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(54) **LEAD-FREE ELECTRIC MATCH COMPOSITIONS**

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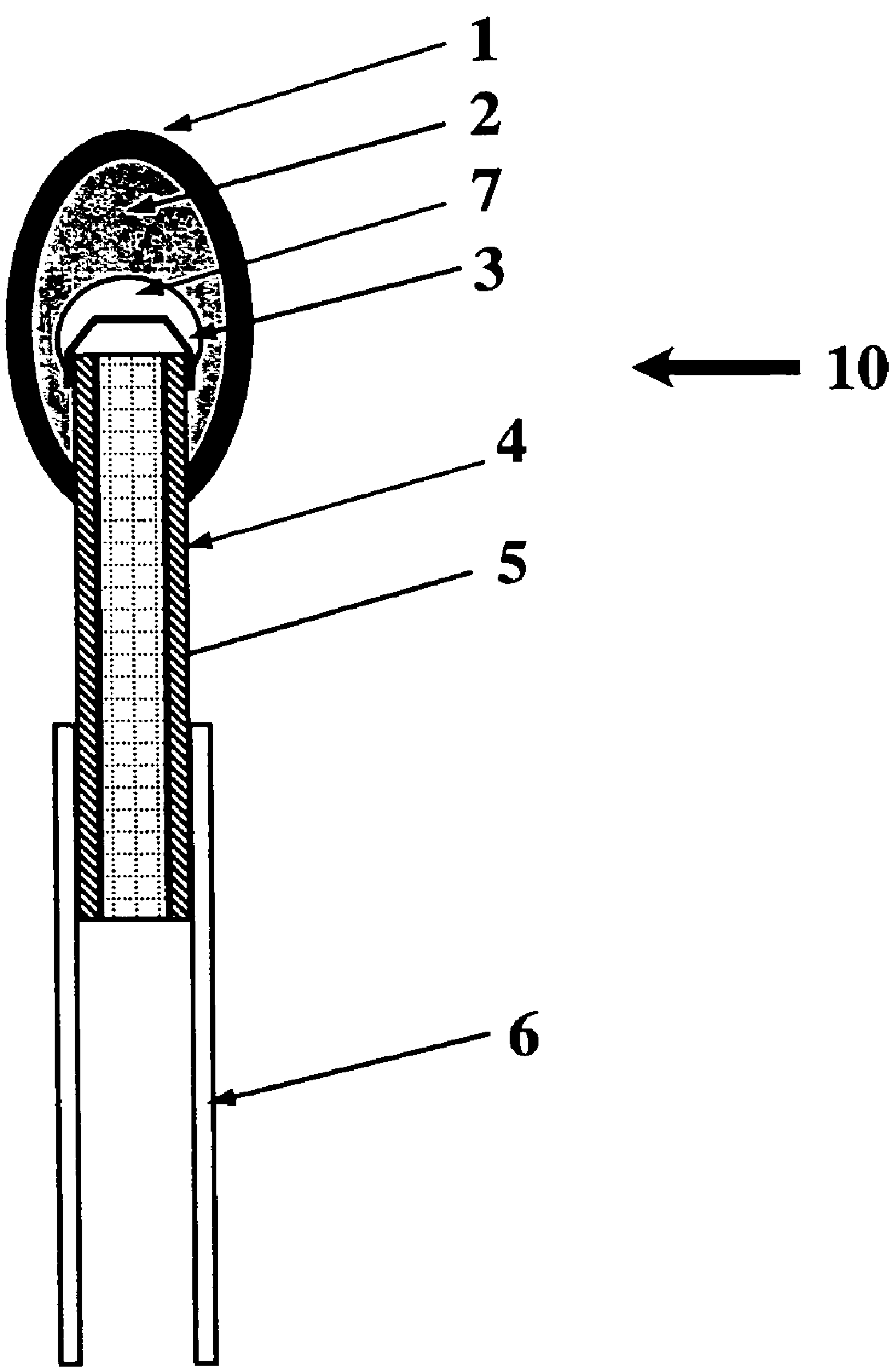
(57) **ABSTRACT**

An electric match including nanoscale particulates of an energetic material and a binder is provided. The energetic material can be a nanoscale thermite metal/metal oxide mixture, a nanoscale intermetallic material mixture, or a nanoscale fuel and oxidant mixture.



