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COMPOSITIONS OF MATTER CONTAINING FERROMAGNETIC  
PARTICLES WITH ELECTRICALLY INSULATIVE COATINGS  
AND NONFERROMAGNETIC ALUMINUM PARTICLES  
IN AN ELASTIC MATERIAL

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FIG. 1

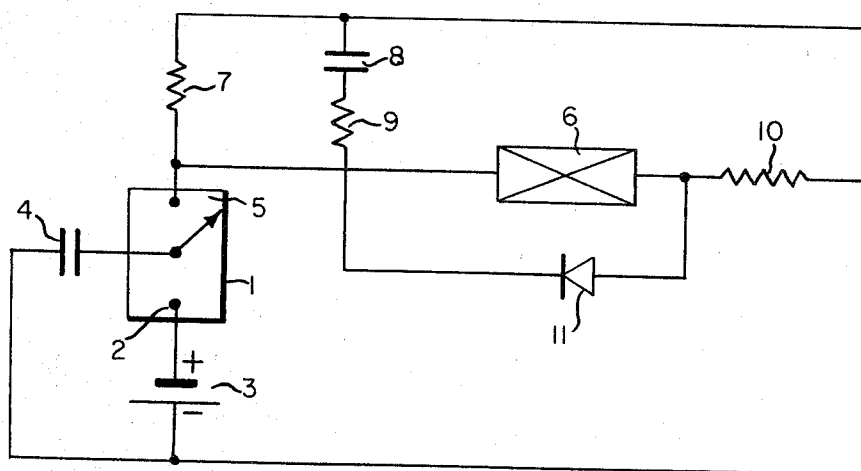
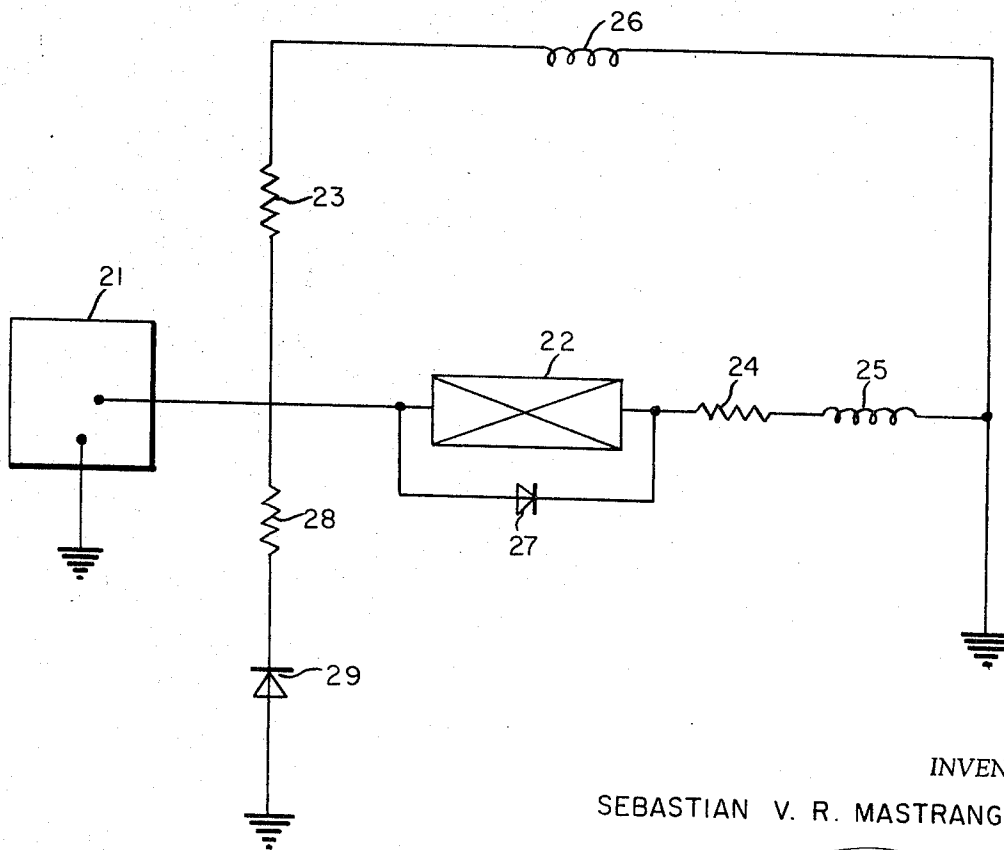


FIG. 2



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## COMPOSITIONS OF MATTER CONTAINING FERROMAGNETIC PARTICLES WITH ELECTRICALLY INSULATIVE COATINGS AND NONMAGNETIC ALUMINUM PARTICLES IN AN ELASTIC MATERIAL

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### ABSTRACT OF THE DISCLOSURE

Compositions of matter comprising aluminum particles, iron or other ferromagnetic particles with electrically insulative coatings and an elastic binder for cementing the particles into a coherent mass.

### BACKGROUND OF THE INVENTION

#### (1) Field of the invention

This invention relates to novel compositions of matter comprising aluminum particles, ferromagnetic particles with electrically insulative coatings and an elastic binder for binding them into a coherent mass. These compositions are particularly useful for making electrical switches.

#### (2) Description of the prior art

Sawyers, McCarthy and Jacoby, in Technical Memorandum SCTM 293-60-52, Sandia Corp., Livermore, Calif. (1960), report that aluminum powder of commercial grade and known to contain magnetic material in appreciable quantities exhibits switching properties when closely bound as finely divided metal particles in a homogeneous mass by means of dielectric filler. Other than a suggestion that the magnetic material is probably iron, the identity, amount and purpose or effect, if any, of the magnetic materials are not disclosed.

Pass in U.S. 3,056,750 discloses a resistance material containing metal particles that are at least partially pre-coated and bonded together by synthetic rubber to form a discrete unit or aggregate of conductive particles. Any metal powder such as iron or aluminum may be used to form aggregates useful in molding electrical resistors with fixed values from 130,000 ohms to as high as 20,000 megohms.

