

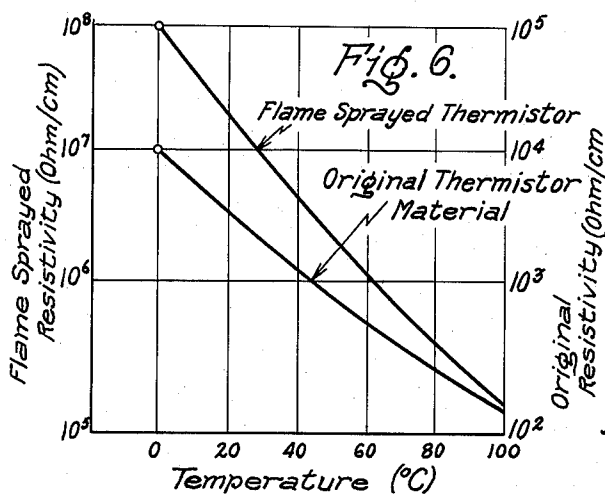
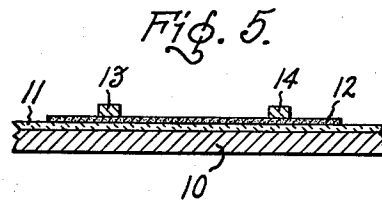
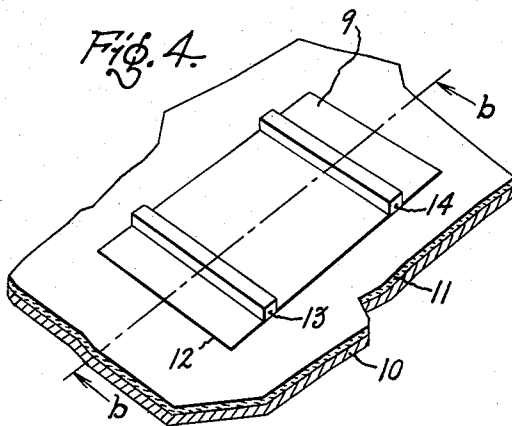
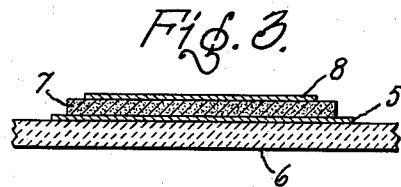
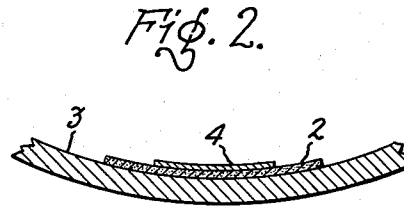
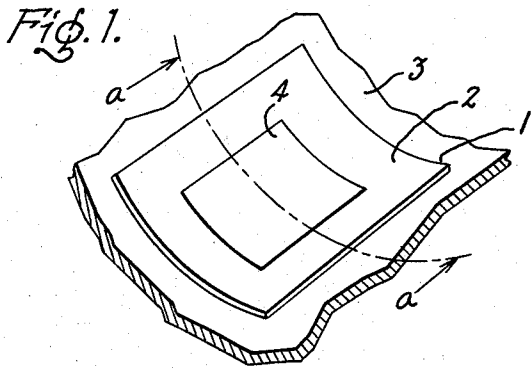
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METHOD FOR MAKING THERMISTORS AND ARTICLE

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METHOD FOR MAKING THERMISTORS
AND ARTICLE

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This invention pertains generally to the preparation of a thermistor from solid semiconducting materials by means of a simplified general technique. More particularly, the invention pertains to the direct preparation of a thermistor by deposition of heated semiconducting materials onto a suitable substrate. Specifically, the invention pertains to the spraying of the semiconducting materials from a heated gas stream to form a thermistor in situ comprising a sintered mass of the material secured to the substrate.

