplitude with a 50% duty cycle (0.5 s pulse, 0.5 s delay) for 1 min. The composite was isolated by gravity filtration through filter paper, air dried, the cake broken up, and then vacuum dried for 1 h.

Branson 400 Watt Digital Sonifier:

In a typical preparation, 20 ml of hexane was added to 0.45 g of 50 nm Al and 0.55 g of MoO_3 (41 nm) in a 30 ml polyethylene vial. The horn was centered in the vial with the tip of the horn about 2–5 mm above the bottom of the vial. The sample was sonicated at 75% amplitude with a 50% duty cycle for 1 min. The composite was isolated by gravity filtration through filter paper, air dried, the cake broken up, and then vacuum dried for 1 h.

C. Lead-Free Electric Primer Preparation

In a typical preparation, the Al/MoO_3 composite was placed in a 50 ml polyethylene beaker, 30 ml of hexane added, a 0.5 in. magnetic stirbar added, then stirred for 2 min. The preground and presieved (150 mesh) BTATz was added to the stirring composite and stirred for 10 min. A hot (60°C) solution of Kel-F in 10 ml of hexane was added to the stirring slurry. The slurry was slowly dried under a slow flow of nitrogen over a period of 1 h. The product was dried in the beaker under dynamic vacuum for 1 h. The product was transferred onto a sheet of aluminum foil on a grounded conductive pad. The composite cake was broken down into a coarse powder with a metal spatula (the operator and spatula must be grounded). The product was transferred into a 100 ml polyethylene bottle, the presieved (150 mesh) carbon added, and the material mechanically mixed for 2 min. The primer material was transferred into a conductive vial for storage.

D. Primer Consolidation and AUR Testing

Hexane (130 mg) was added to 130 mg of the primer material to form a slurry. The slurry was placed in the primer cup, a paper cover added, prepressed, vacuum dried for 4 h, and then pressed at 8000 psi with a dwell time of 15 s. AUR-AT is measured taking the electric igniter discharge as time zero until the projectile leaves the end of the barrel. AUR-AT testing (10–20 per set) of 20 mm rounds in a Mann barrel was performed either at ambient temperature or at low temperature (−40 to −65°F). To achieve low-temperature conditions, the 20 mm round and the Mann barrel gun breach were conditioned to the desired temperature. Each data set consisted of 10–30 all-up rounds and the averages of the sets are reported.

III. Results and Discussion

A. Aging of Nanoaluminum Powders

Three nanoaluminum powders were characterized and stored in a controlled environment at 25°C at 25% relative humidity. Technanogy supplied 50 nm Al powder with 2.7 and 1.7 nm oxide passivation layers and NanoTechnologies provided an 80 nm Al powder with a 1.1 nm oxide layer. The active aluminum content was determined to be 65.6 and 74.8% by TGA and 66.5 and 76.3% by based hydrolysis [16], respectively, for the 50 nm Al powders. The TGA of the NanoTechnologies 80 nm Al gave an initial active aluminum content of 88.8% that corresponds to an average particle size of 80 nm with a 1.1 nm oxide shell. The difference in active aluminum content between the TGA and hydrolysis is due to larger particles in the Technanogy 50 nm Al powder which do not fully oxidize under our standard TGA conditions. The aging of the Al powders were monitored by measuring the active aluminum content by TGA over a prolonged period and is plotted in Fig. 1.