Gibbons and Beadle disclose in Solid State Electronics, Pergamon Press, 1964, vol. 7, pp. 785-797 that films of nickel oxide, films of other metallic oxides, anodized aluminum and aluminum powder held in a suitable insulating binder as in Sawyers' et al. above, all have electrical switching properties. They list these properties of a typical switch operating between high and low resistance states referred to as OFF and ON states:

- (1) It has an OFF-state in which its resistance is approximately 25 megohms.
- (2) It has an ON-state in which its resistance is approximately 100 ohms.
- (3) The device may be turned from its OFF-state to its ON-state by application of a two-hundred volt pulse of 40 microseconds duration. The pulse source impedance should be high (approximately 100 thousand ohms).
- (4) The device may be turned from its ON-state to its OFF-state by application of a 150 milliamp current pulse, 10 nanoseconds in duration.
- (5) Devices made to date have a limited lifetime. The maximum number of repetitive switching cycles obtained thus far is 1000. Furthermore, the device fails

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"short"; that is, it cannot be switched out of its ON-state with normal current amplitudes.

Two problems which commonly arises in switching devices formed from aluminum and/or other materials in an insulating binder are: (1) a tendency to form multiple conductive paths between electrodes when the switch is first subjected to an activating electrical voltage pulse and (2) the maximum number of repetitive switching cycles is limited to about 1000 before the device fails short or "burns-ON."

New compositions of matter have now been discovered which, when contacted with electrodes and activated by an electrical voltage pulse to a state of lower resistance, serves as a useful electrical switch which minimizes both of these problems. Switching devices formed as described herein normally require only 0.1 to 10 milliamperes current pulses to be turned from ON-state to OFF-state, and can be cycled about  $10^8$  times or more without failure.

### SUMMARY OF THE INVENTION

This invention is directed to compositions of matter comprising (a) aluminum particles, (b) iron or other ferromagnetic particles coated with an insulative material, and (c) an elastic binder for said particles, wherein the ratio of ferromagnetic to aluminum particles by weight is in the range of 1:6 to about 3.5:1, and the combined weights of the aluminum particles and the coated ferromagnetic particles is from about 25 to about 85% of the total weight of said particles and the elastic binder.

### DESCRIPTION OF THE DRAWINGS

FIG. 1 is an activating circuit diagram.

FIG. 2 is a diagram of a pulse circuit for repetitive cycling.

### DESCRIPTION OF THE INVENTION

It has been discovered that coating the surfaces of normally conductive ferromagnetic particles to increase their electrical resistance before dispersing them with aluminum particles in elastic binder greatly reduces possible interference with a desired bistable ON-OFF characteristic of electrical switches made from such compositions. The insulative coating on the magnetic particles overcomes an apparent tendency to form multiple conductive paths between electrodes when the switch composition is subjected to an activating electrical voltage pulse, a condition frequently observed when compositions containing non-coated ferromagnetic particles are utilized. Improved switches prepared from the compositions of this invention tend to conduct along a single path when they are turned ON to a low resistance state, and when turned OFF by a current-limited pulse, they do not linger in states of intermediate electrical resistance in transit to an OFF-state of high resistance.

A switching device made from the compositions of this invention can exist in any of three different states, a latent state, an ON-state, and an OFF-state. In the latent state, the resistance of the device is typically greater than  $10^{10}$  ohms; similarly, the resistance in the OFF-state is typically of the order of  $10^{10}$  ohms. However, in the ON-state, the resistance is typically only from  $10^2$  to  $2.5 \times 10^5$  ohms, at least  $10^4$  times less than the latent or OFF-state.

As originally formed, a switching device of this invention is in the latent state. In a manner described below, it can be altered from the latent state to the ON-state.

The transition from the latent state to the ON-state is called activation and is accomplished by applying what is called the activating voltage which is equal to or greater than a critical threshold or breakdown voltage. Typically the activating voltage is between 150 and 400 volts per centimeter and it is applied as a brief pulse.

If the device is in the ON-state, it can be switched to the OFF-state, i.e., turned-OFF, by application of a small current-limited pulse of about 0.1 to 10 milliamperes, less than 10 milliamperes being preferred, and regulated such that at the end of the pulse the current drops very rapidly to a new low value. By a current-limited pulse is meant a brief flow of current kept below a predetermined magnitude by a means such as a resistor in series with the switching device.

If the device is in the OFF-state, it can be switched to the ON-state by application of a voltage, i.e., turn-ON voltage, typically between about 10 volts and 225 volts and regulated such that at the end of the pulse the current drops comparatively slowly to a low value. By "burn-ON" is meant the transition to a state such that the device cannot be switched out of its ON-state. By a "bistable switch" is meant a switch that has two resistance states, an ON-state, and an OFF-state. Such a switch exhibits practically no other discrete resistance values in transit between the ON- and OFF-states, as can be established by viewing on an oscilloscope screen the voltage across a small, fixed series resistor in response to an applied voltage pulse.

The novel compositions of this invention comprise:

- (1) non-magnetic metal particles of aluminum,
- (2) ferromagnetic particles that have been coated with inert, electrically insulative material such that the resistance of one gram of the particles as a layer present between test electrodes one inch in diameter is greater than a million ohms, said coated ferromagnetic particles being present in an amount such that the ratio of ferromagnetic to aluminum particles by weight is in the range of 1:6 to about 3.5:1, and
- (3) elastic binder for said particles.

The ferromagnetic particle surfaces are at least partially enclosed and preferably are practically completely enclosed by the coating. The degree of electrical insulation or resistance introduced between particles is determined by the coating material and its thickness. Improvements in the performance of switches prepared from the compositions of this invention are obtained if the electrical resistance of the coated particles exceeds about a megohm (a million ohms) determined on a one-gram layer of coated ferromagnetic particles pressed between two metal electrodes about an inch square.

Ferromagnetic metal powders useful in the compositions of this invention can be characterized according to methods described by Lark-Horovitz and Johnson, *Solid State Physics*, vol. 6, Part B, p. 204 (1959), Academic Press, as experiencing a measurable body force of a few milligrams in an imposed magnetic field. In general, the ferromagnetic material will have a saturation magnetization per unit volume of at least about 100, preferably at least 500 cgs. units of magnetic moment per unit volume. Ferromagnetic materials useful in this invention include iron and cobalt powders or mixtures thereof with saturation magnetizations of 1752 and 1446, respectively. Iron is preferred in making the compositions of this invention.

