Feasibility Study on the Use of Nanoscale Thermites for Lead-Free Electric Matches

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ABSTRACT

Electric matches are used in the pyrotechnic industry to electrically initiate devices remotely and with precise timing. Unfortunately, most current commercial electric matches contain lead compounds, which when burned produce lead reaction products that may cause environmental pollution and contamination of firing areas. These lead compounds, namely lead thiocyanate, lead nitroresorcinate and lead tetroxide, are used in electric match pyrotechnic formulations because a small diameter resistive bridgewire can reliably initiate them. A possible alternative to lead-containing compounds is nanoscale thermite materials, otherwise known as Metastable Intermolecular Composite (MIC) materials. These super-thermite materials can be formulated to be sensitive to thermal stimuli, such as resistive heating. In the effort to produce a lead-free electric match, a feasibility study was performed using nanoscale aluminum and molybdenum trioxide mixtures in electric match formulations.

Keywords: nanoscale, thermite, lead-free, electric match, metastable intermolecular composite, performance test, sensitiveness test

Introduction

The pyrotechnic industry favors electrical ignition of fireworks and stage special effects over manual ignition when such displays are choreographed to music, when more precise timing is required for an artistic effect, or when ignition must be done remotely. In addition, very large firework shows are better and more safely managed with a central computerized firing station than by teams of personnel in the midst of the display area manually igniting devices. Unfortunately, electric matches are remarkably sensitive to electrical stimuli when compared to initiators sometimes used by other industries (e.g., aerospace, defense and petroleum), such as exploding bridgewires (EBW) or an exploding foil initiator (EFI or slapper). A current as small as 350 milliamps can reliably fire some electric matches, whereas an EBW requires a special capacitive discharge circuit to provide approximately 200 amperes of current and 2 joules of energy for proper functioning. The EFI has even higher power requirements. Although it is generally recognized by the pyrotechnic industry that electric matches are prone to accidental ignition, it is this same industry's demand for simple, relatively inexpensive initiators that has largely determined the performance characteristics of today's electric matches. This, along with the need for inexpensive firing sets and wiring, has played a predominant factor in their development. The need stems from the large number of individual ignitions that are required for a display. For example, a single pyrotechnic show may require hundreds, if not thousands, of electric matches and miles of wire.

For electric matches to fire at such low electrical energies, a thermally sensitive initiating composition is required. The typical means of initiation is a hot Nichrome wire having a diameter no greater than approximately 1 mil (25 microns). Of the compositions that are commonly used, many contain lead compounds in the form of lead thiocyanate, lead nitroresorcinate or lead tetroxide. These lead compounds—when formulated in appropriate ratios and with other constituents—produce the desirable thermally sensitive compositions. But, as expected, these match compositions produce lead reaction products that may cause environmental pollution and contamination of firing areas, which is an undesirable feature. This paper reports on the performance and sensitivity test results of using nanoscale thermite, namely the aluminum and molybdenum trioxide pair, as a substitute for lead-based compositions in electric matches. Nanoscale reactants, which are also known as Metastable Intermolecular Composite—or MIC materials (pronounced "Mick"), were first developed by Los Alamos National Laboratory approximately 8 years ago.[1] Only in recent years, however, has research investigating the utility of MIC been expanded into the fields of explosives, thermobarics, lead-free primers, reactive projectiles, rocket propellants and electric matches.[2]

Match Head Design

While the construction and composition of commercially available electric matches are varied, a common form is diagrammed in Figure 1. The bridgewire, usually a fine filament of Nichrome, is strung and soldered across the edge of a copper-foil-clad substrate somewhat similar to circuit board material. The size of the substrate is approximately 0.4 inch long by 0.1 inch wide and 0.03 inch thick (10 by 2.5 by 1 mm). A bead of pyrotechnic material is formed over the bridgewire by dipping the end of the substrate into a slurry of a pyrotechnic composition. Although not shown in the diagram, a commercial match often contains two distinct layers of composition. The composition most sensitive to initiation by the bridgewire is applied first (generally referred to as the primary coating or layer). This is followed by a secondary coating of a different pyrotechnic mixture. The secondary composition, which is ignited by the primary, produces the desired thermal output (e.g., flame, sparks, molten slag or droplets) that initiates the pyrotechnic device, such as a Black Powder charge. To supply power to the bridgewire, electrical leads (approximately 24 gauge) are soldered at the base of the electric match substrate. The substrate containing the bridgewire and pyrotechnic bead is usually called the *match-head* (or *fuse-head* in other countries).