The active aluminum content for 50 nm Al with a 2.7 nm oxide shell dropped from 66.5% down to 64.3% after 2 weeks and remained constant over the next 27 weeks in air. In contrast, Technanogy's 50 nm Al powder with a 1.7 nm oxide passivation layer and NanoTechnologies' 80 nm Al powder with a thin 1.1 nm oxide layer age severely over a 60 day period when stored in air at 25% relative humidity at 25°C. The active Al content for the 50 and 80 nm Al dropped from 66.4 to 58.4% and from 88.8 to 74.4%, respectively. The active Al content of the 80 nm Al stabilized at 73.6% even after storage in air for a year. The 80 nm Al control sample stored under argon showed no loss in active aluminum content over the same period. Nanotechnologies conducted a similar aging study on 80 nm Al powders with oxide thicknesses between 1.6 and 2.7 nm. The nano-Al powders were stored at 50% humidity at 50°C, monitored over a 200 day period and exhibited aging behavior that confirmed our results. Powders with thin oxide passivation layers severely degraded (84% down to 66% active Al), whereas the Al powder with a 2.7 nm oxide layer exhibited only minor loss of active aluminum content. An aging study of 50 and 80 nm Al, by Puszynski [17], in 43, 75, 83, and 97% relative humidity showed rapid active aluminum loss in 5–40 days. The initial oxide thickness was not determined. However, the calculated oxide thicknesses for the 50 and 80 nm Al powders are 2.2 and 2.1 nm, respectively, based on the reported active aluminum content of 68 and 79.8%. The high

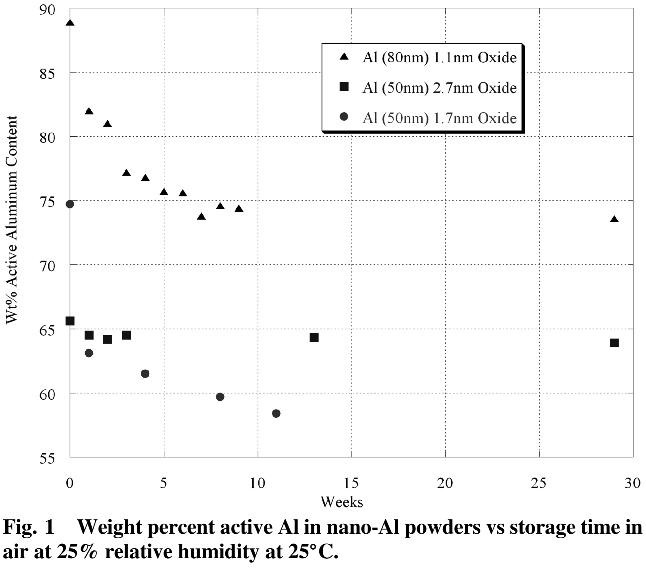


Fig. 1 Weight percent active Al in nano-Al powders vs storage time in air at 25% relative humidity at 25°C.

Table 1 Heat of reaction for nanocomposites

	ΔH pure Al theoretical		ΔH Al (80 nm) 72% active		ΔH Al (50 nm) 64% active		
Chemical reactions	kJ/g	kJ/cc	kJ/g	kJ/cc	kJ/g	kJ/cc	Moles of gas/kg [9]
$2Al + MoO_3 \rightarrow Al_2O_3 + Mo$	−4.70	−18.39	−4.25	−16.63	−4.08	−15.97	2.4
$2Al + 3CuO \rightarrow Al_2O_3 + 3Cu$	−4.11	−20.83	−3.84	−19.08	−3.73	−18.39	5.4
$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$	−3.99	−16.89	−3.63	−15.29	−3.47	−14.57	1.4
$2Al + WO_3 \rightarrow Al_2O_3 + W$	−2.91	−15.96	−2.71	−14.49	−2.63	−13.92	1.4
$2Al + Bi_2O_3 \rightarrow Al_2O_3 + 2Bi$	−2.12	−15.23	−2.04	−14.19	−2.00	−13.71	4.7
M52A3B1	−1.50	——	——	——	——	——	12.1

Table 2 Effect of solvent on sonic mixing

	Bismuth trioxide, Bi_2O_3					
	Aldrich 320 nm		Skylighter 1–3 μm		Sigma–Aldrich 10 μm	
Al powder	hexane	isopropanol	hexane	isopropanol	hexane	isopropanol
Al, 33 nm	good	poor	——	poor	good	——
Al, 50 nm	good	poor	——	poor	good	poor
Al, 80 nm	good	poor	good	good	good	——

aging susceptibility of Al powders with thin oxide layers is due mainly to reactivity with water. Passivation techniques using hydrophobic coatings [18,19] have been shown to reduce the water reactivity of nanoaluminum powders and should be used to maintain high active aluminum content, high reactivity, and long powder shelf-life. Aluminum powders with thin oxide passivation and a thin hydrophobic coating should be stabile in air, more reactive, and have higher active aluminum content. The hydrophobic coating should inhibit hydrolysis/oxidation, enhancing Al powder shelf-life.