The ferromagnetic powder is selected to have an average particle size of 10 to 30 microns and preferably a narrow distribution of sizes around 20 microns.

Ferromagnetic alloys having high saturation magnetization are also available in the desired powder form and particle size range and may be useful in this invention. Such alloys may contain other elements of the Periodic Table in addition to one or more of the three cited.

The aluminum metal powder component preferably meets the following general criteria: (1) an average particle size of from about 10 to 30 microns, more preferably a narrow distribution of sizes around 20 microns, (2) atomized powders that are granular in shape.

Operable amounts of aluminum, ferromagnetic particles, and elastic binder in switch compositions can vary widely.

By the term elastic binder is meant an insulating material which is capable of elongation with substantial recovery of its original dimensions,

Preferably, the elastic binder (when tested without the aluminum and coated ferromagnetic particles) should be capable of being elongated at least 100% (A.S.T.M. D412 test), and still retract to less than 1.5 times its original length.

The elastic binder should be present in an amount such that the combined weights of the non-magnetic aluminum particles and the coated ferromagnetic particles comprise from 25 to 85 percent of the weight of said particles and the elastic binder. The elastic binder may be dissolved in a suitable "carrier solvent" and the aluminum and coated ferromagnetic particles added thereto form a dope.

The nature of the elastic binder itself can vary widely and its composition is not critical provided it is sufficiently elastic as defined. Binders with such elastic properties include natural rubber, synthetic polyisoprene rubber, elastomeric chloroprene polymers, fluoroolefin elastomers, butadiene-styrene rubber, ethylene-propylene-nonconjugated diene rubbers, silicone rubbers and rubbery condensation polymers such as polyurethane obtained by reaction of polyisocyanates with polyalkylene glycols. The elastic binder may also contain fillers, reinforcing agents or plasticizers commonly added to elastomers, providing the properties of the resultant binder remain within the limitations hereinbefore recited.

Stiff polymers with rigid molecular structure such as aromatic polyamides, polyimides and polystyrene result in switches that do not switch off. The elongations of such binders are about 60%, 8%, and 25-58%, respectively, all less than the specified lower limit of 100% elongation.

For convenience in fabricating switches, by casting flexible sheets, for example, on which many switches can be formed side by side, it is desirable to handle fluid or fluidizable compositions from which the final switch composition can be formed in place. Accordingly, instead of the normally solid elastic binder by itself or in a solvent, there can be employed an elastic binder-forming material along with the aluminum and magnetic powder components.

Such elastic binder-forming material includes any one or more of the following:

- (1) preformed polymer which can be further cured to an elastic binder, a curing agent, and optionally a carrier solvent as above,
- (2) preformed polymer and optionally a carrier solvent, said polymer being curable by heat or irradiation,
- (3) polymer precursor, chemical agent to convert said precursor into elastic binder, and optionally an inert volatile solvent as thinner,
- (4) liquid prepolymer, self-curing or containing a curing agent.

By "carrier solvent" as used herein is meant a liquid dispersion medium for transporting one or more substances, such as the particles of this invention, which also is capable of solubilizing other materials such as curing agent or chemical agent for polymerization if such be present, e.g., acetone, xylene, tetrahydrofuran, benzene, toluene, dimethylacetamide, ethyl ether, chloroform and dimethylformamide. Said carrier solvent need not be completely removed by subsequent treatment provided the required criteria for elongation and recovery are met by the resultant binder.

In making these compositions of matter which lie within the spirit of this invention, dopes may therefore be used which are dispersions of aluminum and coated ferromagnetic particles in polymer solutions in volatile carrier solvents as mentioned above, e.g., a solution of hydrocarbon rubber in benzene or toluene. Another type of dope might also contain a reactant in addition to the solvent to promote further polymerization of an elastic binder-forming material that either may or may not yet be sufficiently elastic to meet the required criteria for elongation and recovery; for example, a dope useful in making switches contains 20 wt. percent polyurethane

rubber such as "Adiprene" C, a reaction product of diisocyanate and polyalkylene ether glycol in dimethylformamide containing 3.5 v./v. percent H<sub>2</sub>O whereas other useful formulations include blends of powders in self-curing liquid prepolymers such as silicone rubbers. If desired, elastomers capable of undergoing further reaction, such as chain extension or crosslinking, to harden but still keep products elastic, can be "cured" in situ (in the presence of the metal components). For example, curing agents such as peroxides or sulfur for unsaturated systems represented by hydrocarbon rubbers (including natural and synthetic rubbers derived from olefins and polyolefins) can be incorporated into compositions of this invention and subjected to curing conditions that are well known, for example, curing by heating. Alternatively, rubbers can be cured by irradiation under conditions known to the art for hardening them.

The ferromagnetic particles used in this invention normally conduct electricity and must be made non-conductive for the purposes of this invention by coating individual particles with insulating materials using known techniques. The higher the insulative value of the coating material, i.e., its volume resistivity, the thinner the coating required to meet the resistance test. Although suitable coatings usually range from a fraction of a micron to several microns in thickness, it is more convenient to specify that the weight of a coating as a percentage of the weight of both the coating and the ferromagnetic particles should be in the range of about 0.5 to 6% and preferably about 1 to 3% by weight. To keep the amount of coating material required to a minimum, a type of material is selected that has high volume resistivity, e.g., 10<sup>11</sup> to 10<sup>17</sup> ohm-cm. at 50% relative humidity and 23° C. temperature.

Particularly suitable for insulating the ferromagnetic particles are elastic coating materials including organic and inorganic polymers. These include natural rubber, synthetic polyisoprene rubber, ethylene-propylene-non-conjugated diene rubbers, silicone rubbers, and rubbery condensation polymers such as polyurethanes obtained by reaction of polyisocyanates and polyalkylene glycols. Relatively inelastic polymers such as polyimide polymers, polyamide polymers, and inorganic silicate coatings can, however, also be used.

The coatings should be chemically inert in the presence of other components included in switch compositions, i.e., they should not react chemically with the other substances present so that, once applied, the coating will remain insulative. Not suitable for the purposes of this invention are oxide films on iron or cobalt particles, because they can react with aluminum under activating conditions. As a result of such reaction, switches made with oxide-coated magnetic particles burn-ON.

Coating materials must also be chemically inert toward and insoluble in the particular solvent used in a switch-forming composition.