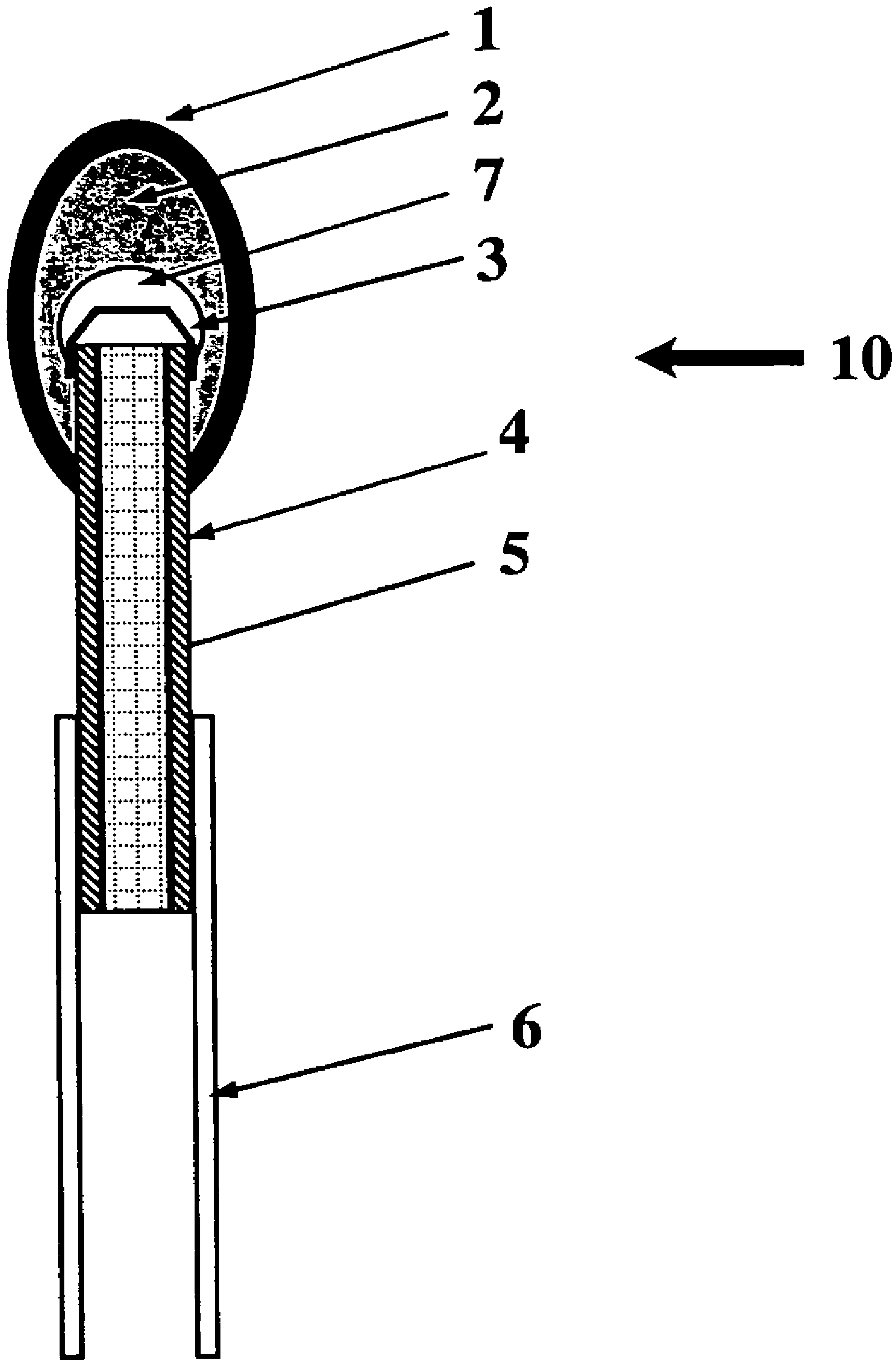


Fig. 1

LEAD-FREE ELECTRIC MATCH COMPOSITIONS

STATEMENT REGARDING FEDERAL RIGHTS

[0001] This invention was made with government support under Contract No. W-7405-ENG-36 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

FIELD OF THE INVENTION

[0002] The present invention relates to electric match compositions, preferably lead-free electric match compositions and to electric matches, preferably lead-free electric matches.