B. Aging of Climax's Nano-MoO_3 Powder

The nano-MoO_3 powders age dramatically in air. The BET surface area of the nano-MoO_3 stored under argon in an Al bag starts at 50.3 m^2/g but after storage in air/light drops to 36.5 m^2/g after 2 days and then down to 31.5 m^2/g after 14 days. The calculated BET average particle size increases from 26 to 35 to 41 nm, respectively. The color changes from a pale yellow to a lime green over the same period. The MoO_3 stored under argon in the light turned blue/purple losing oxygen and forming a small amount of suboxide. The x-ray powder diffraction of Climax's nano-MoO_3 exhibited patterns for the monohydrate $MoO_3 \cdot H_2O$, monoclinic MoO_3, and orthorhombic MoO_3. The TGA of the Climax sample lost 2.1 wt% during heating to 200°C which corresponds to 17 wt% of the MoO_3 hydrate. Air storage increases the hydrate content by converting the monoclinic phase MoO_3 into the hydrate. Storage under inert atmosphere in the absence of light is critical.

The dehydration of molybdenum trioxide hydrate was investigated by powder x-ray by Kuzmin and Purans [20]. The dehydration is described by Eq. (1):

$$Mo\,O_3 \cdot 2H_2O \xrightarrow{60\text{–}80\,^\circ C} MoO_3 \cdot H_2O \xrightarrow{110\text{–}140\,^\circ C} MoO_3\ (\text{monoclinic}) \tag{1}$$

To further explore the dehydration, photosensitivity, and rehydration properties of Climax's nano-MoO_3, a series of heat treatment experiments were performed. The objective was to find conditions to transform the MoO_3 into the pure orthorhombic phase and to determine if the photosensitivity and hydration behavior was due to either the monoclinic or orthorhombic phase. Samples (10 g) were heated to 400°C for 30, 60, 120, and 180 min, to 443°C for 22 min, and to 500°C for 15, 30, and 180 min in a Lindberg furnace. The complete conversion of the monoclinic to orthorhombic phase was obtained for samples heated at 400°C for 120 min, at 443°C for 22 min, and at 500°C for 15 min. Samples containing both the monoclinic and orthorhombic phase continued to exhibit hydration and photosensitivity problems. The pure orthorhombic phase MoO_3 samples were about 200 nm in size as determined by BET and did not form the hydrate or discolor after a month in air.

C. Effect of Solvent on Mixing

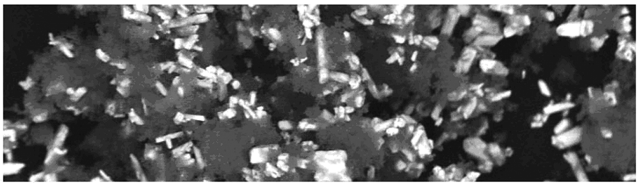
The effect of using a nonpolar (hexane) vs polar (isopropanol) solvent on the mixing was examined for mixtures of different Al and Bi_2O_3 particle sizes. The 1 g samples in 20 ml of solvent were mixed using the 400 W Branson Sonifier at 75% amplitude, 0.5 s pulse with 0.5 s delay for 1 min. The product was isolated by gravity filtration using filter paper. The data is summarized in Table 2.

