United States Patent [19]

Sheran

[11] **3,793,920**

[45] **Feb. 26, 1974**

[54] **PROCESS FOR MAKING A CONDUCTIVE-MIX ELECTRICAL INITIATOR**

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[22] Filed: **Nov. 16, 1972**

[21] Appl. No.: **307,002**

[52] **U.S. Cl.** ..... **86/1 R,** 102/28 R, 102/70.2 R, 149/35, 149/92, 149/16

[51] **Int. Cl.** **C06b 21/02**

[58] **Field of Search** ..... 149/14, 15, 16, 35, 92; 86/1 R; 102/70.2 R, 70.2 A, 28 RP, 46

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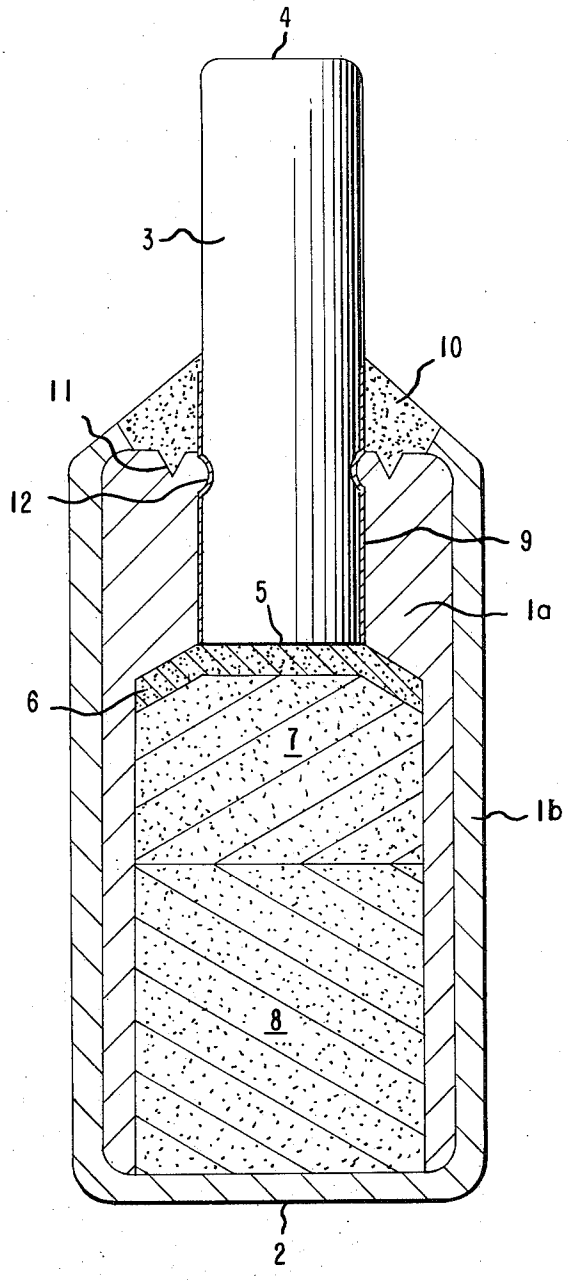
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Primary Examiner—Stephen J. Lechert, Jr.

[57] **ABSTRACT**

A conductive-mix electrical initiator is made more energy-sensitive by applying to at least one electrode surface therein which is to be adjacent the conductive ignition charge, e.g., the end surface of the electrode seated within the initiator body, a coating which increases the resistance of the initiator. Preferably, the coating is applied by chemical or electrochemical conversion coating of the surface, e.g., by acid chromate treatment or a light anodic oxidation.

15 Claims, 1 Drawing Figure


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PROCESS FOR MAKING A CONDUCTIVE-MIX ELECTRICAL INITIATOR

BACKGROUND OF THE INVENTION

This invention relates to a method of producing a conductive-mix electrical initiator, e.g., a detonator or squib, which method provides increased energy sensitivity with a given conductive mix.

Conductive-mix electrical initiators contain, as an ignition mix, an electrically conductive explosive charge comprising a mixture of a heat-sensitive explosive and an electrically conductive material. These initiators function by the application of a voltage to an electrode having one of its ends exposed and its other end adjacent the ignition mix within the body, the ignition mix forming a conductive path through which current flows between this electrode and the initiator body (the other electrode) and the explosive becoming ignited by the heat thereby generated in the mix. Initiators of this type can be miniaturized more easily than standard bridge-wire type initiators, and can be fired at relatively low energy levels, (e.g., below about 5,000 ergs, as contrasted to 50,000–100,000 ergs for standard-size bridge-wire type initiators) making them especially suitable for use in miniaturized form in applications where small initiators and small firing devices are required.