BACKGROUND OF THE INVENTION

[0003] Electric matches are used in the field of pyrotechnics to initiate devices by electrical means rather than by fuses. Fuses have the disadvantage of burning with a long delay before igniting a pyrotechnic device. Electric matches can instantaneously fire a device upon a user's command. In addition, electric matches can be fired remotely at a safe distance.

[0004] Unfortunately, most current commercial electric match compositions contain lead compounds, e.g., lead thiocyanate, lead nitroresorcinate, lead oxides or lead picramate, which when burned, vaporize to produce a lead-containing smoke. For commercial pyrotechnic displays, such lead-containing smoke is a pollutant causing detrimental exposure to a cast, crew and audience. The reason that these lead-containing compounds are used as electric match compositions is that only these mixtures have the required thermal stability while being able to be initiated reliably by a very low energy thermal stimulus, such as spark or resistive heating.

[0005] A typical electric match head consists of an electrically insulating substrate with copper foil cladding, similar to that used for printed circuit boards. The size of the substrate is generally approximately 0.4 inches long by 0.1 inches wide and 30 mils thick. The tip of the match has a small diameter nicrome wire soldered across the edge of the match. Insulated wire leads soldered at the base of the match provide the means of electrically firing the nicrome wire to produce the initiating spark. The match head is coated with the lead-based composition to produce the spark-sensitive bead above the nicrome bridge wire. Normally, the bead is coated with a second layer of composition of a metal fuel such as a magnesium/aluminum alloy or titanium with potassium perchlorate oxidizer. This secondary coat is generally necessary to produce the hot sparks to initiate black powder (or other primers) in pyrotechnic devices. Finally, the bead is generally coated with a nitrocellulose lacquer to provide strength and water resistance. Other similar match designs are well known.

[0006] After extensive and careful investigation, electric match compositions have now been developed free of lead-containing compounds.

SUMMARY OF THE INVENTION

[0007] To achieve the foregoing and other objects, and in accordance with the purposes of the present invention, as embodied and broadly described herein, the present invention provides an electric match composition including nanoscale particulates of an energetic material and a binder. Preferably, the electric match composition is lead-free.

[0008] The present invention further provides an electric match including a match head coated with an electric match composition including nanoscale particulates of an energetic material and a binder. Preferably, the electric match is lead-free.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] **FIG. 1** shows a schematic drawing of an electric match in accordance with the present invention.

DETAILED DESCRIPTION

[0010] The present invention is concerned with lead-free electric match compositions and preparation of lead-free electric matches.

[0011] In the present invention, the electric match materials include nanoscale energetic materials such as nanoscale thermite material mixtures, nanoscale intermetallic material mixtures, and nanoscale fuel and oxidant mixtures, preferably nanoscale thermite material mixtures. Such nanoscale energetic materials are easily ignited, have good energy content and produce high temperature products. Also, the reaction rate is generally very rapid for nanoscale energetic materials such as nanoscale thermite materials and the reaction rate can be further tuned by control of the particle size.