Good samples were homogeneous and showed no signs of material separation. Poor samples were heterogeneous with the gray aluminum on top and the denser yellow bismuth oxide on the bottom. All of the samples prepared in hexane gave homogeneous products. In contrast, for isopropanol, only the Al (80 nm) with Bi_2O_3 (1–3 μm) gave a homogeneous product. The scanning electron micrograph (SEM) of this material mixed in isopropanol and in hexane is shown in Fig. 2:

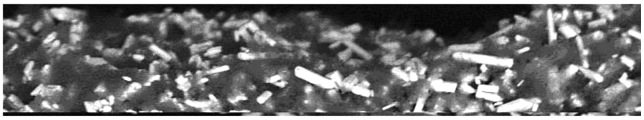
The gray colored material is the nanoaluminum and the white rods are the bismuth trioxide. The mixing of the Al and Bi_2O_3 appears more homogeneous for the product prepared in hexane. The sample prepared in isopropanol has larger regions of segregates of aluminum and segregates of Bi_2O_3.

D. Effect of Sonic Mixing Systems

Energetic nanocomposites have been prepared using a variety of sonic mixing devices. To study the effects of the different mixing systems on the AUR-AT for lead-free electric primers, Al/MoO_3 nanocomposites were obtained from NSWC-IH, Technanogy, and



isopropanol



hexane

Fig. 2 SEM of Al (80 nm) and Bi_2O_3 (2.5 μm) mixed in isopropanol vs hexane.

Table 3 All-up round action times for LFEP using different sources of Al/MoO_3 nanocomposite

Source	Treatment	Wt% BTATz	AUR-AT, ms
NSWC–IH	sonic bath	10.3	3.64
——	——	15.5	3.03
——	——	25.0	2.96
NAWCWD	100 W	20.0	3.65
Technanogy	400 W	20.0	2.98
NAWCWD	400 W	20.0	2.98

also prepared inhouse. For all three sources, the starting materials and composite mixture were identical containing 0.45 g of 50 nm Al powder and 0.55 g of 41 nm MoO_3. An ultrasonic bath was used by NSWC-IH, a GE 100 W Ultrasonic Processor was used by the Naval Air Warfare Center–Weapons Division (NAWCWD), and a Branson 400 W Sonifiers was used by Technanogy and NAWCWD. Even though the three systems represented very different mixing power levels and conditions, they all met the military ambient temperature AUR-AT requirement. The composites were used to make lead-free electric primers with 10–25% BTATz, 2% Kel-F, and 2% carbon. All-up round action times for all samples were all less than 4 ms and no significant differences were observed (see Table 3).

The AUR-AT for the primers made from nanocomposites prepared using the 100 W GE system was slightly higher than for the other systems. A longer treatment time would be needed to reduce the AUR-AT below 3 ms. The effect of preparing nanocomposites with different sonication time (0.5, 1, 2 min) using the 400 W Digital Sonifier was also examined. The composites were used to make our standard primers composed of 76% Al/MoO_3, 20% BTATz, 2% Kel-F, and 2% carbon. The AUR-AT for the three treatment times were similar (3.10 ± 0.11, 2.87 ± 0.13, 2.98 ± 0.16 ms, respectively).

E. Lead-Free Electric Primer Formulation

The general approach for the design of the lead-free electric primer is to develop a composition with similar performance properties to the M52A3B1 primer. The energy content, amount of gas released, mixing efficiency, rates of reaction, gas generating additive, binder, and conductive additive must be factored into the design of the lead-free electric primer. The energy content of nanocomposite primers is a function of the energetic nanocomposite and the Al/MoO_3 system for the electric primer because of its high-energy content (4.7 kJ/g). The calculated heat of reaction for the Al/MoO_3 composite (Table 1) using pure Al, Al (80 nm), and Al (50 nm) decreases from −4.70 to −4.25 to −4.08 kJ/g, respectively. The decrease in energy release is due to the increasing aluminum oxide content with decreasing Al particle size. The effect of using the 80 nm Al vs 50 nm Al powders in primers with a composition of 76% Al/MoO_3, 20% BTATz, 2% Kel-F, and 2% carbon was investigated. The ambient temperature AUR-ATs for the 80 and 50 nm Al compositions gave nearly identical results, 2.90 ± 0.06 and 2.98 ± 0.16 ms, respectively. There is no apparent advantage in using either the 50 or 80 nm Al.

