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Investigation of Alternate Energetic Compositions for Small Electro-Explosive Devices

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Synthesis of 1,1-bis (amino)-3,3,5,5,7,7-hexakis(azido)cyclotetraphosphazene (DAHA) as a lead azide replacement material was accomplished. The DAHA was then loaded into a Mk 1 electric detonator in varying amounts and loading pressure. Detonators were initiated to determine functionality of the new material and output level of the assembled detonator assemblies.

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Investigation of Alternative Energetic Compositions for Small Electro-Explosive Devices for Medium Caliber Ammunition

Technical Objective: The objective of this effort was to identify, evaluate and test environmentally benign compounds that could be used in small electro-explosive devices within medium caliber ammunition, thereby eliminating the existing heavy metal compounds currently used. The effort was to result in a feasibility demonstration of a new small electro-explosive device (EED) design(s) compared to the M100 and PA537 electric detonators.

Background: Small electro-explosive devices are being proposed for use in all new developmental, multi-function medium caliber high explosive rounds. The currently available hardware options center around the M100 electric detonator and its variants. These detonators are small in size and weight and require very low power to initiate, qualities that make them attractive to medium caliber fuze designers as volume and onboard power are two of the most critical design considerations for these size fuzes. Like all other existing initiating charges, from primer material in small arms through detonating charges in large caliber artillery shells and missiles, the M100 contains heavy metal-based primary explosives as part of the initiation train. Because of the environmental and health issues that these lead-based materials produce, The Department of Defense is actively looking into producing heavy metal-free initiating explosives. The work carried out in this effort was specifically directed toward the development of new, non-heavy metal based primary initiating explosives for the production of "green" bridgewire detonators. The US "standard" primary explosives are heavy metal-based compounds (e.g. lead azide, lead styphnate) or mixtures (e.g. NOL-130). The most widely used primary high explosive in US munitions systems is lead azide, either as a neat material, or as in NOL-130, formulated with other ingredients.
Lead azide displays the desirable characteristic of being a near point detonant, a material that will transition from a burning wave front to a detonation wave front in only a few molecules of material. This characteristic makes it ideal for detonator applications as the primary function of the detonator is to initiate the detonation process and pass it along to the main explosive charge. Additionally, at present, there is no production capacity of lead azide in the United States. All the bulk material presently on hand, housed at Lone Star AAP, was produced three to four decades ago, and its composition and viability have recently been called into question. Manufacturing of any new lead-based primary explosive, such as lead azide or lead styphnate, will result in the production of significant quantities of highly toxic hazardous waste. Lead-based materials are cataloged on the EPA Toxic Chemical List (EPA List of 17 Toxic Chemicals). They are regulated under the Clean Air Act as Title II Hazardous Air Pollutants, as well as classified as toxic pollutants under the Clean Water Act, and on the superfund list of hazardous substances.

In a previous developmental effort to replace heavy metal initiating explosives in stab detonators, GEO-CENTERS, INC. prepared a series of phosphazene compounds. Several of these compounds showed promise in their basic characteristics.

Accomplishments. One of the previously developed phosphazene compounds, 1,1-bis (amino)-3,3,5,5,7,7-hexakis(azido)cyclotetraphosphazene (DAHA), was prepared under the present effort for investigation as the initiating explosive in bridgewire detonators. DAHA was chosen as the candidate material for this effort based on its available energy and ease of fabrication. The DAHA was prepared using a two step process. The precursor material 1,1-Diaminohexachlorotetraphophazene was prepared from commercially available octachlorocyclotetraphosphazene by treating it with ammonium hydroxide in sodium sulfate and ether. This diamino compound was then reacted with sodium azide in acetone to obtain the crystalline DAHA.