[0012] The thermite material mixtures used in the present invention are metal/metal oxide compositions including a metal selected from the group consisting of aluminum, boron, lanthanum, magnesium, tantalum, titanium, yttrium and vanadium and a metal oxide selected from the group consisting of silver oxide, boron oxide, bismuth oxide, copper oxide, cobalt oxide, iron oxide, manganese oxide, molybdenum oxide, nickel oxide, silicon oxide, tin oxide, tantalum oxide, titanium oxide, tungsten oxide and vanadium oxide. Among the suitable thermite material mixtures can be included aluminum and silver oxide, aluminum and boron oxide, aluminum and bismuth oxide, aluminum and cobalt oxide, aluminum and copper oxide, aluminum and iron oxide, aluminum and manganese oxide, aluminum and molybdenum oxide, aluminum and niobium oxide, aluminum and nickel oxide, aluminum and palladium oxide, aluminum and silicon oxide, aluminum and tin oxide, aluminum and tantalum oxide, aluminum and titanium oxide, aluminum and vanadium oxide, aluminum and tungsten oxide, boron and copper oxide, boron and iron oxide, boron and manganese oxide, boron and nickel oxide, boron and silicon oxide, boron and tin oxide, boron and tantalum oxide, boron and titanium oxide, boron and vanadium oxide, boron and tungsten oxide, lanthanum and silver oxide, lanthanum and copper oxide, lanthanum and iron oxide, lanthanum and manganese oxide, lanthanum and palladium oxide, lanthanum and tungsten oxide, magnesium and boron oxide, magnesium and copper oxide, magnesium and iron oxide, magnesium and manganese oxide, magnesium and silicon oxide, tantalum and silver oxide, tantalum and copper oxide, tantalum and iron oxide, tantalum and tungsten oxide, titanium and boron oxide, titanium and copper oxide, titanium and iron oxide, titanium and manganese oxide, titanium and silicon oxide, yttrium and copper oxide, yttrium and iron oxide, yttrium and manganese oxide, yttrium and molybdenum oxide, yttrium and nickel oxide, yttrium and palladium oxide, yttrium and tin oxide, yttrium and tantalum oxide, yttrium and vanadium oxide, yttrium and tungsten oxide, zirconium and boron oxide, zirconium and copper oxide, zirconium and iron oxide, zirconium and manganese oxide, and zirconium and silicon oxide. Preferably the thermite material mixtures are aluminum and molybdenum oxide, aluminum and iron oxide, aluminum and copper oxide and aluminum and tungsten oxide. The materials can be added in about stoichiometric amounts, although variations from stoichiometric amounts can be used as well.

[**0013**] The nanoscale intermetallic material mixtures used in the present invention may be material mixtures such as aluminum with nickel, cobalt, copper, iron, molybdenum, niobium, palladium, titanium, or zirconium, alloys of titanium with boron, nickel, cobalt and iron, zirconium boron, and hafnium boron. Preferably the nanoscale intermetallic material mixtures are titanium boron or nickel aluminum.

[**0014**] The nanoscale fuel and oxidant mixtures used in the present invention may include a metal such as aluminum, boron, magnesium carbon, or silicon and an oxidant with a cation such potassium, sodium or ammonium and an anion such as nitrate, chlorate, perchlorate or peroxide. Particular fuel and oxidant mixtures may include: aluminum and ammonium perchlorate; aluminum and ammonium chlorate; aluminum and ammonium nitrate; and, aluminum and potassium nitrate. Preferably, the nanoscale fuel and oxidant mixtures are aluminum and ammonium perchlorate, aluminum and ammonium chlorate, or aluminum and ammonium nitrate.

[**0015**] As mentioned, the energetic materials of the electric match composition are nanoscale size materials. Generally, the materials are particulates with predominant size distributions of from about 10 nm to 1000 nm in smallest dimension, e.g., diameter, thickness and the like, preferably from about 20 nm to 500 nm, more preferably from about 30 nm to 300 nm. Within the particulates, it is not uncommon to find a minor amount of particles significantly outside the mean particle size, e.g., some particles of as large as a micron can be present without detrimental effect. Size distribution within a particular sample of material is another factor. Broader size distributions may be preferable to provide easier ignition and increased spark generation for consistent ignition oif the secondary pyrotechnic composition.

[**0016**] The binder for the nanoscale energetic materials can be any standard material used for binding paticles together. Preferably, the binder is nitrocellulose, but other binders are well known to those skilled in the art. In the electric matches, a nitrocellulose binder is also preferred for binding secondary pyrotechnic composition materials together within the match head as well.

[**0017**] A protective topcoat layer of a suitable waterproof polymer is over the entire match head. Suitable waterproof polymers can include polymers and copolymers of vinyl based materials such as polyvinyl chloride, polyvinyl acetate, polystyrene, polymethyl methacrylate, polyacrylonitrile and the like. Especially preferred is a copolymer of polyvinyl chloride, polyvinyl acetate and 2,3-epoxypropyl methacrylate.