The outer lacquer coating (see Figure 1) protects the match head from physical damage during handling and, if the composition is water sensitive, seals the match head from moisture. In addition, a non-conductive coating such as lacquer can act as an electrical insulator to prevent accidental ignition by electrostatic discharge (ESD). In one possible accident scenario, the current induced by static electricity can travel from a point external to the electric match tip, through the outer match coating and pyrotechnic composition, then to the electrical leads via the bridgewire. In this process, if the ESD energy is sufficient, the electric match composition is ignited. In an earlier study, the outer coating of a number of commercially available matches was examined.[3] It was found that matches with imperfections or holes in the outer coating are much more susceptible to this type of accidental ESD ignition.

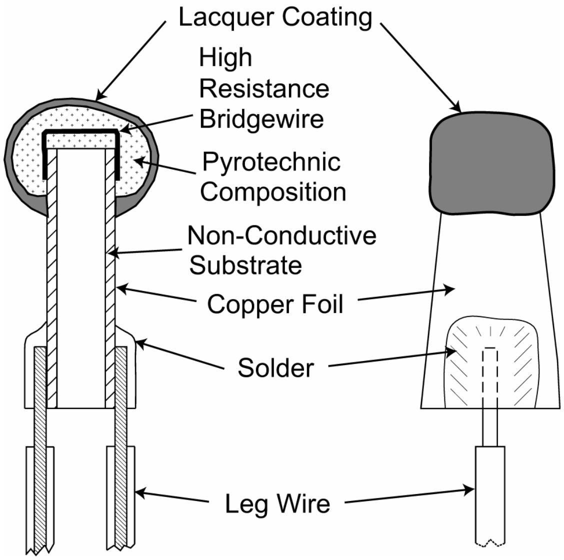

Figure 1. General diagram of an electric match.

The typical bridgewire resistance in commercially available electric matches is between 1 and 2 ohms.[4] Matches with higher resistances function better but are more difficult to manufacture, while those with lower resistances (less than 1 ohm) require more current to fire and are therefore less desirable to the industry. To illustrate the importance of the bridgewire's resistance to overall performance of an electric match, Figure 2 shows an electric match in a typical firing configuration. The electric match, presumably imbedded within a pyrotechnic device, such as a fireworks aerial shell lift charge or star mine, is connected to a fire set by two annealed copper leads of 100 feet (30.5 m) length.

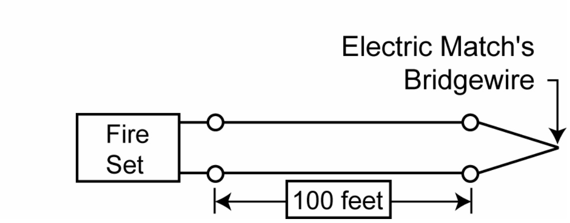

Figure 2. A typical setup for firing an electric match in a pyrotechnic display. A distance of 100 feet between the fire set and the electric match provides a safe operating distance between the fire set and the display site.

For the purpose of this example, the 100 feet distance was arbitrarily chosen as a safe distance between the operator of the fire set and the display site. As the fire set powers the electric match, not all of the energy provided by the fire set is deposited into the bridgewire. The wire leads have electrical resistance that dissipates part of the energy. This is especially problematic when the resistance is substantial in comparison with that of the igniter (i.e., when the leads are long or the wire is of small diameter).

To better illustrate how the wire leads can affect the proper functioning of an electric match, Table 1 lists the resistance and diameter of three example wire gauges that might be used by an operator. (One should note from the table that the resistance of a copper wire increases with decreasing wire thickness, since electrical conductivity is proportional to the cross-sectional area of the wire.) The percentage of electrical energy deposited by the fire set onto the bridgewire (denoted as $\%E_{bw}$) is expressed in the most simple terms by the following equation, where R_{bw} is the resistance of the bridgewire in ohms, and R_w is the resistance of 200 feet of copper wire leads.

Table 1. Measured Properties of Annealed Copper Wire of Three Gauges.

Gauge	Wire Thickness (mils)	Resistance for 100 ft wire at 20 °C (Ω)
18	40	0.64
20	32	1.02
24	20	2.57

Note 100 ft = 30.5 m, and 1 mil = 25 microns.