The ignition sensitivity requirements for low-firing-energy initiators depend on the specific intended use as well as on safety considerations. Ordinarily, response to firing energy on the order of about 2,500 ergs or less may be required for initiation by capacitor discharge (e.g., by the discharge of a 2.2 microfarad capacitor charged to 15 volts), or on the order of about 1.5 volts constant voltage. At the same time, minimum firing energy and current restrictions are imposed for safety reasons, e.g., it may be required that the initiators not fire when subjected to about 40 ergs by capacitor discharge and that they sustain a current of about 10 milliamperes for 30 seconds without firing. The sensitivity to firing energy is directly related to sensitivity to capacitor discharge firing voltage, according to the relationship $W = 1/2CV^2$, where W is energy in joules, C is capacitance in farads, and V is the voltage across the capacitor, and therefore the term "energy sensitivity" when used herein implies "voltage sensitivity" (capacitor discharge) and vice versa.

Whether or not an initiator of a given design is acceptable for field use depends on the degree of reliability of the initiator with respect to its response to firing energy, as well as to its ability to perform the required work, e.g., to bring about the detonation of a secondary explosive or the ignition of a deflagrating composition under a given set of conditions. Regarding response to an energy input, maximum reliability means that as many of the initators as possible after subjection to the handling and storage conditions encountered in use, (a) respond to the selected firing energy level, or pass the all-fire test; and (b) fail to fire at the energy and current levels where firing is undesired, or pass the no-fire test. For maximum reliability, not only must the structure and composition of the initiator be such as to afford consistency of functioning, i.e., functioning of large numbers of initiators, but the potentially active components in the initiator mus be sufficiently stable to assure functioning of the initiator after prolonged storage periods.

Various conductive explosive charges for initiators are known in the arts e.g., those described in U.S. Pats. Nos. 2,918,871 and 3,155,553. Such charges are mixtures of fine particles of a primary explosive, such as lead azide, and of an electrically conductive material, such as a noble metal, carbon, etc. The amount of energy needed to ignite the mixture by application of a voltage to an electrode adjacent thereto depends on the specific explosive employed, the specific conductive material used, the relative proportions of explosive to conductive material, the particle sizes, etc. While greater voltage sensitivity can be achieved to a certain extent by use of a better conductor, and/or a higher conductor/explosive ratio within a specific range, it often is not desirable, in terms of initiator output, or possible, to alter the composition of the mix to achieve a required increase in sensitivity. Thus, a means is needed to increase the voltage sensitivity of a conductive-mix initiator without sacrifice in the long-term no-fire characteristics (current tolerance) of the initiator.

SUMMARY OF THE INVENTION

This invention provides an improvement in a method of making a conductive-mix electrical initiator wherein an electrically conductive explosive charge comprising a mixture of a finely divided heat-sensitive explosive and a finely divided electrically conductive material is positioned between two electrodes, the improvement comprising applying to a surface of at least one of the electrodes, which surface is to be positioned adjacent the conductive explosive charge, a coating which is less electrically conductive than the electrodes and the conductive material in the explosive charge, and thereafter bringing the intact coating on the metal surface into contact with the explosive charge.

One of the electrodes is a metal shell within which the explosive charge is located, a portion of the charge being adjacent the inner wall of the shell, and the other electrode is a solid metal body seated within the mouth of the metal shell in a manner such that one of the solid body's end surfaces is exposed and the other is within the shell adjacent the explosive charge, adjacent surfaces of the solid body and shell being electrically insulated from one another. The coating is applied either to the end surface of the solid metal body to be positioned adjacent the explosive charge, or to the inner wall surface of the shell where the wall is to be adjacent the explosive charge, or to all metal surfaces which are to be adjacent the charge, coating of the end surface, of the solid metal body being preferred. The nature of the coating material and its thickness are such that the resistance of the conductive path from one of the electrodes to the other through the conductive explosive charge is within the range of about from 0.4 to 110 ohms when measured at 10 milliamperes of test current with a conductive charge comprising 70 percent by weight of a lead azide and 30 percent by weight of silver within one hour of contact with the coating.

In a preferred process of this invention, the electrically conductive explosive charge comprises a mixture, in finely divided form, of about from 45 to 90 percent by weight of a metallic azide, most preferably lead azide, and about from 55 to 10 percent by weight of silver, the mixture having been prepared most preferably

by the displacement of silver from a silver salt by magnesium powder in a stirred slurry of fine lead azide substantially as desired in Example 1; and the electrode which is seated within the shell is made of aluminum and has a thin coating, e.g., less than about one-tenth of a mil, applied to its end surface by a conversion coating process, e.g., anodic oxidation or acid chromate treatment.