Encapsulation of the ferromagnetic particles of this invention may be effected by any of the various methods known in the art.

Fluidized bed coating affords a convenient physical means of encapsulating ferromagnetic particles. For example, iron powder of 20 micron average particle size may be suspended as a fluidized bed by proper adjustment of the upward flow of a gas such as nitrogen. A coating solution of a suitable insulating material in a volatile solvent, e.g., a 3% by weight solution of aromatic polyamide reaction product of m-phenylenediamine and 70/30 iso/terephthaloyl chloride in dimethylacetamide solvent could then be added, using a sufficient amount of the solution to form an insulative coating on the fluidized bed particles. After the volatile solvent has passed off with the nitrogen, leaving a coating on the iron particles, a one gram portion of the powder is taken from the bed and the electrical resistance of the powder as a layer between one inch diameter electrodes is meas-

ured. The nitrogen flow is continued and the treatment repeated, if necessary, until the resistance is found to be at least 10<sup>6</sup> ohms.

When a switch is to be formed from the compositions of this invention by casting the coated magnetic component/binder composition in a sheet from a carrier which is a solvent for the binder, the coating for the magnetic component should be selected so as to be insoluble in the solvent for the binder.

For example, a terpolymer of ethylene, propylene, and 1,4-hexadiene is soluble in toluene but has limited solubility in dimethyl formamide containing 3.5% water by weight, a solvent for polyurethane rubbers such as Du Pont "Adiprene" C polyurethane rubber.

Thus, ferromagnetic material coated with the above hydrocarbon polymer may be dispersed along with the aluminum component in the above dimethyl formamide-water solution of the urethane rubber binder without losing its insulating coating.

A preferred procedure for encapsulating ferromagnetic particles to obtain a free-flowing powder with minimal tendency to clump or aggregate is as follows: (It should be pointed out that clumped material is unsatisfactory to make switches, especially banks of switches, due to the uncertainty in uniformity and film thickness.) A dispersion of ferromagnetic powder in a solution of a suitable coating material, such as hydrocarbon elastomer dissolved in toluene solvent, is treated with a non-solvent for the rubber, e.g., acetone which is miscible with the solvent. This causes the precipitation of the coating material onto the surfaces of the suspended ferromagnetic particles. Addition of more non-solvent serves to set or harden the coating. The dispersed particles, now coated, are allowed to settle and the liquid is decanted. The coated particles when settled are washed with non-solvent as needed to remove toluene solvent and, when dried, become a free-flowing powder.

The compositions of this invention may be prepared by simply mixing the components at ambient temperature and atmospheric pressure. The order in which components are introduced is not critical. Normally the insulatively coated ferromagnetic metal powder and the aluminum metal powder are first mixed together. Gentle mixing in a tumbler mixer is preferred to preserve the natural protective tarnish film of aluminum oxide which imparts a characteristically dull gray color to aluminum metal particles handled in air. The mixed coated ferromagnetic and aluminum metal powders are blended with elastic material. Another satisfactory approach is to blend the powders consecutively first one then the other, with elastic material to form the compositions of this invention, the order of addition against not being critical.

In preparing the compositions of this invention, the maximum loading of insulatively coated ferromagnetic powders in the compositions is restricted only by a necessity of having at least about 15% by weight of elastic binder for structural strength and at least about 20% by weight of aluminum powder to readily form the conductive path needed for the ON-state of a switch. Therefore, by subtraction, the weight of coated magnetic material may be as much as about 65% of the total weight. It follows that the ratio of the weight of insulated ferromagnetic powder to the weight of aluminum powder can be as great as about 3.5:1 and still reduce the tendency toward multiple path formation. Preferred range is between 1.5:1 and 2.5:1 for reliable switch performance.

The minimum loading of insulatively coated ferromagnetic powder reduces the current required to turn-OFF a switch to a value less than the high current of about 100 milliamperes required without the ferromagnetic-component present. A reduction is observable at about 1:6 ratio by weight of coated ferromagnetic powder to aluminum powder but the preferred ratio is about 1.5:1 or slightly higher in order to operate at voltages and currents compatible with transistor circuitry.

According to this invention the combined weights of elastically-bound aluminum particles and insulatively coated elastically-bound ferromagnetic particles comprise from about 25 to 85 percent of the total weight of said particles and the elastic material. Compositions containing more than 85 percent generally contain insufficient binder for mechanical strength. Percentages of 60-70% are preferred. Compositions containing less than about 25 percent of the combined weight generally do not contain a sufficient number of particles to activate a switch, i.e., first turn ON the switch by forming a conductive path between electrodes.

As formed by solvent evaporation, melt techniques, or polymerization procedures the compositions described herein typically have electrical resistivities greater than  $10^{10}$  or ten billion ohm-centimeters before activation.

A switching device made from the compositions of this invention may be formed from a dope by shaping the dope, rendering it form-stable, and then applying two nontouching electrodes. The dope may be shaped by spreading it onto a substrate on which it remains when in use or from which it is removed before use. It may be spread onto the selected substrate by brushing, dipping, pouring, use of a doctor-knife, and similar procedures. After the dope has been shaped, it is subjected to heat and/or vacuum to render it form-stable, that is, to remove volatile solvent and bring the properties of the elastic binder into the range hereinbefore recited.

Coated wires are made by using a wire as a substrate and dipping it into the dope. Either before or after the dope has been rendered form-stable, additional electrode or electrodes are placed in contact with it. The wire serves as one electrode, and each combination of the wire, switch material, and additional electrode serves as a switching device.

Fibers may be pulled from the dope of this invention. Either before or after being rendered form-stable, such a fiber can be used to form a switch device by being cemented to two electrodes to form a bridge by the dope of this invention or any conductive cementing material.

Fiber bridges with a common terminal are made into switch arrays with one contact serving as a common terminal for several switches.