Semiconductor materials which possess an electrical resistivity characteristic that varies rapidly with changes in temperature are called thermistors. One particular type of thermistor material having a negative temperature coefficient of resistivity is a semiconducting, non-metallic oxide including one or more of the oxides of manganese, nickel, cobalt, copper, iron, or zinc. A widely used class of this type thermistor material comprises the reaction product of heating a mixture of the mentioned semiconducting oxides and the term "combined oxide" as employed in this specification and the appended claims is intended to define this class of materials. A thermistor is ordinarily prepared from the semiconducting oxides in the form of a solid object such as a disc, block, or bead and fastened to a substrate for use in an electrical circuit. The fabrication of the final thermistor device is a multistep process which includes pressing the combined oxides into the desired shape and size, attaching fastening means to the pressed object, and fastening the object to the substrate. This process necessarily requires the use of materials other than the thermistor composition, fastening equipment, and a time expenditure, all of which requirements increase the complexity and cost of the final assembled thermistor device. It would facilitate the preparation of thermistors generally if the separate steps of forming the final shape and attaching the member to a substrate were combined into a single operation.

It is the principal object of the invention, therefore, to provide a thermistor directly by depositing a semiconducting oxide material onto a substrate.

It is another important object of the invention to provide a thermistor by deposition of a semiconducting oxide material and location of electrodes on the deposited surface so as to control the resistance characteristics of the product in a manner substantially independent of the size and shape of the deposited thermistor.

It is still another important object of the invention to provide a simplified method for the preparation of thermistors on complex shaped substrates such as curved walls and irregular surfaces.

These and other objects of the invention will be apparent from the following description taken in connection with the accompanying drawings.

Briefly, thermistors are prepared according to the invention by suspending combined oxide particles in a heated gas stream at sufficiently elevated temperatures and for an adequate period to sinter at least the surface portion of the particles, depositing the heated particles on a suitable substrate preferably as a thin film and allowing the deposited material to cool to ordinary temperatures whereby a coherent unitary thermistor structure is formed. According to one embodiment of the invention, a thermistor film is obtained simply by spraying the combined oxide powder in a fuel gas-oxygen flame and depositing the

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heated powder particles on an ordinary steel substrate in air. The method can be employed to provide a simplified control circuit for such equipment as a hot water heater wherein the combined oxide is deposited directly on the metal tank with the tank wall serving as one electrode for electrically connecting the thermistor in the control circuit. In another embodiment of the invention, the thermistor is deposited from a heated gas stream as a layer and electrodes secured to the exposed surface of the deposited layer at locations spaced to control the resistance of the thermistor in the electrical circuit. Surprisingly, the response of the deposited thermistors to temperature fluctuations has been improved for at least the combined oxide materials tested compared to the temperature response of the original material. In greater explanation, the change in resistivity with temperature variation is greater at elevated temperature for the thermistors of the invention than for thermistors prepared from the same combined oxides in the conventional manner.

FIGURE 1 is a schematic representation illustrating a thermistor assembly of the invention in which a layer of combined oxide is deposited on a curved metal substrate and an electrode affixed to the exposed surface of the layer;

FIGURE 2 is a sectional view taken along line *a-a* in FIGURE 1;

FIGURE 3 is a sectional view of a thermistor assembly prepared according to the invention wherein the thermistor element comprises an inner layer member between two metal electrodes;

FIGURE 4 is a schematic representation of a different type thermistor deposited on a metal substrate in which two conducting metal electrodes are secured to the top surface of the deposited layer;

FIGURE 5 is a sectional view taken along lines *b-b* in FIGURE 4;

FIGURE 6 shows the relation between resistivity and temperature for a typical thermistor prepared according to the method of the invention compared to a conventional thermistor prepared with the same combined oxide material.

The general nature of the invention having been set forth, the following examples are presented to illustrate but not to limit the preferred means for carrying out the invention.