The need for a gas generating additive becomes clear when the properties of the M52A3B1 primer is compared with the gas release properties of the energetic nanocomposites in Table 1. The M52A3B1 primer releases 2–7 times more gas than the nanocomposites. The gas is needed to propel the hot reaction products of the primer onto the propellant bed. A nanocomposite primer composed of 96% Al/MoO_3 nanocomposite, 2% Kel-F, and 2% carbon that produces little gas had an average ambient temperature AUR-AT of 51 ms. The AUR-AT can be dramatically reduced with the introduction of a gas additive. A wide variety of gas generating additives are available to solve this problem, including pentaerthrol trinitrate (PETN), nitrocellulose, Diamino Azo Tetrazine Oxide (DAATO), BTATz, and other high nitrogen compounds. Bis (triazolyl)amino tetrazine (BTATz) was selected because of its high positive heat of formation ($\Delta H = 883.6$ kJ/mol), gas release properties, and safety properties (flammable solid). The rapid decomposition of BTATz releases nitrogen gas and a solid red-orange $(HCN)_x$ polymeric solid. The effect of the quantity of BTATz on the AUR-AT is plotted in Fig. 3.

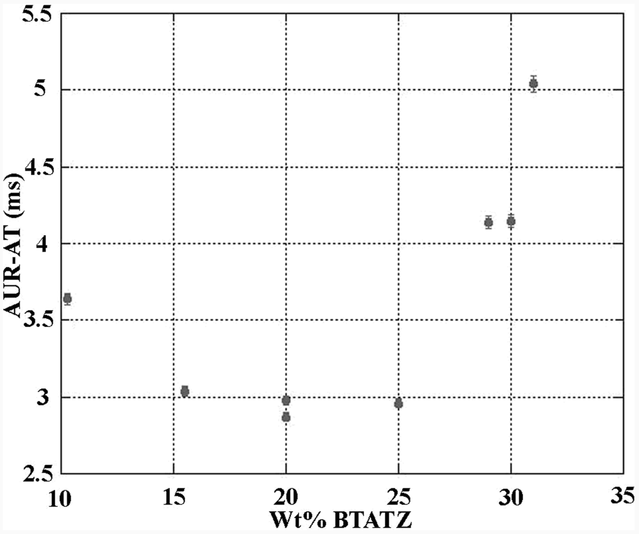


Fig. 3 All-up round action time vs weight % BTATz.

The primers were composed of the standard 45:55 Al (50 nm)/MoO_3 (41 nm) composite, BTATz, Kel-F, and carbon. The amount of BTATz used was at the expense of the Al/MoO_3 nanocomposite, whereas the weight percent Kel-F and carbon were fixed at 2%. Although primer formulations with 10–25% BTATz gave suitable AUR action times, the formulation with 76% Al/MoO_3 nanocomposite, 20% BTATz, 2% Kel-F, and 2% carbon was selected as the optimum formulation. The energy content of the formulation was calculated to be −5.6 kJ/g with a gas release of 12.0 mol/kg of primer, which is almost identical to the gas release of the M52A3B1 primer.

Another factor affecting the primer performance is the aluminum-oxidizer ratio. Assuming most 50 nm Al powders have a 64% active aluminum content, then the standard 45:55 composition has a 2.8 Al to MoO_3 molar ratio. The effect of varying the Al/MoO_3 molar ratio (2.8, 3.0, and 3.1) was investigated in primers with 76% Al/MoO_3, 20% BTATz, 2% Kel-F, and 2% carbon. The AUR-ATs of 2.98 ± 0.07, 3.03 ± 0.21, and 3.65 ± 0.57 ms were obtained, respectively. Both the AUR-AT and the standard deviations increased with increasing Al/MoO_3 molar ratio.