The shape and dimensions of the mass of switch-forming composition are not critical since its intended function as an electrical switch element depends not on its bulk but on its ability when activated to form a wire-like internal path of low resistance from one electrode contact point to another electrode contact point of lateral width not much wider than the diameter of the aluminum particles that join in a conductive path upon activation. Switch length can be as short as 5 mils, e.g., a dip-coated wire or 10 to 50 mils, e.g., a cast film or a brushed-on coating. The lateral dimension, i.e., width of a single switch, need be only about a hundred microns, so that in making one switch in certain of the above forms only a fraction of the volume of a coating is necessary to form a conductive path, since the separation between switches is determined by the shape or form of the substrate, e.g., how a wire is bent or a fiber is supported. The advantage of coatings and cast films is that many switches can be formed side by side either through the thickness of the coating or on its surface with a separation in distance determined only by the condition that a particular switch remains responsive to pulses applied by means of its electrodes in a controlled manner. Separations between switches may be only 50 mils.

Glass, metal, plaster, rubber, wood and paper are satisfactory substrates for the compositions and dopes of this invention; preferences are for polyester film or no substrate at all.

A preferred composition of this invention is made by coating iron particles as above with a hydrocarbon elastomer to electrically insulate the surfaces of the particles and dispersing the free-flowing coated iron particles

with aluminum particles in a solution of polyurethane rubber to form a dope that can be dried in situ to become a switch. More specifically, to form an electrically insulative coating on the iron particles, a non-solvent such as acetone is added to a terpolymer of ethylene, propylene and a non-conjugated diene, e.g., 1,4-hexadiene in toluene solution, precipitating the hydrocarbon elastomer onto the surfaces of iron particles dispersed in the toluene. The precipitated coating is hardened by drying, and remains hard when dispersed in contact with the solvent selected for the polyurethane rubber. The prepared dope is cast into sheets and dried.

Such sheets may be formed continuously by known techniques, e.g., extrusion, to whatever length is required.

Even more preferred is a switch-forming composition prepared by grinding up, i.e., comminuting, the sheet material described above in a micromill, sieving it through a fine-mesh screen and reconstituting it as a dope by mixing the ground-up powder, which is essentially coated iron, aluminum, and elastic binder switch material in each particle with elastic binder forming material as defined earlier, e.g., preformed elastic binder dissolved in a volatile carrier solvent for the binder.

Switches made from either the coated or the coated-comminuted-reconstituted switch-forming composition dopes (switch dopes) show excellent resistance to multiple path formation, i.e., when activated they act as bistable switches having two resistance states, an ON-state and an OFF-state. These switches tend to conduct along a single path between electrodes when they are activated, not multiple paths and therefore do not tend to develop and spend time in states of intermediate electrical resistance between the ON- and OFF-states being pulsed.

In the form of such sheets many applications in the computer or electronic fields are accommodated. For example, electrodes and printed circuitry are formed by photoetching conductive patterns on either side of such sheets for use as read only memories. The sheet is easily cut into any sized or shaped smaller pieces for use as electronic circuit components in flip-flops or oscillators. Electrical contact with the sheet is made with painted electrodes or with suitable spring contact probes.

Variation of the switch sheet or switch plate form includes a metal-backed switch plate made by casting a film of switch dope on a sheet of aluminum foil. The film dries to a reduced thickness and opposing spring contacts are affixed. Other variations include a paper reinforced sheet made by padding various switch dopes on tissue paper, a plastic-baked switch sheet made by casting various switch dopes on pressure-sensitive "Mylar" polyester, and coated printed circuit boards, made by casting various switch dopes on printed circuit boards, with or without printed circuits in place.

Switch-forming compositions described herein typically have electrical resistances greater than  $10^{10}$  or ten billion ohms before activation.

In order to make a useful bistable switch from a latent switch of the compositions of this invention between two electrodes, a voltage pulse must be applied to the switch composition to form a conductive path of less than one megohm resistance per centimeter. By application of such an activating voltage pulse specific resistance values of the initial ON-state can be attained ranging from 100 ohms to 250,000 ohms per centimeter. Once a conductive path has been established its resistance remains essentially unchanged during identification of the On-state by any small testing or "reading" voltage not exceeding a voltage potential which produces enough current to cause a transition to the OFF-state, e.g., less than about 5 volts per centimeter.

The electrical resistance of the initial ON-state depends on the magnitude of the activating voltage as well as the nature, particle size, and amount of dispersed particles. In general the initial resistance is decreased by increasing the activating voltage above a critical threshold

level for activation or by using larger particles. It can, however, also be decreased by reducing the size of a series resistor, nominally maintained at 330,000 ohms, which is used to limit the current which flows when the activating voltage pulse is applied. When the series resistor is reduced in size, the rate of decay of the activating pulse may become so rapid that the switching device is not only activated to the ON-state to become a useful switch, but within the duration of the pulse passes through the ON-state and is left in the OFF-state at the end of the pulse. The reason for this will be better understood following a subsequent description of the nature of current-limited pulses required to turn-OFF switches. Switches activated in this manner are as useful as those activated to an ON-state provided the switch is not impaired by an excessive surge of current. Thus, a switch with desired electrical properties within those practical with the materials used can be obtained from any variety of combinations of activating voltage, current, and particle size and amount of non-ferromagnetic aluminum and ferromagnetic powders.

Two terminal electrodes are needed to apply the activating voltage pulse. Electrode shape, size and form make little difference in switch performance. Silver, copper, and gold paints, copper wire (30 gauge and 18 gauge) straight pins, pressure-sensitive-backed metal foils, rounded spring-loaded pressure contacts and alligator clips have all been used successfully.

Between the two terminal electrodes standing oppositely across a 0.5 cm., sample path for example, a difference in electrical potential or voltage of 150 to 400 volts is normally required to activate the switch. Higher voltages tend to produce ON-states of lower resistance but application of too high a voltage results in switches that will not turn-OFF. In a preferred manner a resistance of less than 250,000 ohms is attained by applying a voltage pulse which is limited so as to be nearly equal to the threshold voltage of the switch and relatively independent of variations in switch-forming compositions. Attempted activation with less than the threshold voltage may have deleterious effects. Incompleted paths may form which may in turn produce multiple paths when breakdown is finally reached or during switching operation.