Example 1

An approximately 0.006 inch thick layer of a commercial thermistor material was flame-sprayed directly onto the interior side wall of a cylindrically shaped conventional hot water tank. The commercial thermistor material was a combined oxide having a chemical composition comprising approximately 82 weight percent manganese dioxide and approximately 18 weight percent nickel oxide with an electrical resistivity at 25° C. of 2100 ohm-centimeters and a resistivity temperature coefficient of 3950 in the temperature range 25-75° C. The thermistor material was prepared for spraying by pulverizing the commercial composition in a conventional manner to provide a free-flowing powder having an average particle size in the range 44-74 microns. The powdered particles were flame-sprayed in an acetylene-oxygen gas stream with a commercial "Thermo-Spray" gun, model P, a product of the Metco Company at gas flow rates of 27.5 standard cubic feet per hour for acetylene and 43 standard cubic feet per hour for oxygen. While the flame-spray temperature was not measured accurately, the temperature of the flame was known to be in excess of 3000° F., during the spraying operation. The powdered particles were sufficiently sintered in the heated gas stream to form a unitary coherent deposit firmly secured to the substrate although the individual particles were not com-

pletely fused by residence in the heated gas stream. The deposit formed was of a dense nature having perhaps only 8% voids by volume.

A circuit element was prepared in the above manner having the configuration shown in FIGURE 1. The circuit element 1 comprises a deposited thermistor 2 on a cylindrical tank wall 3 with a conducting metal electrode 4 secured to the exposed surface of the deposited thermistor. The relative thicknesses between individual members in the circuit element as shown are not believed critical and are intended for the purposes of illustration only. In the present configuration, the thickness of the thermistor layer to achieve a given circuit design resistance is a function of both the thickness and the area of the thermistor layer beneath surface electrode 4. Since the surface electrode area can be varied within wide limits, the sole limitation on the thermistor layer thickness is prevention of contact between the surface electrode and the metal tank wall. The only thickness requisite for the conducting electrode in the configuration is continuity so that essential molecular films of such highly conducting metals as silver, gold, copper, or aluminum are adequate. The conducting electrode is prepared by ordinary techniques including deposition from a solvent or other suspending liquid, vapor deposition, and even brazing, welding, etc. Accordingly, a silver electrode was deposited on the surface of the thermistor layer by applying a thin continuous film of a liquid organic binder suspension of silver, air drying the film, and heat curing the binder. A typical circuit element prepared in the above manner comprises a thermistor layer having a thickness from about 0.001 inch to about 0.010 inch secured to the metal substrate and a top electrode with a thickness generally less than about 0.005 inch. Electrical connection to the circuit element is made with one lead to the top electrode and another lead to the metal substrate at a location adjacent to the thermistor layer.

The electrical conductivity characteristics of a circuit element prepared in this fashion is shown in FIGURE 6 wherein the resistivity of the original thermistor material is plotted on the left ordinate of the graph over the temperature range of the abscissa while the corresponding resistivity of the flame-sprayed product is plotted on the right ordinate. It will be noted from the graph that the rate of resistance change with temperature of a sprayed thermistor is greater than for a thermistor prepared from the original combined oxide material. An increased rate of resistance change with temperature facilitates the design of control circuits for heated devices having closer "on-off" tolerances.

In FIGURE 2 a cross section of the circuit element of FIGURE 1 taken along lines *a-a* is shown to more clearly point out the present embodiment. It must be pointed out that certain pictorial representations in both FIGURES 1 and 2 are primarily for purpose of illustration. For example, the regular rectangular shape of the thermistor shown in the drawings is not generally obtained by merely spraying the powdered combined oxide material on the substrate. This is not to say that a fairly regular shape thermistor member cannot be obtained by flame-spraying since the substrate can be masked with a refractory pattern prior to the flame spraying. Furthermore, a regular shape thermistor member is not required for the circuit element since the resistance of the element can be controlled by the area of the top electrode.