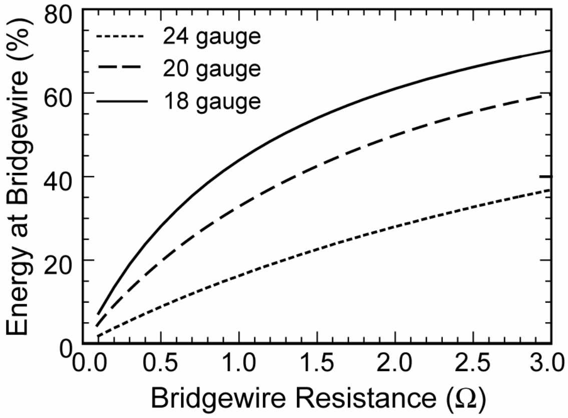

Figure 3. Percent energy at the bridgewire ($\%E_{bw}$) as a function of the bridgewire's resistance and the type of wire leads used. The upper curve represents two 100 feet wire leads with 18 gauge thickness; the middle curve represents that for 20 gauge; and the bottom curve is that for 24 gauge.

$$\%E_{bw} = \frac{R_{bw}}{R_{bw} + R_w} \times 100$$

Figure 3 shows the change of $\%E_{bw}$ as the resistance of the bridgewire, R_{bw}, is varied from 0.1 to 3 ohms for the three different wire gauges. It can be seen that the energy deposited at the bridgewire significantly decreases for a bridgewire resistance less than 1 ohm, especially when thin wires—with relatively high resistances—are used. For this reason, commercially available electric matches intended for pyrotechnic displays generally have a bridgewire resistance of 1 ohm or more. To approximate the industry standards, the electric match chosen for this study had a resistance of about 1 ohm.

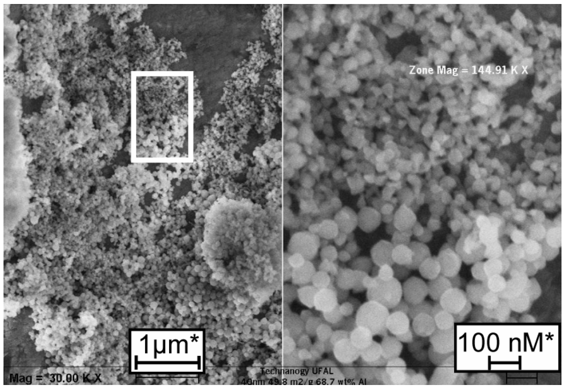

Figure 4. SEM of 40-nm Technanogy aluminum.

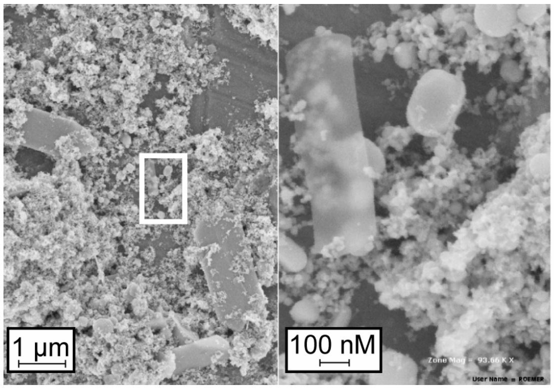

Figure 5. SEM of Climax molybdenum trioxide.

Materials Used

Nanoscale Thermite

Interest in nanostructures has grown since it has been demonstrated that the reactivity of MIC materials is much greater than those composed of micron-sized grains. For example, aluminum and molybdenum trioxide mixtures with an average particle size ranging from 20 to 50 nm react more than 1000 times faster than mixtures using conventional micron-sized or larger particles. The reason for such reactivity has been attributed to the large reduction in the diffusion barrier between reactants.[1] One process for manufacturing nanoaluminum involves vaporization of the metal from a resistively-heated ceramic boat followed by rapid condensation of the vapor in an inert atmosphere (argon or helium). Particle size and distribution can be controlled using various techniques.[5] Because pure aluminum of such small particle size is pyrophoric, the surface of the aluminum is passivated by controlled addition of oxygen (to form an oxide coating on the metal surface) soon after the aluminum has condensed. The oxidant of the thermite pair, molybdenum trioxide, is also produced in a similar fashion, except the addition of passivating oxygen is not needed.