DAHA has found to be thermally stable (DSC decomposition temperature = 230 °C.) and sensitivity testing shows it to behave as a primary explosive (ball drop impact: 8 inches; BAM friction: GO at 50-gram load). DAHA, however has a low melting point (72 - 74 °C) when considered for munitions applications and will have to be re-formulated, possibly as a salt, for any follow-on developmental efforts.

Once sufficient DAHA had been synthesized, a simple test was done to check the viability of DAHA as a bridgewire-sensitive initiator material. DAHA was partially dissolved in an organic solvent to create a de-sensitized slurry. Nichrome 60 wire (34 gauge) was bent into a U-shape, and dipped into the slurry. The wire was then removed and the solvent allowed to evaporate from the applied material. This process was repeated several times to coat the wire surface. The total length of wire coated was approximately 0.25" in length. Coating was verified by visual inspection; no quantification as to the amount of material or the coating thickness was done. Three separate wires were coated in this manner. After sufficient repetitions of the process were accomplished to achieve the appropriate coating level, the wires were allowed to sit at room temperature for 15 minutes to insure that any remaining solvent had completely evaporated. The wires were attached to electrical leads and functioned by closing the circuit with a 9-volt battery. The wires became hot and all three resulted in a visual flash and sharp, audible crack when the DAHA decomposed/detonated. The third test wire was broken by the reaction/detonation.

The next step was to determine if a quantity of DAHA could initiate a quantity of main explosive material. A quantity of DAHA was loaded into a MK-1 detonator using RDX, CL-20, or both materials as the secondary/output energetics. The MK1 detonator was selected because it is larger that the M100, and offered better control (and safety) of the energetic materials loading. Results of these tests are summarized in Table 1.

Table 1: MK1 Detonator DAHA Testing

	Weight (mg)			
Cup #	DAHA	CL-20	RDX	Result
1	Not measured	---	Not measured	DAHA initiated. Large flash. RDX initiated. Complete detonation transition.
2	Not measured	Not measured	---	DAHA initiated. Larger flash than in 1. CL-20 initiated. Complete detonation transition.
3	Not measured	---	---	Large flash and flame.
4	Not measured	Not measured	Not measured	Complete detonation transition.
5	Not measured	Not measured	---	Cup confined, fired against Al witness plate: detonation, plate cracked.

The final step was to determine if DAHA could be substituted as the initiator and transition material within a complete detonator and then properly function a full detonation train. MK-1 detonators were loaded with DAHA/RDX/CL-20 and functioned against A-5 booster pellets. Six aluminum cups were loaded with energetics, as detailed below, and a MK-1 bridgewire pressed into the tops of the cups in contact with the DAHA. For cups 1-3, Cl-20 was added to the aluminum sleeve, in two or three increments, and hand pressed to a dial reading of 15 after each incremental addition. DAHA was placed on top of the CL-20 and hand pressed to a dial reading of 15. A MK1 bridgewire was then pressed into the top of the cup so that the bridgewire was in contact with the DAHA (Figure 1.)

For cups 4-6, RDX was added to the aluminum sleeve in one increment and hand pressed to a dial reading of 15. CL-20 was placed on top of the RDX and hand pressed to a dial reading of 15. DAHA was placed on top of the CL-20 and hand pressed to a dial reading of 15. A MK1 bridgewire was then pressed into the top of the cup so that the bridgewire was in contact with the DAHA. The weight of CL-20 was reduced from 300 mg to 250 mg for cup # 6, because it was thought that the total pressed volume would not allow for sufficient space to press in the bridgewire.

