Nano Energetics for US Navy Percussion Primer Applications

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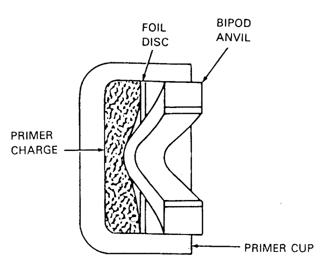
Background

The US Navy has been conducting a program to eliminate toxic ingredients used in pyrotechnic and explosive compounds currently employed in Navy weapons systems. The elimination of these toxic ingredients will result in significant benefits to the Navy, including reduced environmental risk during manufacture, testing, use, and DEMIL operations with these systems. Two primary explosives used extensively by the Navy, lead azide [$Pb(N_3)_2$] and lead styphnate [$C_{12}H_4N_6O_{14}Pb$] were selected for investigation for possible replacement compounds. Both of these explosives are used individually and in mixtures with other compounds in a variety of explosive and pyrotechnic trains found in Navy weapons systems.

This paper addresses the replacement efforts for lead styphnate in one major application – the PVU-1/A percussion primer (Figure 1). This primer is used primarily as the initiator for Cartridge Activated Devices (CADs) and Propellant Actuated Devices found in most aircraft in the Navy fleet. The charge in the primer is 24% by weight lead styphnate. The majority of CADs are either impulse cartridges, which employ their ballistic output to perform work functions (stores release, for example), or as delay cartridges used to time critical events in aircrew escape systems. The PAD devices generally consist of small rockets used to catapult ejection seats from aircraft and to stabilize them in preparation for man-seat separation and parachute deployment.



Primer Mix 5086

Ingredient	Weight %
Normal Lead Styphnate	24.0
Barium Nitrate	43.5
Tetracene	2.0
Calcium Silicide (Treated)	10.5
Antimony Sulfide	20.0

Figure 1 – PVU-1/A Percussion Primer and Charge Composition

Al/MoO_3 MIC Primer Evaluation

At the time the Navy lead styphnate replacement program was begun, lead-free percussion primers were already under development at the Los Alamos National Laboratory using nano-scale thermite-like mixtures developed there by Joe Martin and his associates[1,2]. Several of these metal/metallic oxide mixtures, dubbed MIC (referred to as either Metastable Interstitial Composites or Metastable Intermolecular Compounds) compositions had been evaluated and these exhibited high caloric output and fast burning rates. One in particular, a 55/45 weight percent Al/MoO_3 composition had been loaded into commercial No. 41 percussion primers and were in the process of evaluation for use in small arms ammunition at the Army Research, Development, and Engineering Command (ARDEC) at Picatinny Arsenal, NJ. The nano-scale aluminum used in the composition was approximately 50 nanometers in diameter, having a 1.5-2.5 nanometer oxidation layer, resulting in an active aluminum content of about 65-75 wt%. The commercially available MoO_3 used was somewhat larger, on the order of 100 – 200 nanometers. Given the similarity between the No. 41 and the PVU-1/A, several lots of PVU-1/A hardware were loaded with the Al/MoO_3 MIC composition and shipped to the Indian Head Division, Naval Surface Warfare Center (IHDIV, NSWC) for evaluation.

These primers were subjected to a variety of tests, many of which are normally conducted on percussion primers and CADs undergoing development and qualification for service use. These included the following, for which the test results are briefly summarized below:

- Open Air Flame Tests
- Ball Drop Sensitivity (Ignition Energy)
- Cartridge Performance
- Environmental Tests

The tests revealed that the visible flame from the PVU-1/A primers was typically 2 to 6 inches long and persisted for about 1.0 msec. For the Al/MoO_3 MIC primer, a luminous “flame” more than twice as long as that from the PVU-1/A was observed that lasted considerably longer, about 27.0 msec. This behavior is believed to enhance the performance of the MIC primer.

Ball-drop sensitivity tests are conducted on representative samples of percussion primer production lots to establish all-fire and no-fire energies for the lot. Any replacement primers for the PVU-1/A must meet the PVU-1/A specification so that there is no loss in reliability or performance margin with the new primers. This is especially important for the man-rated systems in which the PVU-1/A is used.