Multiple paths can be detected by displaying the switch current, e.g., by taking a voltage signal from a fixed resistor in series with a switch, and displaying it on the screen of an oscilloscope as the switch is cycled between ON- and OFF-states by alternate application of current-limited and voltage pulses. If multiple paths exist, additional horizontal lines or steps will appear between the two widely separated horizontal lines or steps characteristic of the ON- and OFF-state during each switching cycle. Occasionally one or even several such lines of faint brightness may be seen indicative of a tendency to conduct along one or more conductive paths other than the activated path of lowest resistance. If all the intermediate lines are very faint, operation of a switch as a bistable element is usually not impaired; however, when one such line approaches the brightness of either the ON- or OFF-state, or becomes as bright as the OFF-state line, bistable switching may become uncontrollable.

The latent switches prepared from the compositions of this invention should therefore be activated by circuitry that will standardize and produce uniformity in switch characteristics and performance. A typical circuit for activation of a switching device, prepared from the compositions of this invention, from its latent state to its ON-state is shown in FIG. 1. This circuit is optimized for a switch with about 1 cm. spacing between electrodes. An initially open single-pole double throw switch 1 is thrown to terminal 2, allowing a source of electric potential 3 of 400 volts strength to energize a 0.01  $\mu$ f. capacitor 4. Switch 1 is then thrown to make connection with terminal 5, whereupon the potential difference across latent switching device 6 raises at a rapid but controlled rate until its activation occurs.

Two means of control are provided. A parallel circuit path consisting of a 270,000 ohm resistor 7 provides a finite time constant for discharge of the energizing capacitor 4 since the latent switching device has too high a resistance to do so, typically  $10^{10}$  ohms, before activation. Secondly, a 100  $\mu$ f. time delay capacitor 8 serves to slow down the rate of rise by receiving electrical charge flow from the energizing capacitor 4. The capacitor 8 establishes a time constant for potential difference rise determined by the product of the value of the adjacent 10,000 ohm resistor 9 and its own capacitance in farads equal to one microsecond. Within this order of time a threshold voltage between about 150 and 400 volts is thereby reached for the activation of the latent switching device, changing its electrical resistance from a high value typical of its latent state to a low value characteristic of its ON-state. Thereafter a 300,000 ohm resistor 10 in series with the device limits the resultant increase in current through it as the potential difference that persists is rapidly dissipated. Finally, a 1N-4005 silicon diode 11 shorts out any reverse transient voltages that might develop.

If the potential difference is allowed to rise too rapidly, the voltage value may overshoot the threshold or breakdown voltage and produce a switch that will not turn-OFF.

If the current is not limited when the switching device is activated, it will tend to pass through the ON-state and be turned-OFF by the current surge. Sometimes actual destruction of the device will occur.

If the diode is omitted, the reverse transient voltages are capable of sometimes destroying the device.

By observing these criteria for composition preparation and switch activation, the current to switch OFF is greatly reduced as is the tendency to form multiple conductive paths between electrodes and a degree of reliability is achieved which has been missing in switches made without the addition of a coated ferromagnetic component. The current needed to turn-OFF the switches is normally 0.1 to 10 milliamperes and most frequently from 1 to 5 milliamperes, instead of 10 to 200 milliamperes characteristic of switches made without the addition of ferromagnetic powder. An ordinary switching circuit will not, however, suffice unless it provides rapid decay of the trailing edge of the turn-OFF pulse. This is evident, for instance, because an activated switching device will not turn-OFF in response to a 60 Hz. or even a 1000 Hz. pulse form.

A typical circuit useful for turning-OFF a switching device that is initially in its ON-state is shown in FIG. 2. Voltage source 21, when interrupted, results in rapid decay of circuit current. Voltage source 21 consists of a common Schmitt trigger circuit working off a sine wave generator into a one-shot multi-vibrator section and a coupling capacitor to provide a shaped current pulse as desired. Upon application of a first pulse, the switching device 22 is turned-OFF by the rapidly decaying current, but electrical charge tends to remain on both sides of the switch. Such charge, if left unattended, may develop sufficient potential difference to turn-ON the switch again. Typical means for removing excess charge promptly is shown in FIG. 2. It may bleed through a parallel resistor 23 to ground. At the other side of the switch it may bleed through variable series resistor 24 to ground. Further difficulty may still arise because of difference in the time constants for bleeding off charge from both sides of the switch. It can be overcome by those skilled in the art by introducing pulse time delay inductors 25 and 26 as shown, for example, in series and in parallel with the switching device. A switch by-pass consisting of a 1N-4005 silicon diode 27 serves to eliminate transient voltages in the circuit. An additional path to ground composed of resistor 28 and a silicon diode 29, such as a 1N-4005, serves to shape and limit the amplitude of turn-OFF pulses.

The above circuit is not only useful for turning-OFF a switch, but can be used for repetitive cycling between ON- and OFF-states. This is possible because once a switch is turned-OFF it develops a much higher resistance than the internal resistance of voltage source 21. Hence, essentially the full voltage of voltage source 21 can then be made to appear across the switching device in its OFF-state. By voltage regulation the next pulse to be supplied is therefore adjusted in value to that required to turn-ON the switching device to complete a cycle between ON- and OFF-states. Repetitive cycling rates may be varied from relative low frequencies to frequencies of 10,000 Hz. or more and individual pulse widths from about 1 to 50 microseconds using a typical Schmitt trigger. Visual observation of alternating ON- and OFF-states may be followed by suitable use of an oscilloscope in testing the life of switching devices of this invention. Life tests show that switching devices prepared from the compositions of this invention can be cycled over 10<sup>8</sup> times or more without failure using the circuitry of FIG. 2.

As stated above, the turn-OFF current can be as little as 0.1 milliamperere. The extended current range makes possible a novel, three-lead, high speed switching device with an isolated second lead. Preferably such a device comprises two bistable switches as described previously in series such that the first switch requires a current to turn-OFF by virtue of its improved composition, particle size, and shape, that is less than either the current to turn-OFF or the current that corresponds to the voltage to turn-ON the second switch. The first bistable switch must be turned-OFF initially. The characteristics of the two switches can be selected so that "write" (ON) and "erase" (OFF) pulses for the second switch pass through the first switch to reach the second switch, yet the first switch is always OFF whenever the ON or OFF condition of the second switch is "read," i.e., determined using an isolated second lead between the two switches. Such a lead is electrically isolated from the "write" and "erase" circuits by the high resistance of the first switch when "read" operations are carried out. Momentarily, however, during the "write" and "erase" pulses the first switch is in its ON-state although it is OFF at the end of the pulse.