Technanogy, Inc.[6] provided the three sizes of nanoaluminum that were used in this study, specifically 40, 121 and 132 nm powders (T40, T121 and T132, respectively). These sizes represent the approximate mean of their particle distributions. Only one type of nanoscale molybdenum trioxide was used as the oxidant with the above aluminums; this material was purchased from Climax Corporation.[7] Figures 4 and 5 are scanning electron micrographs (SEM) of the 40 nm aluminum and the Climax molybdenum trioxide powders, respectively. Unlike the nanoaluminums, the molybdenum trioxide has a more varied morphology and distribution of particle size, consisting of thin sheets and rounded particles. From small-angle scattering analysis, the sheet thickness was measured to be approximately 15 nm.[8]

The aluminum and molybdenum trioxide thermite mixtures used for the test matches were composed of approximately 40 to 45 percent aluminum (by weight) with the remainder being molybdenum trioxide. The exact amount of aluminum used in the thermite mixtures depended on the thickness of the oxide coating for a given aluminum sample. The procedure for quantifying free aluminum was by thermogravimetric analysis (TGA), where the aluminum sample mass was monitored with increasing temperature in the presence of oxygen. Oxidation of the aluminum causes the sample mass to increase until all of the aluminum has reacted. Knowing that the increase in mass is attributed to the conversion of free aluminum to aluminum oxide, the amount of free aluminum can therefore be calculated.

Simple mechanical mixing of the thermite mixture does not produce a homogeneous mixture of nanosized reactants; rather coarse agglomerates of each reactant are formed. To break up the agglomerates, hexane is added to the dry mixture and the resulting slurry was sonicated for about 30 seconds. The hexane was

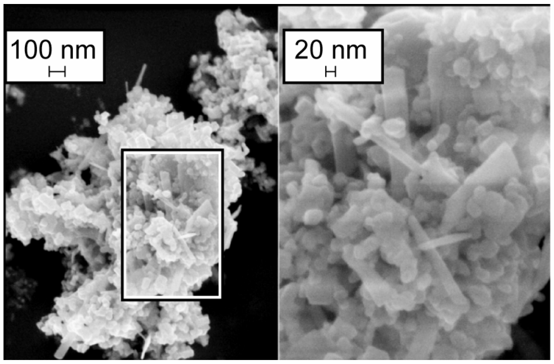

Figure 6. SEM of a 40 nm aluminum and molybdenum trioxide mixture.

then evaporated and the resulting granulated powder sieved through a 45 mesh screen to break up the mass of powder. Because the resulting powder is ESD sensitive, small amounts (about 0.5 gram) are mixed and handled to minimize the hazards of an accidental initiation. Scanning electron micrographs (see Figure 6 for one example) have verified that the sonication procedure produces a highly intimate mixture of fuel (aluminum) and oxidant (molybdenum trioxide).

Three different batches of electric match composition were prepared during the course of this study and are designated as Batch Nos. 1, 2, and 3. The differences between the batches are the types and amounts of MIC powders used in the primary formulations, which are given in greater detail below. (In general, the reactivity of the MIC powders increases with smaller particle size distribution.)

Blank electric matches (i.e., without pyrotechnic material dipped on the bridgewire) for this study were obtained from two sources. Batch No. 1 test matches used blank match heads purchased from Firefox Enterprises, Inc.[9] Unfortunately, these match heads had a bridgewire resistance of less than 0.1 ohms, and while they were deemed not suitable for firing current tests, they were suitable for most of the sensitiveness tests. To have match heads with a higher resistance and a narrower range of resistance values, other blank match heads were obtained from Martinez Specialties, Inc.[10] These blanks had a distribution of resistance values of approximately 0.9 ± 0.1 ohm. This resistance is somewhat low as compared to other commercially available matches[4] but is within the acceptable range. With these blanks, Batch Nos. 2 and 3 of electric matches were prepared for additional performance testing.

The first manufacturing step was to prepare the slurries for each layer in the match. The first layer, the primary, consisted of 91% MIC and 9% nitrocellulose (13.5% nitrogen content), which was dissolved with ethyl acetate containing 0.3% FC 430 surfactant from 3M, Inc. Depending on the viscosity of the slurry, the primary layer was built up on the bridgewire by dipping the match head three or four times. The secondary composition was composed of 56.1% potassium perchlorate (sieved through 120 mesh screen), 27.0% 12μ German black aluminum, 8.6% nitrocellulose, 8.1% sponge titanium (–80 to +100 mesh), 0.2% super-fine iron oxide[11] as a catalyst for decomposition of the potassium perchlorate, and enough ethyl acetate solvent to form a thin slurry. Approximately 6 to 8 dips into the secondary composition were needed to build up the match head to the desired size. The outer protective coating was produced by dipping the match head in a vinyl solution.[12] For Batch No. 1 test matches, only a single dip in the vinyl solution was performed; for Batch Nos. 2 and 3, four dips were performed. Between each of these 3 layers (primary, secondary and vinyl coating), the match heads were dipped once in 10% nitrocellulose lacquer to serve as a barrier between each layer.