The ball-drop sensitivity test consists of dropping a 1.94 ounce steel ball from various heights onto a firing pin assembly containing the primer. The height and standard deviation at which 50% of the primers will fire is determined statistically, and the all-fire and no-fire energies are calculated from the following formulas:

$$\text{All-Fire Energy} = W(H_{50} + 5\sigma) \qquad \text{inch-ounces}$$
$$\text{No-Fire Energy} = W(H_{50} - 2\sigma) \qquad \text{inch-ounces}$$

Most of the testing that was conducted with MIC primer formulations used the Neyer method with 30 primers from each lot to determine H_{50} and σ. Initial testing conducted with the LANL MIC primers revealed that they did not meet the PVU-1/A all-fire requirement of 25.4 inch-ounces. However, early in the program, nano-aluminum production was started at several organizations, including ARDEC, NSWC, and some commercial manufacturers. These new manufacturing sources produced nano-aluminum with greater active (non-oxidized) aluminum than that made at LANL. Subsequent testing with these improved nanoreactants showed that primers using the higher purity aluminum and commercial MoO_3 met the PVU-1/A all-fire requirement. From the test results it was concluded that the use of commercially available aluminum and MoO_3 would allow Al/MoO_3 MIC primers to meet PVU-1/A all-fire and no-fire requirements. This realization was at least partly responsible for cessation of nano-aluminum production activities at both IHDIV, NSWC and ARDEC.

As part of the Navy test program for the LANL MIC primers, cartridge performance testing was conducted with two different impulse cartridges and two different delay cartridges. The tests were performed in the lot acceptance test (LAT) fixture appropriate to each over a temperature range of –65 F to +200F and compared the performance with cartridges loaded with standard PVU-1/A primers against those containing the LANL MIC primers. Virtually identical test results were obtained with both sets of primers[3,4].

As commercial sources of nano-aluminum became available, some of the cartridge tests were repeated with Al/MoO_3 MIC formulations using the improved aluminum. The MIC primers used in these tests met the PVU-1/A all-fire requirement. Once again, it was found that the cartridge performance with Al/MoO_3 MIC primers was identical to that with PVU-1/A primers. Thus, it was established that performance-wise, the MIC primer could function as a drop-in replacement for the PVU-1/A.

Environmental testing was conducted on several lots of Al/MoO_3 MIC primers produced at NSWC with commercial nano-aluminum and MoO_3. The tests were done to determine the capability of the primers to withstand various storage an handling environments. The tests included the usual cartridge qualification tests of 28 day thermal shock, humidity, and altitude cycling (TSH&A), random vibration, and high temperature storage at 160 F. All testing was conducted on bare primers rather than loaded into cartridges, and an off-center hit test was also conducted to simulate primer performance in worn firing mechanisms. Ball-drop sensitivity and dud tests at the PVU-1/A all-fire height (13 inches) were used to measure primer performance before, during, and after the tests. In addition, the effects of shellacking the output side of the primers drying the MoO_3 prior to mixing and loading were investigated.

The 28 day TSH&A results showed that the 50% all-fire height was unaffected for baseline lot, although the standard deviation increased remarkably to an unacceptable level. Both the shellacked and “roasted” MoO_3 lot showed similar effects and an increase in 50% all-fire height as well. The number of no-fires in the dud test also increased.

Similar results were obtained for the baseline and “roasted” MoO_3 lots in the random vibration tests, which showed a slight increase in 50% all-fire height , increased standard deviation, and increased dudding. The shellacked lot was largely unchanged, however, it was unacceptable to begin with.

Surprisingly, it was found that high temperature storage at 160 F degraded primer performance for a 45 day storage period, but actually improved performance when the storage period was extended to 90 days. These results suggest that water absorption, possibly by the MoO_3, may be an important factor in Al/MoO_3 MIC primer performance.

The off-center hit results show that both the shellacked and unshellacked primers show susceptibility (increased all-fire height) to offsets of as little as 0.010 inches.

<u>Oxidizer Investigation</u>

While the replacement of the LANL nano-aluminum with one with higher active aluminum content resulted in MIC primers that met the PVU-1/A all-fire specification, there was continued difficulty with the Al/MoO_3 formulation. Acceptable solutions to the adverse effects of exposure of loaded primers to vibration and moisture could not be found, and eventually it became evident that the dry mixing and loading techniques used to manufacture the primers was also a problem. This was evidenced by inadvertent firings of primers during loading operations. While these occurred relatively infrequently (roughly one incident in every 700 primers) they were not restricted to any one phase of the loading operations, but occurred randomly throughout the whole range of operations. This circumstance was perceived to be a safety issue and a major obstacle to eventually scaling up to automated mixing and loading operations to the kilogram range.