The loaded detonators were tested in the configurations illustrated in Figure 2. A sleeve was created by center drilling a hole thru the block, the hole diameter being equal to the outer diameter of the assembled detonator. A larger bore was made from the bottom of the block, its diameter being that of an an A-5 booster pellet. The depth of the hole was half of the original length of the block. The booster pellet was inserted into the bottom hole. The detonator was inserted into the top hole so that the bottom of the detonator cup butted up against the top surface of the booster. The fixture was centered on an aluminum witness block and the completed setup taped together (Configuration I in Figure 1.) A second test setup was constructed by

adding an upper confinement sleeve created by drilling a hole the diameter of the detonator through an additional aluminum block (Configuration II in Figure 2.)
For safety reasons, each setup was placed inside a test confinement cylinder and remotely functioned. Test results are summarized in Table 2.
Figure 3 shows an original set of configuration II test blocks (left side) and the test blocks from test #5 (Table 2.) In five of the six test firings, DHA initiated a detonation in the secondary explosive loaded in the detonator cup. In three of these firings, the detonation was then successfully transitioned to an A-5 booster pellet.

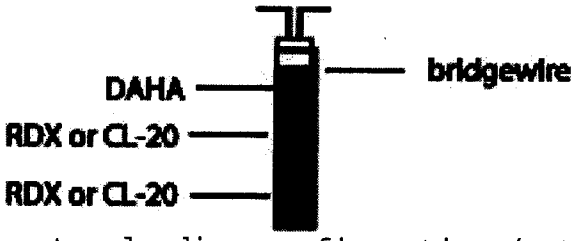

Figure 1: MK-1 detonator loading configuration (not drawn to size)

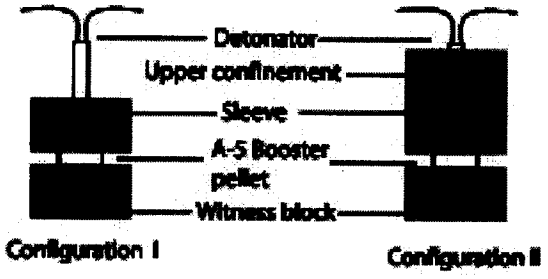

Figure 2: Testing configuration (not drawn to size)

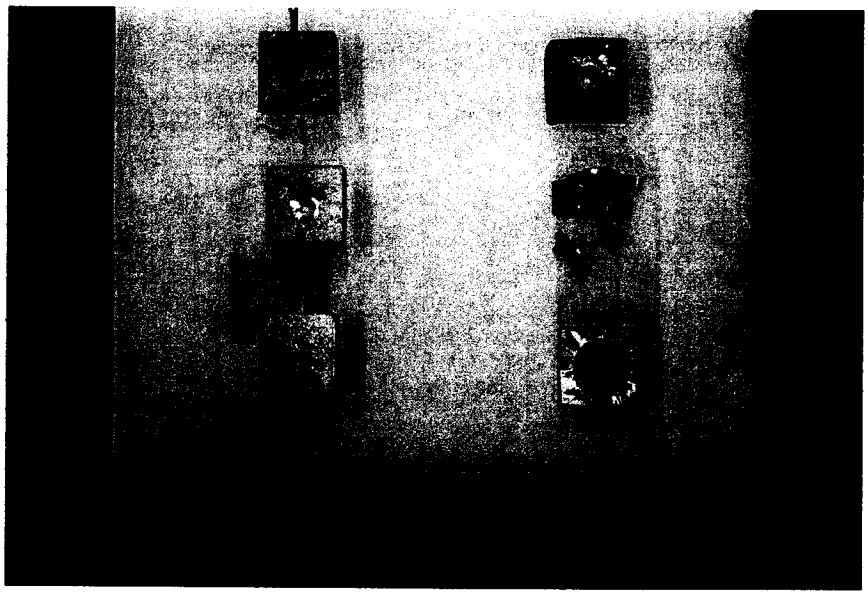

Figure 3: Aluminum test blocks: Unused (left side) and after firing (right side)

Table 2: DAHA Testing: Full detonation train

	Weight (mg)				
Cup #	DAHA	CL-20	RDX	Configuration	Result
1	100	800	---	I	DAHA initiated. Cup split. CL-20 still in cup.
2	150	800	---	II	Complete detonation transition. Large dent in witness plate.
3	200	800	---	II	Complete detonation transition. Witness plate destroyed, only small pieces found.
4	100	300	500	II	Detonator functioned, but did not initiate A-5. Detonator may not have been in contact with the booster pellet.
5	150	300	500	II	Complete detonation transition. Large dent in witness plate. Center sleeve destroyed.
6	200	250	500	II	Detonator functioned, but did not initiate A-5. Powdered A-5 floating in air above test confinement cylinder.