As previously mentioned, the amount and type of MIC in the primary formulations were different for the three batches. For Batch No. 1, the aluminum portion of the thermite mixture was composed of 60% T121 and 40% T132. For Batch No. 2, only type T132 aluminum was used. Batch No. 3 matches were made somewhat differently from Batch No. 2, whereby the blank match head was dipped once in a thermite formulation composed with T40 aluminum only. Thereafter, the primary layer was built up with two to three successive dips into a thermite slurry composed with T132 aluminum. This was done to see if less electrical current would be required to fire a nanoscale thermite composed with 40-nm aluminum rather than that containing the 132-nm aluminum. Previously, matches were made using a primary composition that contained only the T40 aluminum.

However, when these matches were fired, it was found that their reactivity was too great. These matches exploded or ignited violently and had difficulty in fully igniting the secondary composition. Therefore, to reduce the quantity of the most reactive T40 aluminum in the primary layer, the T40 thermite was limited to a single dip on the bridgewire. Then the less reactive T132 thermite was used to complete the build up of the primary layer. Again, as stated previously, only one type of molybdenum trioxide, obtained from Climax, was used as the oxidant pair in all of the above thermite mixtures.

Results and Discussion

A reasonably thorough study of electric match sensitiveness has been published for ten different match types from four commercial suppliers in a series of short articles in *Fireworks Business* as well as in this journal.[3,13] Since testing of the prototype MIC matches was performed under similar conditions using the same equipment, some comparisons can be made between data of the MIC test matches and the data reported for the commercial matches. However, because of the voluminous amount of data that has been presented in these published works, the authors do not wish to reprint the data, but rather compare the results in qualitative terms. Furthermore, since these MIC matches are the first prototypes (i.e., not finalized designs for commercial production) and future iterations with improved performances are expected, strict interpretation of the test results may be considered superfluous. (Readers wishing for more information on the setup and conduct of the testing than is given below should consult reference 3.)

Impact Sensitiveness

The impact sensitiveness test apparatus is of a standard drop hammer design, except that a lighter than normal drop hammer (1 kg) was used. To better simulate the typical use environment of an electric match in a fireworks display (e.g., electric match inside the paper tube of a piece of quick match), the test match was inserted inside the fold of a 0.01-inch (0.25-mm) thick card stock, and the hammer was allowed to fall onto the assembly. For these tests, the match heads had their wire leads removed, as it was believed that the thickness of the solder connection and wire could absorb some of the impact energy. Earlier testing had shown that a protective shroud on electric matches provided a substantial decrease in their impact sensitiveness. However, at this time, the impact sensitiveness of these test matches covered with a shroud was not investigated. The impact result, typically reported in inches of hammer drop height, was determined for the test match heads following the standard stair-step (Bruceton) method for 20 samples from Batch No. 1.[14] A value of 56 cm (22 inches) was obtained for the test matches using the 1 kg drop hammer. This was significantly better than all of the commonly used commercial matches.[3] Only the low-sensitiveness matches had better performance (the Daveyfire *AN 26 F*, the Luna Tech *Flash* and the Martinez Specialties *Titan*).

The match head samples were also subjected to impact testing in the presence of Black Powder. In these tests, the inside surface of the card stock was heavily painted with a slurry of Black Powder (bound with 5% dextrin) and thoroughly dried. Using the previously obtained impact height of 56 cm, ten matches were consecutively struck at that height. A result of five ignitions out of ten suggests that the presence of Black Powder does not appear to increase their sensitivity to impact.

Friction Sensitiveness

Because a standard friction apparatus is more suitable for powdered samples, a modified test apparatus was used for friction testing the match heads. In these tests, the test match was used as the striker, held at a 45° angle to a moving abrasive surface (#100 grit sand paper). Each test consisted of a set of three trials of three matches at the lowest force setting (a 1.5 N force holding the match head to the abrasive surface). If the matches failed to ignite, a greater force (3.0 N) was used for another set of three trials. Again, if there was no ignition, a still greater force of 6 N was applied on a final set of three matches. Test matches from Batch No. 1 demonstrated no ignition, even at the maximum force setting of 6 N. This is better than all of the commonly used commercial electric matches and as good as any of the low sensitiveness matches that were tested.[3]