[**0018**] **FIG. 1** shows an electric match head in accordance with the present invention. Match head **10** includes standard match parts such as a high resistance bridgewire **3**, electrical insulator **5** with conductive foil cladding **4** and wire leads **6** soldered to the foil cladding **4**. Primary coating layer **7** including the nanoscale particulates of an energetic material and a binder is on bridgewire **3**. Over primary coating layer **7** is secondary pyrotechnic composition layer **2**. Finally, a protective waterproof topcoat polymer layer **1** is over secondary pyrotechnic composition layer **2**.

[**0019**] While not as preferred as a protective waterproof topcoat polymer layer over the entire match head, nanoscale particulates may be coated with a fluorosilane to provide protection from water and oxygen.

[**0020**] The present invention is more particularly described in the following example which is intended as illustrative only, since numerous modifications and variations will be apparent to those skilled in the art.

EXAMPLE 1

[**0021**] A bare electric match head was dipped into a sample composition for the primary layer. The sample composition had been diluted with ethyl acetate containing 0.3 weight percent FC 430 (from 3M) surfactant. The primary layer included about 6 milligrams (mg) of a mixture of 9 percent by weight of 13.5 percent nitrogen content nitrocellulose (NC), and a 91 percent by weight of a mixture of 121 nm nanosize aluminum (from Technanogy, Inc., Irvine Calif.), 132 nm nanosize aluminum (from Technanogy, Inc., Irvine Calif.) and a nanoscale MoO_3 material obtained from Climax Corp. having a sheet thickness of about 15 nm. Nanoscale aluminum (45 percent by weight) and nanoscale molybdenum trioxide (55 percent by weight) had been previously mixed by sonication to obtain the desired thermite metal/metal oxide mixture. After the primary layer, a thin barrier coating of nitrocellulose was deposited by dipping the match head into a nitrocellulose/ethyl acetate lacquer.

[**0022**] A secondary pyrotechnic composition included 56 percent by weight finely ground potassium perchlorate, 27 percent by weight 12 micron black aluminum, 8 percent by weight titanium (80-100 mesh), 0.3 percent by weight superfine iron oxide, 8.7 percent by weight nitrocellulose and sufficient ethyl acetate solvent to form a viscous slurry. The match head was dipped into this secondary material several times with intermediate drying to build up the quantity of secondary pyrotechnic composition, followed again by a protective coat of nitrocellulose using the same nitrocellulose/ethyl acetate lacquer as with the primary layer.

[**0023**] A protective waterproof topcoat polymer layer was finally deposited onto the match head by dipping each match head into a composition of a copolymer of polyvinyl chloride, polyvinyl acetate and 2,3-epoxypropyl methacrylate dissolved in a mixture of methyl ethyl ketone and toluene.

[**0024**] The resultant electric match head was found to have reasonable mechanical strength.

EXAMPLE 2

[**0025**] Aging tests were conducted on the final electric match heads. The protective topcoating had been used to keep moisture from contact with the nanosize aluminum.

The final electric match heads were submerged in water for three weeks and continued to perform reliably.

EXAMPLE 3

[0026] Impact tests (2.5 kg weight onto bare anvil) were conducted on the lead-free matches by placing the match head sample between two sheets of thick paper card stock and allowing a 1-kg drop weight to fall onto the sample. It was determined from twenty samples that the 50% probability of ignition (as described by Paine et al., Inorg. Chem., vol. 38, pp. 3738-3743 (1999)) was approximately 56 kg-cm. Identical tests on seven other commercially available electric matches of standard construction and performance gave results that ranged between 9 kg-cm and 23 kg-cm.

EXAMPLE 4

[0027] Thermal ignition tests on these lead-free matches were performed by placing the match heads in a heated block and measuring time to initiation. The match heads did not undergo initiation within five seconds when placed in a 300° C. environment. Comparatively, five commercially available electric matches of standard construction and performance showed initiation in five seconds at temperatures between 215° C. and 280° C.