Example 2

A flame-sprayed thermistor was prepared according to the general method described in Example 1 with a powdered combined oxide material having a composition comprising approximately 56.9 weight percent manganese dioxide, approximately 15.2 weight percent nickel oxide, and approximately 27.9 weight percent cobalt oxide. The electrical resistivity of the composition was 300 ohm-

centimeters at 25° C. with a resistivity temperature coefficient of 3580 over the range 25-75° C. The physical characteristics of the flame-sprayed thermistor were substantially comparable to the product of Example 1 in appearance, porosity, and adherence to the substrate. Also, the desirable electrical resistivity changes in the thermistor material after flame-spraying noted in the said example were obtained for the present product.

Example 3

A circuit element was prepared by the same general method and having the same configuration as previously described. The chemical composition of the powdered combined oxide flame-sprayed onto the metal substrate comprised approximately 45.9 weight percent manganese dioxide, approximately 16.2 weight percent nickel oxide, approximately 27.9 weight percent cobalt oxide, and about 10 weight percent copper oxide. The electrical resistivity of the composition was significantly lower than for the preceding compositions illustrated being 30 ohm-centimeters at 25° C. with a resistivity temperature coefficient of 3000 over the range 25-75° C. The top surface electrode applied on the deposited thermistor layer also differed from the electrodes of the previous examples and comprised an approximately 0.005 inch thick aluminum layer prepared by flame-spraying aluminum wire.

The performance characteristics of the circuit element prepared in the above manner were substantially comparable to the results obtained in the preceding examples. While the electrical resistivity of the flame-sprayed thermistor element is lower due to the lower initial resistivity of the combined oxide employed, the difference in resistivity can be compensated for by decreasing the area of the surface electrode to obtain a given resistance for the circuit element. It is possible by practice of the invention, therefore, to prepare thermistor elements having approximately the same total resistance from combined oxide materials having widely different resistivities simply by adjustment of the electrode area. In contrast thereto, compensation for resistivity differences of the combined oxides in conventional thermistor elements generally requires volume adjustment with perhaps additional modification of the means for fastening the element in the circuit.

In FIGURE 3 there is shown a different type circuit element incorporating a flame-sprayed thermistor which is suitable for preparation of the element on a non-conducting substrate. A circuit element is prepared having the illustrated configuration by first depositing a base electrode 5 of an inert, thermally stable conducting material, such as platinum on the non-conducting substrate 6 in a conventional manner as hereinbefore described. The thermistor layer 7 is deposited from a heated gas stream onto the exposed surface of the lower electrode member 5 and secured thereto by sintering action. A top electrode 8 of a conducting material is adhered to the thermistor layer having an area fixed by the desired resistance for the circuit element. Leads are connected to electrodes 5 and 8 by such known processes as soldering, welding, or use of an electrically conducting cement.

FIGURE 4 shows a schematic representation in perspective view of a circuit element 9 having two electrodes and prepared in situ on the porcelainized exterior metal wall 10 of a conventional hot water tank. The porcelain layer 11 provides suitable electrical insulation so that the current path in the element will be contained to the thermistor layer. A thermistor layer 12 is deposited directly upon porcelain layer 11 and electrodes 13 and 14 affixed to the exposed surface of the thermistor layer in the usual fashion. The resistance of the circuit element 9 is controlled by the spacing between electrode members. The location of electrodes at a given design resistance for the circuit is determined simply with probe measurements using a conventional electrometer device. One advantage for the present configuration compared

with the type circuit elements heretofore described is substantial independence of the circuit element resistance from the electrical characteristics of the metal base layer. Another comparative advantage for the present type circuit element is faster response since the location of both electrodes on a single surface requires only a surface temperature change to alter the resistance of the element. It will be noted that a thermistor circuit element having two electrodes on the surface of the thermistor can be prepared with said thermistor layer deposited directly on a metal substrate. This modification of the circuit element in FIGURES 4 and 5 eliminates an electrically insulating barrier layer between the thermistor layer and the metal base layer and requires only that the thickness of said thermistor layer be substantially greater than the distance between electrodes. The modified construction creates in effect a parallel circuit with the resistance path between electrodes being smaller than any path through the metal base layer and thereby directs the current between the electrodes.