Thermal Sensitiveness

Two thermal test methods were employed for characterizing the match samples. In the first test, described as a *Ramp Ignition Temperature* test, electric match heads were placed inside individual small wells drilled into an aluminum block, which was heated at a rate of 5 °C per minute—beginning at room temperature. The test was concluded when all of the test matches ignited or a temperature of 300 °C was reached. With Batch No. 1 test matches, it was found that no matches ignited below 300 °C, which was as good as any of the electric matches tested previously, including the commercially produced low sensitiveness matches.[3]

Because some electric match compositions can slowly decompose without producing an ignition event while the temperature is ramped up, a second test method, described as a *Time to Ignition* test, was employed using the same heating block. However, the block was heated to a specific temperature and held constant. Then a single match was inserted into a well. If the match ignited within approximately 5 seconds, the temperature of the block was taken as an indication of its thermal sensitiveness. For those matches not igniting at this temperature, the block's temperature was increased by ten degrees and the test repeated. Similarly, if the match ignited in less than 5 seconds, the block's temperature was reduced 10 degrees and the test repeated. For the test matches, the time to ignition at the highest temperature attainable of 300 °C was 28 seconds. Again, this result was as good as any of the electric matches previously tested, including the commercially available low sensitiveness matches.[3]

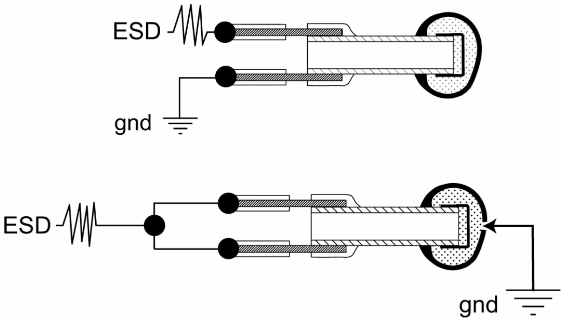

Figure 7. Illustration of the two basic ESD test configurations used in this study.

ESD Sensitiveness

Two tests were performed on the prototype matches to characterize their ESD sensitiveness. In the first test, sensitiveness to electrostatic discharge through the bridgewire was determined by passing discrete amounts of discharge energy through the bridgewire in much the same fashion as the intended firing current (see top configuration, Figure 7). Using an energy storing power supply, the electric match is subjected to electrical discharge energy at a low setting and a positive or negative ignition is noted. The discharge energy is increased incrementally until an ignition is achieved. Much like the impact testing, the discharge energies are raised or lowered following the standard stair-step (Bruceton) method for a series of approximately 20 match tests. The resulting stair-step value provides an ESD energy value that should initiate approximately half of the matches. This test was performed on Batch Nos. 2 and 3 test matches. For Batch No. 2 matches, the ESD energy value was measured at 230 mJ, which is significantly better than all of the commonly used commercially produced electric matches and on a par with the low sensitiveness matches. For Batch No. 3 matches, which contained the more reactive T40 aluminum, the ESD result dropped to 120 mJ, which is comparable to the least sensitive of the commonly used matches.[3]

In the second series of tests, the discharge current is typically passed from the bridgewire through the pyrotechnic composition to ground, as illustrated in Figure 7 (bottom configuration). However, the test results can at times be difficult to interpret because they are highly dependent on the nature of the outer coating. All commercial matches have a protective coating that covers the pyrotechnic composition. This coating strengthens the match head, limits physical damage during normal handling, and, if the composition is water sensitive, offers protection of the match head from moisture. However, an important characteristic of a non-conductive coating is that it can act as an electrical insulator to prevent accidental ignition by an electrostatic discharge through the composition. Unfortunately, imperfections in the coating seem to occur frequently, whether such imperfections are created at the time of manufacture or as a result of abrasion or crushing during rough handling. The effect is that such imperfections can greatly increase the sensitiveness of the match to electrostatic discharge through the composition.[3] Thus, before the test matches were subjected to this electrostatic discharge test, the integrity of the coatings was inspected.