BRIEF DESCRIPTION OF THE DRAWING

The attached drawing is a cross-sectional view of a detonator which can be made by the process of this invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

Referring to the drawing, a metal shell is comprised of an inner shell component 1*a*, made, for example, of aluminum or steel, and a surrounding outer shell component 1*b*, made, for example, of aluminum, steel, or stainless steel. The two-component, or dual-walled, shell structure is a convenient one for use in the mechanical assembling of the detonator. The closed bottom end of the shell is formed by the closed end 2 of outer shell component 1*b*. The open top end of the shell is located in the inner shell component 1*a*, which has a smaller internal-diameter portion near the top end, and a larger interal-diameter portion for the remainder of its length. Solid metal body 3, e.g., a wire, made of aluminum or steel, for example, is seated within the opening in the top end of the shell, fitting in the smaller internal-diameter portion of shell component 1*a*, and has one exposed end surface 4 and an internal end surface which has a thin coating 5, e.g., less than about one-tenth of a mil, of a material which is less electrically conductive than the metal from which solid body 3 and shell component 1*a* are made, e.g., an oxide or other oxygen-containing compound of a metal, coating 5 being in contact with the ignition mixture, i.e., an electrically conductive explosive charge 6, located within the larger internal-diameter portion of shell component 1*a*, e.g., a mixture of about 70 percent finely divided lead azide and about 30 percent finely divided silver (by weight). Ignition charge 6 is in contact with a priming charge 7, e.g., lead azide, which in turn is in contact with the base charge of secondary explosive 8, e.g., HMX (cyclotetramethylenetetranitramine). Thus, there is a continuous reaction train containing ignition charge 6, primary charge 7, and base charge 8.

Solid metal body 3 (one of the electrodes) has a layer of electrically insulating material 9, e.g., "Formvar," a polyvinyl formal insulating resin, applied to its convex peripheral surface where this surface is adjacent to the internal surface of shell component 1*a* (the other electrode). Thus, when voltage is applied to electrode 3, current flows from one electrode to the other through coating 5 and conductive ignition charge 6, the heat generated in ignition charge 6 causing the ignition of the explosive in the mixture, which in turn causes the detonation of priming charge 7 and base charge 8. A moisture-resistant seal 10, e.g., an epoxy resin, surrounds electrode 3 in the area where it emerges from the shell, the seal covering the ends of inner and outer shell components 1*a* and 1*b*, respectively, and extending beyond the end of insulating layer 9. Annular notch 11 in the end surface of shell component 1*a* is produced by staking the surface, thereby laterally deforming shell component 1*a* so as to produce an annular depression 12 in the periphery of electrode 3, which thus becomes locked securely in position.

In the present process, a metal surface in a conductive-mix initiator which is to be adjacent to the conductive ignition charge, e.g., an inner wall surface of the initiator body and/or the end surface of the electrode seated within the body, has applied thereto a coating which has a lower electrical conductivity than the electrodes, and the conductive material in the ignition charge, thereby increasing the resistance of the conductive path between the electrodes through the ignition charge. The resistance of this path depends on the composition of the ignition charge, and in the absence of the coating, is essentially zero with a charge containing a noble metal such as silver or gold as the conductive component, and slightly higher with charges containing a material such as carbon as the conductive component. It has been found that increasing the resistance of the initiator to a controlled degree has the effect of increasing the voltage sensitivity of the initiator without unduly increasing the long-term sensitivity to firing current. The composition and thickness of the resistance-increasing coating are such that the resistance of the conductive path from one electrode to the other through the ignition charge is greater than about 0.4 ohm, and preferably at least about 0.8 ohm, and no greater than about 110 ohms, these resistances being measured under the conditions specified above. The suitability of a given coating can be determined by making a resistance measurement under the above-specified conditions although it will be understood that the resistance obtained with a coating which meets the above-specified requirement may be above the 0.4–110 ohms range when the coating is used in an initiator containing a different ignition charge than the 70/30 lead azide/silver charge used for the test. The requirement that the test resistance measurement be made within one hour of the time that the coating and test charge are brought into contact is prescribed to offset the possibility that with some charges the resistance may increase with time.