FIGURE 5 is a cross-sectional view along lines *b-b* of FIGURE 4 for the purpose of showing in greater detail the construction of the circuit element in FIGURE 4.

With regard to both FIGURES 4 and 5, it will be noted that although substrate 10 is shown as being of metallic material, the present circuit element configuration can be prepared on such non-conducting refractory substrates as glass, ceramics, etc.

It is not intended to limit the method of the invention to the preferred process employed in the preceding examples. It will be apparent that other known methods for heating powdered materials can also be suitably employed in the preparation of thermistors according to the invention. For example, it is not critical to the practice of the invention to employ a flame-spray method for depositing the thermistor layer since streams of inert gases such as nitrogen, helium, or argon heated in a plasma jet can be suitably employed. It is preferred to employ a neutral or slightly oxidizing gas stream for heating the powdered particles to minimize chemical reaction during deposition. Likewise, it is not intended to limit the method of the invention to deposition of heated combined oxide particles on a cooled substrate since the substrate can be heated to increase the rate of deposition. It will also be obvious that the powdered combined oxide particles being refractory in nature can be preheated before residence in the gas stream to again permit faster deposition of the sintered layer. The method of the invention in a broad sense includes the deposition of heated combined oxide particles on a suitable substrate and the sintering of the deposited particles to form a coherent mass which is secured to the substrate all in a single unitary operation.

The thermistor composition which can be employed in the practice of the invention can be selected from the class of refractory combined oxides generally prepared by sintering a mixture of the oxides at elevated temperatures. Suitable thermistor materials must not be degraded unduly in the gas stream, have reasonably adhesive characteristics in the sintered state and not be overly sensitive to impurities likely to be encountered in the present method of preparation. Commercial thermistor materials with these characteristics are available having resistivities at 25° C. ranging from 12 ohm-centimeters to about 57,000 ohm-centimeters.

These commercial materials contain 40-80 weight percent manganese oxide with the remainder of the composition comprising at least two of the following three oxides in the proportions 2-55 weight percent cobalt oxide, 0-20 weight percent nickel oxide, and 0-15 weight percent copper oxide.

The preferred thermistor materials are those described in the above examples and the materials can be characterized as stabilized combined oxides. The stabilized

materials are well known in the art and comprise combined oxides prepared in the usual fashion but given an additional thermal treatment after the sintering operation which reacts the oxides. The added thermal treatment comprises heating the combined oxide at temperatures in the approximate range 1100-1450° C. for a sufficient period to insure reproducible resistivity response of the material in subsequent use. Since the stabilization temperatures are above the use temperatures, it can be expected that the refractory combined oxides will not thereafter exhibit much change in use. Surprisingly, the stabilized oxides employed in the practice of the invention retained a reproducible resistivity response even though the materials had been heated to temperatures above the stabilization temperature and sintered during the spraying operation. More particularly, even though the absolute resistivity of the sprayed thermistor material was increased by spraying in the manner illustrated in FIGURE 6, the material retained its stability characteristic of reproducibly returning to a specific resistivity during repeated temperature cycling.