The three-lead switch can be used, for example, to store binary information, e.g., as a computer memory element by either

passing an electrical voltage pulse in series through the first and second switches, which first switch is turned-ON and then turned-OFF by said pulse, and which second switch is turned-ON and left turned-ON, i.e., turned-ON by said first pulse, or

by passing an electrical current pulse in series through said first and second switches, which first switch is turned-ON and then turned-OFF by said pulse, which second switch is left turned-OFF, i.e., turned-OFF by said pulse,

in a manner consistent with the binary form of information to be stored as a conductive condition of the second switch.

Both the two- and three-lead switches utilizing the compositions of this invention demonstrate reliable characteristics that have advantages in computer logic and memory systems as well as in modulation and control of other electrical devices. Other advantages are the simplicity of design and fabrication, particularly the ease of interconnecting switches for use in high capacity memories for the more advanced type of computers or learning machines. Switching times are faster than a microsecond and, as a result of the low turn-OFF current, banks of switches of this invention have extremely low power requirements and high packing density capability. These and other applications of the current switch prepared from the compositions of this invention are as electronic circuit ele-

ments in oscillators, multivibrators, or flip-flops, relays, circuit breakers, flashers, electronic displays.

## EXAMPLES

The following examples are intended to be merely illustrative of the invention and not in limitation thereof. Unless otherwise indicated, all quantities are by weight.

### Examples 1-8

Two separate fluidized beds of iron particles were prepared by in each instance placing 20 grams of iron powder (Baker and Adamson 1807 with an average particles size of 20 microns) on a fitted glass filter and suspending the iron particles by upwardly flowing nitrogen gas at 10 to 30 liters per minute.

Two solutions of 0.2 gram and 0.4 gram respectively of terpolymer of ethylene, propylene, and 1,4-hexadiene (Du Pont Nordel® 1070 hydrocarbon rubber) in 100 cc. of toluene were then prepared. Each solution was then applied to coat one of the two suspensions of iron powder in the fluidized beds.

After 24 hours a gram of each of the coated iron powders was taken from the fluidized beds and each was pressed between two one inch diameter electrodes to form a uniform layer several particles thick. The resistance between electrodes was determined to be over 10<sup>8</sup> ohms using a Simpson Volt-Ohmyst® meter.

The iron powder coated with 0.2 gram rubber/20 grams of iron was mixed with aluminum powder (Alcan Aluminum Co. MD-2000 aluminum) at different iron-to-aluminum ratios as indicated in Table I (Examples 1 through 5), and each mixture was dispersed in 5.56 grams of an 18% solution of "Adiprene" C urethane rubber (430% elongation, A.S.T.M. D412 test), a reaction product of diisocyanate and polyalkylene ether glycol in dimethylformamide containing 3.5 (v./v.) percent H<sub>2</sub>O, i.e., 1 gram urethane rubber in a non-solvent for the hydrocarbon rubber on the iron particles. The iron powder coated with 0.4 gram rubber/20 grams of iron was used to prepare test switches in similar manner and their performance is indicated in Table I as Examples 6 through 8.

### Comparative Examples 1-A to 8-A

Examples 1 through 8 were repeated except the iron used in making the switches was not coated with rubber. Table I shows that coating the iron with electrically insulative material is effective in reducing the number of multiple paths particularly at iron-to-aluminum ratios near 2:1. At lower ratios, where multiple paths are not normally as troublesome a problem, the coating of the iron resulted in improved or greater percentage response to current pulses to turn-OFF such switches. Additionally, it is noted that a 25% increase in the amplitude of the voltage pulse used to turn-ON each switch produced less change, i.e., deterioration, of the performance of switches made with coated iron, especially at the higher iron-to-aluminum ratios.

TABLE I

Example	Grams		Ratio Fe:Al	Number of multiple paths	Percent Switch-OFF
	Fe	Al			
1	1.0	1.0	1:1	0	
1-A	1.0	1.0	1:1	1	
2	1.5	1.0	3:2	1	90-95.
2-A	1.5	1.0	3:2	1	0 (burned ON).
3	2.0	1.0	2:1	0	
3-A	2.0	1.0	2:1	3	
4	2.0	1.5	4:3	0	95.
4-A	2.0	1.5	4:3	0	85.
5	3.0	1.5	2:1	0	
5-A	3.0	1.5	2:1	3	
6	1.0	1.5	2:3	1	
6-A	1.0	1.5	2:3	2	
7	1.5	1.5	1:1	1	95.
7-A	1.5	1.5	1:1	1	75.
8	3.0	1.5	2:1	1	
8-A	3.0	1.5	2:1	3	

Iron powder, 100 grams of Baker and Adamson 1807, was dispersed into a solution of 3 grams of Nordel® 1070 hydrocarbon rubber, a terpolymer of ethylene, propylene, and 1,4-hexadiene in 500 cc. toluene. The mixture was stirred while 150 cc. of acetone was added slowly. This caused an initial precipitation of the hydrocarbon rubber on the iron powder. An additional 750 cc. of acetone was added with thorough mixing to harden the coating. The solution was then allowed to settle and the liquid decanted. The mixture was again stirred with acetone and the solvent again decanted. This was repeated three times to extract toluene and then the iron powder was air-dried to form a free-flowing coated iron powder which exhibited an electrical resistance of 100 megohms as a particle layer pressed between test electrodes.

25 grams of the free-flowing coated iron was mixed with 15 grams of aluminum powder (Alcan Aluminum Co. MD-2000 aluminum powder) and dispersed in 55.6 grams of an 18% solution of "Adiprene" C polyurethane rubber (430% elongation, A.S.T.M. D412 test), a reaction product of diisocyanate and polyalkylene ether glycol in dimethylformamide containing 3.5 v./v. percent H<sub>2</sub>O, i.e., 10 grams urethane rubber in a nonsolvent for the hydrocarbon rubber coating on the iron particles.

Switches were prepared by casting this dope into sheets varying from 10 to 50 mils in thickness when dried at 40-50° C. for 2 hours and then thoroughly dried at 150° C. in air for 12 to 16 hours. Two electrodes were then painted on a section of the 10 mil sheet, using conductive silver paint, and the latent switch, so formed, was activated with a voltage of about 400 volts. The resultant switch showed excellent response to ON- and OFF-pulses when driven by automatic circuitry at millisecond intervals for millions of cycles. In addition, it showed practically no tendency toward multiple path formation and the stability at increased turn-ON voltage was excellent, i.e., no change in performance was observed.