When the coating provides insufficient resistance to produce more than 0.4 ohm in the above-specified test, the initiator cannot be fired reliably when a 2.2 microfarad capacitor charged to 30 volts (5,000 ergs) is discharged through it, whereas reliable initiation at less than 30 volts is achieved when the coating provides a resistance of more than 0.4 ohm in the test. A coating which provides sufficient resistance to produce at least an 0.8 ohm resistance in the above-specified test is preferred inasmuch as an initiator having such a coating can be fired reliably when a 2.2 microfarad capacitor charged to less than 15 volts is discharged through it. The coating applied to the electrode surface(s) should not be so resistant as to produce a resistance above about 110 ohms with the lead azide/silver charge, because when the resistance becomes this high, the minimum firing current drops excessively, and the interior begins to show some tendency to fire when subjected to a current of about 10 milliamperes for 30 seconds. The coating can be applied to any or all of the metal surfaces of the electrodes which are to be located adjacent the conductive charge in the initiator, e.g., the inside wall surface of the shell or initiator body (shell component 1*a* in the drawing), the end surface of the solid metal body seated within the shell, or both. Pref-

erably, the coating is applied to the smaller area surface, e.g., the end surface of the solid metal body, inasmuch as the required resistance increase may be more readily achieved therewith.

The chemical composition *per se* of the coating is not a critical feature of the process of the present invention, provided that its electrical conductivity is low enough to afford the resistance required to achieve the desired voltage sensitivity, and also provided that it can be applied in a thin enough layer, generally less than about one ten-thousandths of an inch, to assure that an excessively high resistance will not result. In any case, the coating should be sufficiently nonreactive with the electrically conductive explosive charge employed as the conductive ignition mixture that the resistance does not become excessive over prolonged storage periods.

Various procedures can be used to apply the coating to the electrode surface, e.g. dipping or immersion in a film-forming material of suitable resistance and stability. A convenient technique is to apply a conversion coating, which is a film formed by a reaction in which a portion of the base metal is converted to one of the components of the film. The conversion coating can be chemical or electrochemical. For example, with an aluminum electrode, any of the well-known chemical conversion coating processes can be used, e.g., those which produce amorphous phosphate or chromate coatings, such coatings being described more fully, for example, in U.S. Pat. No. 2,796,370; in a paper entitled "Surface Preparation of Aluminum for Painting," presented by R. F. Reeves et al. at the Aluminum Finishing Seminar sponsored by the Aluminum Association, Detroit, Michigan, Jan. 30—Feb. 1, 1968; and in *Aluminum Vol. III, Fabrication and Finishing*, K. R. Van Horn; Ed., American Society for Metals, 1967, Chapter 17. The chemical conversion procedure which produces an amorphous chromate coating employs a bath which contains at least two ingredients, i.e., a source of hexavalent chromium and a source of fluoride; that which produces an amorphous phosphate coating additionally contains phosphate. The coatings are postulated to contain aluminum in the form of an oxide or hydrated oxide, and a chromium salt (e.g., a chromate or phosphate). When the coating is formed by a chemical conversion coating procedure, e.g. with a solution of an "Alodine" chemical (Amchem, Ambler, Pa.), the thickness of the coating produced, depends on the coating conditions used, e.g., concentration of the solution, temperature of the solution, and contact time. In general, a concentration of about 7.5 grams of "Alodine" 1200S per liter of water, with a 3-minute contact at room temperature, is sufficient to provide the required resistance, usually in a thickness of about 0.00002–0.00007 inch. Concentrations in the range of about from 3 to 15 grams per liter have been employed successfully, as well as temperatures up to 180°F. and contact times of up to 10 minutes. It may be desirable to avoid the use of a combination of the most strenuous conditions, however, to assure that not too thick, and therefore too resistant, a coating is produced.

Another suitable method of applying the coating consists in producing an electrochemical or anodic conversion coating. For example, an aluminum electrode may be subjected to a light anodic oxidation, the anodizing current and time being controlled so as to produce a thin (less than one ten-thousandths of an inch) aluminum oxide coating on the aluminum. This can be accomplished by making aluminum the anode in a suitable electrolyte, e.g., sulfuric, chromic, or oxalic acid, with a metal or carbon cathode, and passing an electric current through the cell. The procedure is described more fully in the above-cited book edited by Van Horn, Chapter 19. For coating an aluminum electrode in the present process, a suitable coating of oxide, i.e., a layer about from 0.00002 to 0.0001 inch thick, is produced with an 0.5 milliampere current, an anodizing time of about from 2 to 10 minutes, and a 15 percent sulfuric acid solution.

Whatever the method employed to produce the coating on the metal surface, it is essential that the coating be thin, that it have the required conductivity relative to the other conductors in the initiator, and that it be a preformed coating made under controllable conditions, keeping in mind that too thick, i.e., too resistant, a coating results in increased current sensitivity, and finally leads to complete failure of the initiator.

One of the electrodes is a solid (i.e., not hollow) metal body, the surface configuration of which can be as desired. For miniature initiators, e.g., detonators no more than about 0.5 inch long and 0.33 inch in diameter, the electrode usually is a wire, pin, or screw. The end surfaces of the electrode can be flat, curved, or pointed, a substantially flat surface adjacent the conductive explosive charge being preferred.