Findings & Conclusions.

Findings:

Bridgewire heating from a 9-volt circuit successfully initiated the DAHA material it was in contact with.

When loaded in MK-1 detonator hardware, DAHA initiated with a bridgewire stimulus successfully initiated CL-20 and RDX.

Detonators loaded with DAHA as a replacement for the lead based initiator materials detonated A-5 booster pellets in 50% of the tests conducted.

Conclusions:

DAHA has shown the positive potential to be a replacement material for lead based chemicals in small electro-explosive devices.

Future Work:

Several concerns still need to be addressed during any future work with DAHA.

1) Although DAHA is thermally stable (DSC decomposition temperature = 230°C), it has a low melting point (72 - 74°C). This would not be acceptable in a fielded munition where specified maximum storage temperatures are usually 71° C. Other materials have been developed with this same problem and the usual method used to raise the melting point is to create a salt using the basic material.
2) The starting material for DAHA has been dropped from the commercial market. A devoted preparation process of the precursor material would have to be done in-house or contracted out, increasing DAHA's production cost.
3) Although DAHA was successfully functioned with a MK-1 bridgewire it has not been demonstrated in the smaller detonators, e.g. a M100 or PA537.

In a parallel program, two additional phosphazene-based materials have been identified for testing in a follow-on program: HNP (tris(spiro(N,N"-ethylene dinitramino))cyclotriphosphazene), and EDNAP (spiro(N,N"-ethylene dinitramino)-3,3,5,5-tetrakis(azido)cyclotriphosphazene). GEO-CENTERS, INC. has prepared a series of organic polyazides that have promise as heavy metal-free initiating explosives. These compounds have been prepared under an ARDEC program and can be easily transitioned into a future Green Detonator program. All starting materials for these energetics are commercially available. A number of the new small molecule organic polyazides are solids, while several are liquids at ambient temperature. The liquids may be derivatized to convert them into solids, mixed with a polymeric material to form a gel, or precipitated with another solid energetic material to form a co-crystalline complex. Crystal engineering techniques can be used to produce co-crystalline complexes of the organic azides (solid or liquid) with secondary explosive materials such as TNAZ or CL-20. The performance

of the initiating explosive will be enhanced by incorporating a more powerful energetic material into the crystal lattice. These materials could then be successfully utilized as the energetic fill in small volume detonators.

A two-year program would be necessary to prepare, characterize, test, and transition the new materials for fielding in green detonators. During the first year the new materials will be synthesized on-site at ARDEC in quantities sufficient to fully characterize their physical, sensitivity, and energetic properties. These materials will be characterized by standard spectroscopic, physical, and thermal methodologies. After complete physical characterization the materials will be submitted for standard sensitivity testing prior to loading into detonator fixtures for testing as green initiating explosives. Small-scale function testing in bridgewire detonators will be carried out in the test chambers in Bldg. 3024. Promising candidates will be downselected for further investigation. In the second year of the program, the preparation of the candidate materials will be scaled up and optimized. Function testing of the materials will be conducted with a variety of bridgewire detonators against a series of fuze board approved booster materials. A second downselection of materials will then be done, and production will be transitioned to a GOCO or commercial plant for pilot production and loading.

Recommendation:

Based upon the accomplishments attained in this effort and the preliminary results that have been achieved in the PP1364 and the NSWC stab detonator program, it is recommended that a full program proposal be prepared and submitted combining the two programs. The scope of the single full program will be to further develop the promising environmentally benign replacement compounds for lead azide.