Early lead-free primers prepared without binders were difficult to consolidate and resulted in a crusty, brittle ceramic with poor firing reliability. The addition of a binder, Kel-F, at the 2% level improved the consolidation properties and firing reliability.

The effect of conductive nanocarbon was explored by preparing primers with 0, 2, 4, and 6% carbon. Primers without the carbon additive could not be ignited except at very high power levels. The low-temperature AUR-AT for 2, 4, and 6% were 3.65 ± 0.57, 3.63 ± 0.18, and 5.91 ± 5.81 ms, respectively. At 6% carbon loading, the action time degraded badly and 2% carbon loading was selected for the primer formulation.

The material safety properties are a major concern for energetic nanocomposites. The properties, in general, are similar to primary explosives. The human body ESD (HBESD) sensitivity and ABL friction sensitivity of the lead-free electric and M52A3B1 primers were determined and compared. The HBESD test data are plotted in Fig. 4.

The lead-free electric primer (LFEP) composition appears safer than the current M52A3B1 primer. The M52A3B1 primer exhibits a lower ignition threshold where some ignite at less than 1 kV and reaches 100% ignition at 5 kV. The ignition threshold for the new LFEP is greater than 2.5 kV (0% fired) and reaches 100% ignition at 7.5 kV. The LFEPs will not ignite from inadvertent discharges of 2.5 kV or less. The ABL friction sensitivity of both the M52A3B1 and LFEP were greater than 10 N.

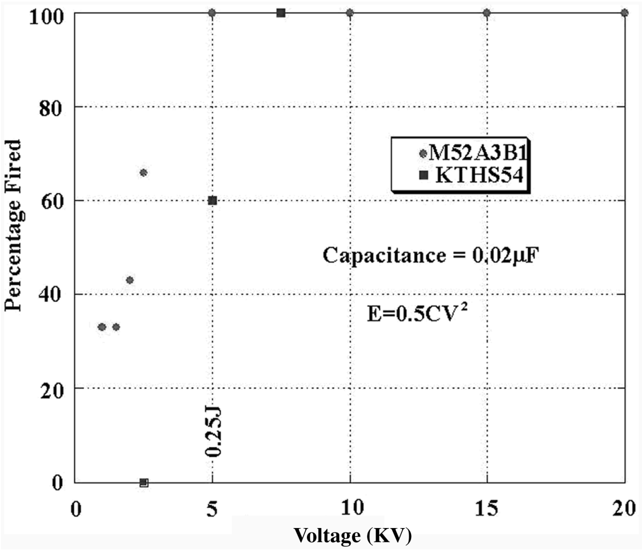


Fig. 4 Human body electrostatic discharge simulator comparison of the M52A3B1 and lead-free electric primer.

F. Aging Effect on AUR-AT

The effect of aging of primers on the AUR-AT was evaluated by using Al powder (80 nm Al with a 1.1 nm oxide shell) that is prone to aging. Typically, primers made from 50 nm Al from Technanogy (2.7 nm oxide shell) showed no aging effect after storage for more than 6 months in air. Al/MoO_3 composites were prepared from 80 nm Al powder that had been stored in air for 5 days and had an active Al content of 82.7%. Three energetic nanocomposites with active Al/MoO_3 ratios of 2.04, 2.70, and 3.03 were prepared and used to make primers with the composition 76% Al/MoO_3, 20% BTATz, 2% Kel-F, and 2% carbon. Primers with an Al/MoO_3 ratio of 2.04 were used as the baseline and three additional sets of primers with an Al/MoO_3 ratio of 2.04, 2.70, and 3.03 were used in the aging study. The baseline primers were loaded and fired to give an ambient AUR action time of 2.90 ± 0.06 ms. The other three sets of primers were aged under uncontrolled ambient conditions for 3 months, loaded, and fired. Only the aged primers with the Al/MoO_3 ratio of 2.04 were fired at ambient temperature and had a slightly high average AUR-AT of 4.48 ± 1.76 ms. However, low-temperature AUR-ATs for the three sets of primers were 32.39 ± 3.87, 4.46 ± 1.02, and 4.23 ± 1.21 ms, respectively. Aging increased the action times at ambient and low temperatures and also increased the scatter resulting in larger standard deviation. None of the aged primers gave acceptable action times. The most probable cause is the change in active Al to MoO_3 ratio. The active Al content of the NanoTechnologies 80 nm Al powder dropped from 89 to 74% after storage in air for 49 days at 25% humidity and 25°C. The primer samples were stored under uncontrolled conditions for 90 days and the active Al content may have decreased well below 74%. The primers with higher starting Al/MoO_3 ratios nearly met the 4 ms action time requirement. If the active Al content of the 80 nm Al powder dropped to 74%, the actual Al/MoO_3 ratios were 1.73, 2.29, and 2.56, respectively, and may explain the 32 ms action time for the worst set of primers.