The coating applied to the metal surface which is to be adjacent the conductive ignition charge in the initiator generally is a substantially continuous layer, although in view of the extreme thinness of the coating, discontinuities and/or nonuniformities may be detected on a microscopic scale in the as-applied coating. Such imperfections are entirely acceptable, having no deleterious effect with respect to the achieving of the required resistance and sensitivity. On the other hand, the presence of the less-conductive coating in the electrode-to-electrode circuit is critical in the present process, and it is neither necessary nor desirable to remove a portion of the coating after the application or formation thereof so as to expose a portion of the surface for contact with the ignition charge. Therefore, in the present process the intact coating is contacted with the ignition charge, i.e., there is no intentional removal of a portion of the coating after its formation on, or application to, the electrode's surface to the extent that the resistance is decreased thereby to a value below about 0.4 ohm in the test specified above.

The application of a coating as specified above to the electrode in a conductive-mix initiator increases the voltage sensitivity of the initiator regardless of the specific conductive explosive charge employed. Therefore, the process can be employed with any conductive charge desired, e.g., a mixture of a detonating explosive and a conductive material when the initiator is a detonator, and a mixture of a detonating or deflagrating explosive and a conductive material when the initiator is a squib. For a given charge, the voltage sensitivity is increased when the present process is employed to produce the initiator. A preferred ignition charge, especially for detonators, is a mixture of about from 45 to 90 percent by weight of a finely divided metal azide, e.g., lead azide or silver azide, and about from 55 to 10 percent by weight of a finely-divided noble metal, e.g., silver or gold, or carbon. A particularly preferred charge is one which comprises a mixture of about from 60 to 80 percent by weight of finely divided lead azide

and 40 to 20 percent by weight of finely divided silver, prepared by the displacement of silver from a water-soluble silver salt such as silver nitrate by magnesium powder in a stirred slurry of fine lead azide. Where maximum stability of the firing characteristics, especially the sensitivity to current, of the initiator over prolonged storage periods is desired, the lead azide/silver mixture can be prepared as described in Example 1, i.e., by contacting the silver salt with an aqueous suspension of the lead azide, to which magnesium powder has been added, thereby precipitating silver. The components of the ignition charge should be in the finely-divided form, e.g., smaller than about 20 microns, and well mixed.

The initiator made by the process of the present invention can be any device which features, in a metal shell, an electrode/conductive ignition mixture assembly, wherein the ignition mixture can be the sole explosive charge present, or it can be in initiating relationship with another explosive charge which is located at the bottom of the shell, the bottom charge being a detonating, or high, explosive in the case of an electric detonator or blasting cap, and a deflagrating explosive composition in the case of a squib. Regardless of the number of explosive charges in the shell, the nature of the bottom charge and the initiator's output capability, in the initiator produced by the present process the ignition mixture is an electrically conductive explosive charge which is in contact with a coating on an electrode, the coating being less electrically conductive than the electrodes and the conductive material in the ignition mixture, and causing the resistance of the conductive path from one electrode to the other through the ignition mixture to be in the range of about from 0.4 to 110 ohms when measured as described previously, the resistance remaining within this range after prolonged storage periods in initiators containing maximum stability ignition charges. This means that these initiators meet low firing-voltage specifications along with no-fire current requirements as-made as well as for extended periods after production. This stability of firing characteristics is dependent, of course, not only on the proper mode of application or production of the coating, but also on the provision of an ignition mixture which is substantially stable with respect to the coating in contact therewith.

The conductive ignition charge can be the sole explosive charge in the initiator, or it can be present in a continuous reaction train with another explosive charge located at the bottom or base of the initiator. The nature of the difference between the ignition and base charges can vary and depends on the intended use for the initiator. For example, in a detonator, the base charge will be a secondary high (detonating) explosive and thus usually will be chemically different from the ignition charge, which is a mixture of a primary high explosive and a conductive material. A detonator also will usually have a priming charge of high explosive between the ignition and base charges. In a squib made by the process of this invention, the ignition charge may be chemically different from the base charge, or the difference may be a quantitative one, with the base charge being of the same chemical structure as the ignition charge but of different density.

The body structure of the initiator is not critical, provided it affords the required protection of the active ingredients from the environment, as well as from possible damage in handling. Although not required, the dual-walled shell structure shown in the accompanying drawing is a preferred one both from the standpoint of strength as well as adaptability to mechanized loading techniques. Firm seating of the electrode within the body, so that the electrode is unable to move from its required position adjacent the conductive ignition charge, is essential. For this reason, an initiator in which the end surface of the body has been staked so as to cause the electrode to be swaged in place, as is shown in the drawing, is preferred. As is shown in the following examples, the initiator made by the process of this invention is particularly suited for use in miniature form, making it particularly useful in military applications requiring small fuze train components responsive at low energy levels. However, the initiator's utility should not be construed as being limited to initiators of miniature size.