Because of these problems, the potential use of other metallic oxidizers was investigated. The primary objectives of the investigation were to maintain caloric output as much as possible, meet the PVU-1/A all-fire requirement, and hopefully find an oxidizer that could be wet-loaded. To these ends, the thermal properties of over 30 common metallic oxides were looked at, with most of them dismissed on grounds of hygroscopicity or thermal instability. For the remainder, the stoichiometric gravimetric and volumetric heat release was calculated assuming complete oxidation of aluminum. Also considered was melting point, as it was thought this would be important for rapid burning. A comparison of these parameters with those corresponding to MoO_3 shows that Bi_2O_3, which has only a slightly higher melting point than MoO_3 and slightly lower volumetric heat release might be a good replacement oxidizer, especially in light of its known lack of reactivity with water. Despite its higher melting point, CuO was also considered as a candidate because of its high heat release. Based on the calculations, several oxidizers were selected for tests at LANL in a miniature closed bomb specifically designed for small percussion primers. The tests were conducted with oxidizers obtained from a variety of sources which were mixed with 80 nm aluminum obtained from Nanotechnologies, Inc. (Austin, TX). Some of the test results have been reported elsewhere(5).

Hot wire and YAG laser ignition tests performed at LANL with loose powder mixes revealed that several of the candidates (MgO, SiO_2, TiO_2, and ZnO) were either very difficult to ignite or could not be ignited at all. The remaining candidates (WO_3, CuO, Bi_2O_3, and Fe_2O_3) were tested in a closed bomb. For the loose powder tests, a micron sized Bi_2O_3 oxidizer was found to produce the highest peak pressure. This oxidizer also produced the highest peak pressures for primer mixes loaded into No. 41 primer hardware. The CuO oxidizer produced the highest burn rates (greater than 500 m/sec), while the Bi_2O_3 mixture was somewhat slower, around 400 m/sec.

Based on the above very promising results, the Al/Bi_2O_3 mixture was selected for additional testing at NSWC and Innovative Materials and Processes (IMP) in Rapid City, SD. Wet loading investigations were also carried out at IMP for both Al/MoO_3 and Al/Bi_2O_3 nano-powders. For water-based loading of Al/Bi_2O_3 nanopowders, it is necessary to protect the aluminum from further oxidation due to a hydration reaction. Fortunately, since the wet-loaded primers are dried immediately after loading, the aluminum has to be protected for only a few hours. Hydrophobic coatings for nanosized aluminum investigated at IMP included oleic acid, succinic acid, and ammonium di-hydrogen phosphate. While all three were successful in protecting the aluminum during all phases of mixing and loading, it was found that the degree of mixing depended on the particular oxidizer as well as the coating on the aluminum. Thus, the coating has to be tailored for each different mixture. It was also found that the length of time the aluminum could be protected was a strong function of temperature. For the Al/Bi_2O_3 mixture, a wet mixing and loading procedure was developed using the ammonium di-hydrogen phosphate coating on the aluminum. This process provides a time window of approximately 8 hours to complete mixing, loading, and drying at 25 C ambient temperature, sufficient for production of primers in PVU-1/A hardware. At 10 C, the window is approximately 48 hours.

The new mixing and loading procedure has been successfully used to manufacture several lots of primers without incident. Subsequent ball-drop testing of Al/Bi_2O_3 primers using micron sized Bi_2O_3 has resulted in all-fire energies of around 12-13 inch-ounces, about half that of the PVU-1/A. Thus, there is ample margin for tailoring the output while meeting all PVU-1/A performance specifications.

Conclusions

Initial results with the Bi_2O_3 oxidizer are very encouraging. The new oxidizer appears to have solved many of the problems encountered with Al/MoO_3 primers, namely over-sensitivity to environmental exposures and loading operations. Much additional testing is still required, however, to verify these results. Also of importance is whether the mixing and loading process with the Bi_2O_3 oxidizer can be successfully scaled up to large batches.

Future Plans

Performance testing of the Al/Bi_2O_3 primer is being funded through the DoD Environmental Security Technology Certification Program. This demonstration program will include performance testing in five different US Navy cartridges and US Army 5.56 mm small arms ammunition. The tests are expected to be completed in FY07.

Also in FY07, scale-up of the wet mixing and loading process will be investigated at NSWC and IMP.

References

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