[0028] From all these results, it was concluded that lead-free match heads in accordance with the present invention, had properties comparable or exceeding those of commercially available electric matches of standard construction and performance.

[0029] Although the present invention has been described with reference to specific details, it is not intended that such details should be regarded as limitations upon the scope of the invention, except as and to the extent that they are included in the accompanying claims.

What is claimed is:

1. An electric match composition comprising nanoscale particulates of an energetic material and a binder.

2. The electric match composition of claim 1 wherein said binder is nitrocellulose.

3. The electric match composition of claim 1 wherein said energetic material is selected from the group consisting of a nanoscale thermite metal/metal oxide mixture, a nanaoscale intermetallic material mixture and a nanoscale fuel and oxidant mixture.

4. The electric match composition of claim 3 wherein said nanoscale thermite metal/metal oxide mixture includes a metal selected from the group consisting of aluminum, boron, lanthanum, magnesium, tantalum, titanium, yttrium and vanadium and a metal oxide selected from the group consisting of silver oxide, boron oxide, bismuth oxide, copper oxide, cobalt oxide, iron oxide, manganese oxide, molybdenum trioxide, nickel oxide, silicon oxide, tin oxide, tantalum oxide, titanium oxide, tungsten oxide and vanadium oxide.

5. The electric match composition of claim 3 wherein said nanoscale thermite metal/metal oxide mixture is selected from the group consisting of aluminum and copper oxide, aluminum and iron oxide, aluminum and molybdenum trioxide, and aluminum and tungsten oxide.

6. The electric match composition of claim 3 wherein said nanoscale thermite metal/metal oxide mixture is of aluminum and molybdenum trioxide.

7. The electric match composition of claim 3 wherein said intermetallic material mixture is selected from the group consisting of titanium boron and nickel aluminum.

8. The electric match composition of claim 3 wherein said nanoscale fuel and oxidant mixture includes a metal fuel selected from the group consisting of aluminum, boron, magnesium, carbon and silicon and an oxidant including a cation selected from the group consisting of potassium sodium and ammonium and an anion selected from the group consisting of perchlorate, chlorate and nitrate.

9. The electric match composition of claim 1 wherein said nanoscale particulates have a mean size of from about 40 nm to 500 nm in smallest dimension.

10. The electric match composition of claim 1 wherein said match is lead-free.

11. An electric match comprising a match head coated with an electric match composition including nanoscale particulates of an energetic material and a binder.

12. The electric match of claim 11 wherein said energetic material is selected from the group consisting of a nanoscale thermite metal/metal oxide mixture, a nanoscale intermetallic material mixture and a nanoscale fuel and oxidant mixture.

13. The electric match of claim 11 wherein said binder is nitrocellulose.

14. The electric match of claim 11 wherein said match head includes a first layer coating including nanoscale particulates of an energetic material and a first binder, a second layer coating including secondary pyrotechnic composition and a second binder, and a protective waterproof topcoat polymer layer.

15. The electric match of claim 14 wherein said first binder and second binder are nitrocellulose.

16. The electric match of claim 14 further including a layer of nitrocellulose between said second layer coating and said protective topcoat layer.

17. The electric match of claim 14 further including a layer of nitrocellulose between said first layer coating and said second layer coating and a layer of nitrocellulose between said second layer coating and said protective topcoat layer.

18. The electric match of claim 12 wherein said nanoscale thermite metal/metal oxide composition includes a metal selected from the group consisting of aluminum, boron, lanthanum, magnesium, tantalum, titanium, yttrium and vanadium and a metal oxide selected from the group consisting of silver oxide, boron oxide, bismuth oxide, copper oxide, cobalt oxide, iron oxide, manganese oxide, molybdenum oxide, nickel oxide, silicon oxide, tin oxide, tantalum oxide, titanium oxide, tungsten oxide and vanadium oxide.

19. The electric match of claim 12 wherein said nanoscale thermite metal/metal oxide mixture is selected from the group consisting of aluminum and copper oxide, aluminum and iron oxide, aluminum and molybdenum trioxide, and aluminum and tungsten oxide.

20. The electric match of claim 12 wherein said nanoscale thermite metal/metal oxide mixture is aluminum and molybdenum trioxide.

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