The following examples describe different ways in which the process of the invention can be employed to produce a miniature detonator having the structural features shown in the drawing.

EXAMPLE 1

Solid metal body or electrode **3** is made from a 0.209-inch long, 0.0508-inch diameter wire made of 5056–0 aluminum having a 0.0031-inch-thick "Formvar" insulation coating on its peripheral surface, and having bare substantially flat end surfaces. Inner shell component **1***a* (the other electrode) is fabricated from an open-ended shell of 2024–T4 aluminum, which is 0.249-inch long, and has an outer diameter of 0.120 inch and an internal cavity having a 0.0545-inch diameter for 0.079 inch of length and a 0.100-inch diameter for 0.170 inch of length. The change in diameter of the cavity is effected through a tapered portion which forms a 30° angle with the horizontal axis.

The insulated wire, the end surfaces of which are free of corrosion products, heavy oxide, grease, etc., is placed in a solution of "Alodine" 1200S, a conversion coating chemical for aluminum produced by Amchem Products Inc., Ambler, Pa., and containing a source of hexavalent chromium and a source of fluoride. The concentration of the solution is 7.5 grams of "Alodine" 1200S powder per liter of cold tap water. The wire is maintained in the stirred solution for three minutes, after which time it is removed from the solutions rinsed in running water for five minutes, and dried at 120°F for about 4 hours. This treatment applies to the end surfaces of the wire a thin coating (about 0.00002 inch), yellowish to tan in color, of an amorphous chromate. The coated wire then is positioned in the smaller-internal-diameter portion of the cavity in shell component **1***a* and swaged in place by applying an annular stake to the end surface of shell component **1***a* around the wire and coaxial therewith. Staking of this surface produces an annular notch **11** in the end surface and lateral deformation of shell component **1***a* so as to produce an annular depression **12** in the periphery of the wire, thereby locking the wire securely in place. The "Formvar" insulation is stripped from the protruding portion of the wire (now electrode **3**) to within 0.020 inch from the end surface of shell component **1***a*, and the thin coating on the protruding end surface **4** of electrode **3** is removed.

Ignition charge **6** then is loaded into shell component **1***a* and pressed tightly against coating **5** at a pressure of

about 12,800 psi. Charge **6**, weighing 10 milligrams, is a mixture of 70 percent finely divided lead azide and 30 percent finely divided silver prepared by the displacement of silver from silver nitrate by magnesium powder in a stirred slurry of fine lead azide according to the following procedure:

In a 2.5-liter vessel, a suspension of lead azide is prepared at room temperature by rapidly adding 401 milliliters of a sodium azide solution containing 89.69 grams/liter sodium azide to 398 milliliters of a lead nitrate solution containing 229.9 grams/liter lead nitrate with vigorous stirring to assure fast mixing. After about two minutes of stirring, the suspended material is allowed to settle, the liquid is decanted off, and the solids washed four times, with 1.3 liters deionized water in each wash, by reslurrying and decantation. Following the washes, about 800 milliliters deionized water is added to the solids, and the stirrer restarted. After about two minutes of stirring, 3.89 grams of magnesium powder in sufficient (S.D.A.–3A) denatured alcohol to permit suspension of the powder is poured slowly into the suspension. Immediately thereafter, a solution of 54.33 grams of silver nitrate in 200 milliliters deionized water is added, and stirring is continued for one hour. The solids are allowed to settle and are washed four times (about 1.3 liters each wash) with deionized water by reslurrying and decantation followed by two washings (about one liter each wash) with denatured alcohol by reslurrying and decantation. The solids are then dried under ambient conditions. Photomicrographs of the solid material show that it consists of a homogeneous mixture of about 70 percent by weight of lead azide particles about 2.5–5 microns in size and about 30 percent by weight of dendritic silver particles about 0.1–10 microns in size.

Twenty-eight milligrams of priming charge **7** is pressed into shell component **1***a* against ignition charge **6** also at a pressure of about 12,800 psi. Charge **7** consists of the so-called RD–**1333** lead azide, a finely divided product which meets military specification No. MIL–L–46225A, dated Mar. 29, 1963. The base charge **8** of the detonator is 18.5 milligrams of HMX and is pressed into shell component **1***a* against charge **7** at a pressure of about 12,800 psi.