An instrument designed to make high resistance measurements was used to evaluate the resistance from the coating to the bridgewire. In this analysis, the leg wires of the electric match are tied to one terminal of the instrument and a test probe is connected to the other terminal. The test probe applies up to 200 volts (but with limited current) to help induce a dielectric breakdown at the match surface as the probe is moved over the match tip to find points of low resistance. A good protective coating with no defects was generally found to provide more than 500 megohms (MΩ) of resistance. Some matches, specifically those with surface defects, register much lower surface resistance values. For Batch No. 1 test matches, which were coated with only one dip in vinyl lacquer, the surface resistance values varied greatly, measuring from less than 1 MΩ to approximately 200 MΩ. The consequences of the poor coating was demonstrated by subjecting these same matches to 18 mJ of electrostatic discharge energy through the coating; out of 10 matches tested, 9 ignited. Compared to some of the commercially produced matches, the Batch No. 1 matches faired poorly.[3] Gaining insight from these test results, Batch Nos. 2 and 3 matches were coated with four dips of vinyl instead of one, with the hope of covering any imperfections, such as tiny bubbles or cracks. The surface resistance values of 10 test matches from Batch No. 2 yielded only one match with 400 MΩ resistance, with the remainder registering 500 MΩ. For Batch No. 3, all were greater than 500 MΩ, which was the limit of the testing device. Undoubtedly the additional coats improved the surface resistance values. Out of 10 Batch No. 2 matches that were subjected to 18 mJ of electrostatic energy, 3 ignited; for Batch No. 3, only 1 match out of 10 ignited. For Batch No. 3, an additional 10 matches were subjected to 180 mJ of electrical discharge energy, and again only one ignited. While these results are positive, they do demonstrate that the matches are not entirely free of surface defects. An inspection using light microscopy indeed revealed the occasional presence of tiny bubbles in the vinyl coating.

Because it cannot be assumed that the electric match coatings will be in sufficiently good condition to completely protect the matches from discharges through the composition, the second type of ESD test was performed on matches that had intentional coating damage inflicted upon them. In this way, the test would be a measure of the ESD sensitiveness of the electric match composition only and not the degree of protection afforded by the coating. In this test, a portion of the outer coating of the electric match was removed using emery paper before they were subjected to the electrostatic discharges. Similar to the first test described above, the matches are exposed to increasing increments of discharge energy until initiation is observed. Using the Bruceton method, the discharge energy is raised or lowered for a series of 20 matches. From these results, an approximate 50% ignition energy value is obtained (i.e., the energy that would initiate 50% of the matches tested). Only Batch No. 1 matches were tested, which yielded an ESD value of 0.7 mJ, which is very low, but not quite as bad as the worst of the commonly used matches.[3] This is not surprising to the authors, as the aluminum–molybdenum trioxide MIC thermite has been previously demonstrated to be ultra-sensitive to spark initiation.[15] Attempts to reduce the spark sensitivity of MICs by using fluorocarbon coatings have produced positive results, but how such coatings may affect other performance and sensitivity parameters have yet to be investigated.

Table 2. Estimates of the Likely No-Fire, All-Fire and Recommended Firing Currents for Batch Nos. 2 and 3 Prototype Electric Matches.

Batch No.	Resistance (Ω)		Current (Ampere)		
	Average	Range	No-Fire	All-Fire	Recommended
2	0.9	0.8–1.0	0.45	0.90	1.4 / 1.8
3	0.9	0.8–1.0	0.35	0.70	1.1 / 1.4

Firing Current Tests

The preferred electric match is one where its sensitiveness to friction, impact and other stimuli are low, while leaving the match with a recommended firing current that is less than 1 ampere. This value is not arbitrary, but rather a performance criterion that has been shaped by the electrical firing equipment in use by the pyrotechnic industry. However, the recommended firing current of commercially available matches fall into two groups.[4] One group, which consists of the electric matches most sensitive to accidental ignition by all causes, has a range of recommended firing currents between 0.5 and 1.0 amperes. The second group, with recommended firing currents of 2.0 to 3.5 amperes, is much less sensitive to accidental ignition. That is to say, the least sensitive matches are also the most difficult to ignite intentionally. What would be ideal, and what was hoped for with the MIC electric matches, is that they would combine general low sensitiveness to accidental ignition and yet have a firing current below 1 ampere (i.e., similar to those in the most sensitive group). Table 2 lists the no-fire, all-fire and recommended firing currents for Batch Nos. 2 and 3. These values are only estimates, since the number of electric matches made and tested was not sufficient to develop very accurate firing current values. The two values listed as recommended firing current are for firing individual matches (1.5 times the approximate all-fire current) and matches in series (2 times the approximate all-fire current). Because the matches of Batch No. 1 had relatively heavy gauge (large diameter) bridgewire, with resistance values around 0.1 ohms, they were deemed not suitable for current testing. For the prototype MIC electric matches, it appears that the firing current needed for ignition lies somewhere between those recommended for the sensitive and insensitive groups of commercially produced electric matches. It appears that less current was needed for Batch No. 3 matches (all-fire current of 0.70 ampere), which contained the most reactive T40 nanoaluminum. Batch No. 2 matches, having a primary composition composed entirely of the lesser reactive 132-nm aluminum, required a slightly higher current (all-fire current of 0.90 ampere).