The switch was used to light a neon bulb biased to just below its threshold voltage with the switch in its OFF-state of high resistance. When the switch was pulsed ON by a voltage pulse of about 2 to 3 volts through a 47,000 ohm resistor, the increased voltage across the neon lamp turned-ON the lamp. When the switch was turned-OFF by a current pulse through a 4,700 ohm resistor, the voltage across the neon lamp decreased and it turned-OFF. In this way the switch behaved like a relay switch that could be pulsed to turn a lamp ON or OFF.

#### Example 10

A film or sheet formed from the dope prepared according to preceding Example 9 was ground up, i.e., comminuted using a micromill with a plastic-covered blade. The resulting powder was sieved through a 50-mesh screen and dispersed in a 10% (v./v.) solution of "Adiprene" C polyurethane rubber in chloroform, in proportions varying from about 5.0 to 5.5 grams comminuted powder to 2.5 grams urethane rubber to form switch dopes. The switch dopes were then cast on microscope slides and activated by a 400 volt pulse through two electrical contacts. The activated switches showed no trace of multiple path formation whereas switches made from the cast, dried sheet before comminution had shown some tendency to form states of intermediate resistance between ON- and OFF-states.

The life of an activated switch prepared as above with 5.0 grams of comminuted powder was tested using the circuit shown in FIG. 2. Voltage source 21 consisted of a Schmitt trigger delivering 200 volt DC pulses 1.0 microsecond in duration at a repetitive cycling rate of 8000 Hz. through a 0.0003  $\mu$ f. coupling capacitor. The parallel charge bleed resistor 23 was 50 ohms and the series bleed resistor 24 was 22,000 ohms. The series inductor 25 was 1 microhenry, and the parallel inductor 26 was 100 micro-

henrys. The resistor 28, useful in controlling the turn-OFF pulse, was 1000 ohms. The switch was cycled repetitively for 8 hours through 112 million cycles. The switch was still running and did not fail "short" or burn-ON.

Coated iron switch material which was comminuted and reconstituted in elastic binder as above is considered reliable enough to be a candidate for computer memory applications in which an error frequency of one in about 10<sup>8</sup> switching cycles is permissible.

The foregoing detailed description has been given for clarity of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to exact details shown and described for obvious modifications will occur to one skilled in the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A composition of matter comprising:

(a) aluminum particles,

(b) ferromagnetic particles coated with an insulative material, and

(c) an insulative elastic binder for (a) and (b), the binder being different from the insulative material, wherein the ratio of ferromagnetic to aluminum particles by weight is in the range of 1:6 to about 3.5:1 and the combined weights of the aluminum particles and the coated ferromagnetic particles is from about 25 to about 85 percent of the total weight of said particles and the elastic binder.

2. A composition according to claim 1 wherein the ferromagnetic particles are iron powders.

3. A composition according to claim 1 wherein the elastic binder is an elastic binder capable of being elongated at least 100 percent and still retract to less than 1.5 times its original length.

4. A composition according to claim 3 wherein the elastic binder is selected from the group consisting of natural rubber, synthetic polyisoprene rubber, elastomeric chloroprene polymers, fluoroolefin elastomers, butadiene-styrene rubber, ethylene-propylene-non-conjugated diene rubbers, silicone rubbers and polyurethane rubbers.

5. A composition according to claim 3 wherein the elastic binder is in a carrier solvent.

6. A composition according to claim 1 wherein the ratio of ferromagnetic to aluminum particles by weight is from 1.5:1 to 2.5:1.

7. A composition according to claim 1 wherein the combined weights of the aluminum particles and the ferromagnetic particles is from 60 to 70 percent of the total weight of said particles and the elastic binder.

8. A composition according to claim 1 consisting essentially of

(a) aluminum particles,

(b) iron particles coated with a terpolymer of ethylene, propylene and unconjugated diene, and

(c) polyurethane rubber binder.

9. A composition according to claim 1 which is in sheet form.

10. A composition according to claim 8 which is in sheet form.

11. A composition according to claim 10 wherein the composition has been hot-pressed into sheets.

12. A composition according to claim 1 wherein the ferromagnetic particles are coated with an insulating coating material having a volume resistivity of from 10<sup>11</sup> to 10<sup>17</sup> ohm-cm. at 50 percent relative humidity and at a temperature of 23° C.

13. A composition according to claim 12 wherein the coating material is selected from the group consisting of natural rubber, synthetic polyisoprene rubber, ethylene-propylene-non-conjugated diene rubbers, silicone rubbers, polyimide polymers, polyamide polymers, inorganic silicates and rubber condensation polymers obtained by the reaction of polyisocyanates and polyalkylene glycols.

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14. A composition according to claim 1 wherein the weight of the insulative coating material is from about .5 to about 6 percent by weight of the total weight of the ferromagnetic particles and the insulative coating material.

15. A composition according to claim 14 wherein the weight of the insulative coating material is from about 1 to about 3 percent by weight of the total weight of the ferromagnetic particles and the insulative coating material.

16. A composition according to claim 1 which has been activated by the application thereto of a voltage pulse to form a conductive path of less than one megohm.

17. An activated composition according to claim 16 which has two resistance states and which is capable of being switched between these two resistance states.

18. An activated switch composition which is prepared by

- (a) insulatively coating iron particles with a hydrocarbon elastomer;
- (b) mixing aluminum particles with the coated iron particles;
- (c) dispersing the coated iron particles and the aluminum particles in a solution of polyurethane rubber to form a dope;
- (d) casting the dope into sheets;
- (e) comminuting the sheets;
- (f) sieving the comminuted sheets through a fine-mesh screen;
- (g) mixing the resultant sieved and comminuted sheets with an elastic binder forming material; and

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(h) applying to the resultant composition a voltage pulse to form a conductive path of less than 1 megohm resistance, wherein the ratio of coated iron to aluminum particles by weight is in the range of 1:6 to about 3.5:1 and the combined weights of the aluminum particles and the coated iron particles is from about 25 to about 85 percent of the total weight of said particles and the elastic binder.

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