The loaded shell component **1***a* is inserted into an AISI 305 stainless steel cup, which forms outer shell component **1***b*. The thickness of the bottom of the cup, which forms closed end **2** of the shell, is 0.007 inch. The cup is 0.272 inch long and has an outer diameter of 0.136 inch and an inner diameter of 0.122 inch. The top of the cup is roll-over crimped to the top surface of shell component **1***a*, and the top end of the assembly is sealed by applying an epoxy resin sealant **10** around electrode **3** and the ends of components **1***a* and **1***b*. The length of the exposed portion of electrode **3** (from sealant **10** to the exposed end surface **4**) is about 0.100 inch.

In a typical sampling (e.g., about 100) of miniature detonators made as described above, the resistances measured within one hour of assembly, at 10 milliamperes of test current, fall within the range of about from 0.4 to 35 ohms. Detonators in such a sampling which have a resistance of at least about 0.8 ohm all fire (the explosive in the conductive charge ignites) in 10 microseconds when a 2.2 microfarad capacitor charged to 15 volts (ca. 2,500 ergs) is discharged through the electrode/conductive charge/electrode circuit, the specific firing voltage range being about from 3 to 13 volts. Detonators at the lower end of the resistance range, i.e., about from 0.4 to 0.8 ohm, generally fire when the 2.2 microfarad capacitor is charged to 30 volts, and some fire at less than 15 volts. All of the detonators in a typical sampling fire when subjected to a constant voltage of 1.5 volts from a battery or other power supply.

None of the detonators in the typical sampling fire when a 10 milliampere current is applied to the electrode-to-electrode circuit for 30 seconds, or when a 2.2 microfarad capacitor charged to 2 volts is discharged therethrough. The minimum firing current for these detonators, within one hour of assembly, is about from 62 to above 500 milliamperes.

After storage for about six months at ambient conditions, the detonators in the sampling have resistances in the range of about from 3.8 to 100 ohms. The firing voltage range is essentially unchanged. All of the detonators still pass the 10 milliampere current no-fire test, the minimum firing current range being about from 90 to above 500 milliamperes.

With respect to the output characteristics, the detonators in the sampling, as-assembled as well as after six months' storage consistently detonate a pellet of pressed tetryl over an air gap of 0.045 inch and through a mild steel barrier 0.008 inch thick.

CONTROL EXPERIMENT 1

A detonator is made according to the procedure described in Example 1 except that the application of coating **5** to the end surface of electrode **3** is omitted. This detonator, in a typical sampling, has a resistance, as-made, of 0 to 0.4 ohm, and does not fire when a 2.2 microfarad capacitor charged to 30 volts is discharged therethrough.

EXAMPLE 2

The procedure of Example 1 is repeated except that coating **5** is applied to the end of electrode **3** by an electrolytic procedure in which a length of the aluminum wire is connected to the positive side of a power supply and a lead strip to the negative pole. Both metals are placed in a 15 percent sulfuric acid solution, and a 0.5 milliampere current passed through for two minutes. This treatment produces an approximately 0.00003-inch coating of aluminum oxide (resistivity at 25°C. is about 10^{14} ohm-cm.) on the bare end of the aluminum wire. The resistivity of aluminum at 25°C. is 2.6 microhm-cm.

In a sampling of 10 detonators made as described in Example 1 with the electrode coated by anodic oxidation, resistances measured within one hour of assembly, at 10 milliamperes of test current, are within the 0.4 to 110 ohm range. The firing voltage range, with a 2.2 microfarad capacitor, is about from 3 to 8 volts.

CONTROL EXPERIMENT 2

When the procedure described in Example 2 is repeated with the exception that a 1.0 milliampere current is passed through for 15 minutes, the oxide coating has infinite resistance and all 5 detonators in a sampling fail to fire at 25 volts.

EXAMPLE 3

The procedure of Example 1 is repeated except that ignition charge **6** is a mechanical mixture of 70 parts by weight of RD–1333 lead azide and 30 parts by weight

of channel black. The resistances of a ten-detonator sampling measured with the ignition charge described in Example 1 are the same as given in Example 1. With the lead azide/channel black ignition charge, the detonators fire by the discharge of a 2.2 microfarad capacitor charged to 9–14 volts.

CONTROL EXPERIMENT 3

Detonators made as described in Example 3, except that the coating on the end surface of the electrode is omitted, fire by the discharge of a 2.2 microfarad capacitor charged to 17–28 volts. One out of ten of the detonators tested is not fired by discharge of the same capacitor charged to 30 volts.

EXAMPLE 4

The procedure described in Example 1 is repeated with the exception that inner shell component **1***a* also is treated with the "Alodine" 1200S solution so as to produce an amorphous chromate conversion coating on the internal and external surfaces thereof. Thus, charge **6** is in contact with coating **5** on the end surface of electrode **3** as well as with the coating on the internal surface of shell component **1***a*.