IV. Conclusions

The use of energetic nanocomposites as alternative lead- and barium-free formulations is under development for both percussion and electric primers. The ambient AUR-AT (51 ms) for primers without gas additives was found to be too high for medium caliber ammunition applications. However, lead-free electric primer formulations with 76% , 20% BTATz, 2% Kel-F, and 2% carbon met the ambient and low-temperature AUR-AT requirement of 4 ms. The 4 ms AUR-AT requirement was met using several sources of energetic nanocomposite and with different mixing devices used in its preparation. The ambient temperature AUR-AT was met with primers using Technanogy's 50 nm Al or NanoTechnologies' 80 nm Al powders and with untreated and heat-treated nano-MoO_3 powders. The ability to meet the stringent requirements with a variety of different starting materials, sonication devices, and sources is extremely promising for ultimate commercialization and deployment of this technology.

The aging of the nanocomposite has been shown to negatively impact the performance of the lead-free electric primers in medium caliber ammunition. Primers made using 50 nm Al powders with a 2.7 nm oxide layer did not exhibit loss of performance after storage in air for more than 6 months, whereas primers made using 80 nm Al powder with a thin 1.1 nm aluminum oxide layer exhibited severe performance loss after storage in air for only 3 months. The main source of primer aging is thought to be due to the aging of the Al powder. Aluminum nanopowders with thin aluminum oxide passivation layers (1.1–1.7 nm) aged rapidly in air, whereas powders with thicker oxide layers (2.7 nm) exhibited only mild aging. For military applications, nanoaluminum powders should be passivated with at least a 2.7 nm aluminum oxide layer or they should be stabilized with hydrophobic coatings. Aging of the oxidizer, Climax's nano-MoO_3 is also a problem. It ages in air and light by forming a hydrate and by forming a suboxide by photochemical reduction. Both by-products change the fuel to oxidizer ratio and impact the reaction rate of the nanocomposite. This behavior can be mitigated by conversion of Climax's MoO_3 to pure orthorhombic MoO_3 via heat treatment. It is essential to reduce or eliminate the aging pathways to meet the 20 year life-cycle requirement.

The addition of 2% Kel-F binder greatly improved the consolidation and firing reliability of the primer formulations. Without the binder, the primer firing reliability was poor at best. For electrically ignited primers, ohmic heating is the primary ignition mechanism. Conventional primers use conductive additives such as $CaSi_2$ and carbon. Considering the high-conductivity of aluminum metal and the high nanoaluminum powder content (33%), the need for a conductive additive was not obvious. However, nanoaluminum powders are inherently nonconductive due to the aluminum oxide shell. The weight fraction of alumina in nanopowders is much higher than for conventional powders and the electrical properties are more similar to alumina than aluminum. The addition of conductive carbon powder was required for primer ignition and 2 wt% was found sufficient for high primer ignition reliability.

The current primer formulation has been shown to meet military requirements for electric primers but it is also a viable candidate for lead-free percussion applications for small and medium caliber ammunition. The ESD and friction properties are similar or less sensitive than the M52A3B1 primer currently used for electrically initiated medium caliber ammunition.

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S. Son
Associate Editor