A potential problem was discovered during the performance of the current-firing tests. It appears that the matches occasionally become non-ignitable when moderate currents, somewhat less than the no-fire current, are first passed through the bridgewire.[16] Thereafter, increasing the current only causes the bridgewire to fuse without initiating the composition. This occurred most often with those matches containing the less reactive 132-nm aluminum. It is speculated that the hot bridgewire, while not sufficiently hot to initiate the composition, is hot enough to decompose some of the material around the bridgewire, which creates a gap around it, thus thermally decoupling the wire from the remaining composition. This problem could be attributed to the decomposition of the nitrocellulose binder in the primary formulation. Future work may investigate the effect of binders on the reactivities of MIC thermites. It should be noted that some of the most commonly used electric matches also have a similar *fuse but no fire* problem when they are subjected to gradually increasing firing current.

Additional Discussion

There is concern that matches that contain nanoaluminum may not have good long-term storage, since moisture and atmospheric oxygen can oxidize the aluminum and render the composition useless. Such aluminum has extremely high-surface area and special care must be afforded to its storage, especially in humid environments. However, two simple and severe tests demonstrated that the vinyl coating used on the prototype matches appears to serve as an excellent barrier to moisture. In one test, five test matches were submerged in a container of water for 1 week before they were removed and test fired. All of the matches ignited properly. In the second test, two matches were exposed to steam by suspending them over boiling water for 14 hours. Again, the matches fired readily despite the vinyl coating taking on a cloudy and wrinkled appearance.

While a secondary formulation with good ignitability characteristics (aluminum and potassium perchlorate mixture) was employed for these prototype electric matches, more difficult-to-ignite (and generally less sensitive) secondary formulations could be used instead. In one example, matches were prepared with a T132 aluminum and molybdenum trioxide primary composition, followed by a secondary composition of aluminum powder alone. In both compositions about 10 percent of nitrocellulose was used as a binder. This aluminum had a broad particle distribution that centered at 200 nm but contained particles of up to 1 micron in diameter. Igniting this match produced an entirely unique effect; a half dozen sparks were thrown to a distance of 6 feet and burned white hot for approximately 2 seconds. It is thought that the aluminum burned slowly because it was dispersed as large fragments whose burn rate was limited by the availability of atmospheric oxygen. It would seem that such matches, with pure aluminum as the secondary component, would be less sensitive to accidental ignition from stimuli such as friction and impact.

Insofar as the aluminum–molybdenum trioxide MIC thermite appears to have functioned well in our feasibility study, there is no doubt that some improvements could be made. Only one thermite pair was investigated for this study, but scores of other thermites exist, as well as intermetallic reactions. It may very well be that an altogether different primary composition can be employed with better results. Fischer and Grubelich[17] produced an extensive compilation of these reactions along with their respective energy output. In addition to thermites and intermetallic reactions, simple oxidant–fuel combinations could be used. Recently, potassium perchlorate has been produced as nanoscale particles with the hope of having enhanced reactivity.[18] Such materials and their use in electric matches in primary compositions have yet to be investigated.

Conclusion

The utility of a nanoscale aluminum–molybdenum trioxide thermite as an initiating composition for electric matches was examined. These nanoscale reactants, otherwise known as Metastable Intermolecular Composite (MIC) materials, were demonstrated to be sufficiently sensitive for electric match use. The estimated recommended firing current for the MIC matches lies approximately between those of the least and most sensitive matches that are commercially available. Best results for minimum firing currents were achieved for matches with the most reactive aluminum (i.e., 40-nm particle distribution). In addition, the sensitiveness of these test matches was measured and compared to commercial electric matches. The prototype matches faired very well in impact, friction and thermal stability tests, equal or better than the most commonly used matches. The same matches were on a par with the most commonly used commercial matches in electrostatic discharge tests, both through the bridgewire and through the composition. Improvements in the manufacture of the protective outer coating should alleviate much of the electrostatic discharge sensitivity. In addition, a myriad of yet uninvestigated nanoscale thermites, reactants, or intermetallic pairs may prove more useful as electric match compositions.

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14) A measured impact height using the Bruceton method correlates to a height where there is a 50% probability of initiation.

15) ESD tests on nanoscale thermites were performed at Los Alamos National Laboratory, Los Alamos, NM, USA.

16) In this test, the current was applied for 5 seconds or until an ignition event occurred. However, no match that did fire took longer than about 150 ms to fire (i.e., no ignition occurred in the interval between 150 milliseconds and 5 seconds in any of the test matches).

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