The resistances of ten detonators prepared in this manner, measured within one hour of assembly at 10 milliamperes of test current, range from about 1.8 to 60 ohms. All of the detonators fire in 10 microseconds when a 2.2 microfarad capacitor charged to 15 volts is discharged through them, the specific firing voltage range being about from 5 to 10 volts.

EXAMPLE 5

The procedure described in Example 1 is repeated with the exception that the application of coating **5** to the end surface of electrode **3** is omitted, and inner shell component **1***a* alone is treated with "Alodine" 1200S solution, so that charge **6** is in contact with the amorphous chromate coating on the internal surface of the shell component **1***a*. Detonators prepared in this manner and having resistances above about 0.8 ohm fire in the range of about from 6 to 14 volts (2.2 microfarad capacitor discharge).

I claim:

1. In a method of making a conductive-mix electrical initiator wherein an electrically conductive explosive charge comprising a mixture of finely divided heat-sensitive explosive and a finely-divided electrically conductive material is positioned between two metal electrodes, the improvement which comprises applying to a surface of at least one of said electrodes, which surface is to be positioned adjacent said conductive explosive charge, a coating which is less electrically conductive than said electrodes and said conductive material in said explosive charge, and thereafter bringing the intact coating on said metal surface into contact with said explosive charge.

2. A method of claim **1** wherein the composition and thickness of said coating are such that the resistance of the conductive path from one of said electrodes to the other through said electrically conductive explosive charge is within the range of about from 0.4 to 110 ohms when measured at 10 milliamperes of test current with a conductive charge comprising 70 percent by weight of lead azide and 30 percent by weight of silver within one hour of contact with the coating.

3. A method of claim **1** wherein said coating is about from 0.00002 to 0.0001 inch thick.

4. In a method of making a conductive-mix electrical initiator wherein a solid metal body is seated within the mouth of a metal shell in a manner such that one end surface thereof is exposed and the other end surface thereof is within said shell adjacent an electrically conductive explosive charge comprising a mixture of a finely divided heat-sensitive explosive and a finely divided electrically conductive material, said explosive charge being adjacent the inner wall of said shell, and adjacent surfaces of said metal body and said metal shell being electrically insulated from one another, the improvement which comprises applying to at least one of the metal surfaces which is to be positioned adjacent said explosive charge a coating which is less electrically conductive than said solid metal body, said shell, and said conductive material in said explosive charge, and thereafter bringing the intact coating on said metal surface into contact with said explosive charge.

5. A method of claim **4** wherein said coating is applied to the end surface of said solid metal body.

6. A method of claim **4** wherein said coating is applied to the inner wall of said shell.

7. A method of claim **5** wherein said end surface to which said coating is applied is substantially flat.

8. A method of claim **1** wherein said electrically conductive explosive charge is comprised of about from 45 to 90 percent by weight of a metallic azide and 55 to 10 percent by weight of a conductive material selected from the group consisting of the noble metals and carbon.

9. A method of claim **8** wherein said electrically conductive explosive charge is in a continuous reaction train with a secondary high explosive.

10. A method of claim **8** wherein said conductive material is silver.

11. A method of claim **2** wherein said coating is applied by a conversion coating process.

12. A method of claim **11** wherein said electrode is made of aluminum and said coating is applied by treatment of said electrode surface with a solution containing a source of hexavalent chromium and a source of fluoride.

13. A method of claim **5** wherein said solid metal body is made of aluminum and said coating is applied by anodic oxidation of the end surface of said body.

14. In a method of making a conductive-mix electrical initiator wherein a solid metal body is seated within the mouth of a metal shell in a manner such that one end surface thereof is exposed and the other end surface thereof is witin said shell adjacent an electrically conductive explosive charge comprising a mixture of finely divided heat-sensitive explosive and a finely divided electrically conductive material, said explosive charge being adjacent the inner wall of said shell, and adjacent surfaces of said cylindrical body and said shell being electrically insulated from one another, the improvement which comprises employing a conductive explosive charge comprising 45 to 90 percent by weight of lead azide and 55 to 10 percent by weight silver and applying to at least one of the metal surfaces which is to be positioned adjacent said explosive charge a coating which is less electrically conductive than said solid metal body, said shell, and silver, and thereafter bringing the intact coating on said metal surface into contact with said explosive charge, said charge having been

prepared by contacting a silver nitrate with an aqueous suspension of finely divided lead azide and magnesium powder, whereby silver is precipitated, and separating the solids.

15. A method of claim 14 wherein said coating is applied to the end surface of said solid metal body by a conversion coating process.

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