The products of the invention comprise thermistor elements prepared in situ by heating combined oxides in a gas stream at temperatures at least above the sintering temperature of the combined oxides and depositing the heated oxides on a substrate to form a unitary sintered mass. The thermistor member is bonded to the substrate solely by adhesion between oxide particles and the substrate. The sintered product can be further characterized as having a negative temperature coefficient of resistance and being utilizable directly in its then present form as a resistive member in an electrical circuit. The porosity of the sintered products can be varied over a wide range by varying the particle size and particle size distribution of the powdered combined oxide employed to prepare the thermistor layer. Thermistor layers have been prepared with sufficient porosity to make it advisable to deposit a layer of a non-conducting refractory material, such as colloidal silica, on the exposed surface of the thermistor layer so that a relatively smooth substrate is obtained for subsequent deposition of a top electrode member. The deposited non-conducting material fills the void spaces between adjacent cohered thermistor particles in such a manner that the electrode material contacts only thermistor particles at the exposed top surface of the thermistor layer and produces uniform resistance over essentially the complete area of the electrode. The deposition of the non-conducting material on the surface of a relatively porous thermistor layer prepared according to the invention can be accomplished in any conventional manner. Excess material over that required to fill surface voids is removed simply by wiping the surface clean.

The preferred products of the invention are circuit elements incorporating a thermistor layer deposited directly on a conducting metal substrate. The construction has a wide range of applications because of the common use of such conducting metals as steel, iron, copper, brass, etc., for structural members and does not require any special electrical insulation of the thermistor layer from the conducting substrate. Thermistor elements of this construction can be used directly in many applications including temperature control, thermometers, temperature compensators, switching devices, regulators, pressure gages, flow meters, time-delay and surge suppressors, oscillator and amplifier controls, timing devices, etc. For example, a circuit element prepared directly on the bare metal wall of a hot water tank has been incorporated successfully in an otherwise conventional bolometric type temperature control circuit. The especially preferred circuit element has the general configuration of FIGURE 1 in that a thermistor layer is deposited directly on the metal substrate and a surface electrode affixed thereto. The especially preferred circuit element can be prepared as shown with very thin films of a therm-

istor composition which minimizes the problem of adherence between the members due to differences in thermal expansion and provides efficient use of the thermistor composition. An additional advantage of the construction compared to the modified configuration of FIGURE 4 having both electrodes on the exposed surface of the thermistor layer is shorter response time of the element since generally smaller volumes of thermistor material need be heated or cooled to effect a resistance change in the element.

From the foregoing description it will be apparent that the preparation of thermistors in situ has been provided by a method which obviates manufacture to specific sizes and shapes for a given resistance. A thermistor layer can be deposited on almost any surface regardless of shape and contour having improved thermal contact with the substrate and secured thereto by simple adhesion. Additionally, circuit elements employing thermistors deposited in situ have been shown incorporating novel means for controlling the resistance of the thermistor element. It is not intended to limit the invention to the preferred embodiments above shown, since it will be obvious to those skilled in the art that certain modifications of the present teaching can be made without departing from the true spirit and scope of the invention. It is intended to limit the present invention, therefore, only to the scope of the following claims.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A method for the preparation of a thermistor in situ which comprises suspending a powdered combined oxide consisting essentially of from about 40 to 85 percent by weight manganese dioxide, up to 55 percent cobalt oxide, up to 20 percent nickel oxide, and up to 15 percent copper oxide having a negative temperature coefficient of resistance in a heated gas stream at temperatures at least above the sintering temperature of the combined oxide, heating the powdered oxide to the sintering temperature, and depositing the powdered oxide on a substrate to form a unitary sintered mass.

2. A method for the preparation of a thermistor in

situ which comprises suspending a powdered combined oxide consisting essentially of from about 40 to 85 percent by weight manganese dioxide, up to 55 percent cobalt oxide, up to 20 percent nickel oxide, and up to 15 percent copper oxide having a negative temperature coefficient of resistance in a heated gas stream at temperatures at least above the sintering temperature of the combined oxide, heating the powdered oxide to the sintering temperature, depositing the powdered oxide on a substrate to form a unitary porous sintered mass, and filling the surface pores in the sintered mass with a non-conducting material.

3. A thermistor member which comprises a flame sprayed sintered mass of stabilized combined oxide particles having a negative coefficient of resistance bonded to a substrate by adhesion between oxide particles and the substrate.

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