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J. A. BECKER ET AL

2,633,521

HIGH-TEMPERATURE COEFFICIENT RESISTOR AND METHOD OF MAKING IT

Filed June 28, 1949

2 SHEETS—SHEET 1

FIG. 1

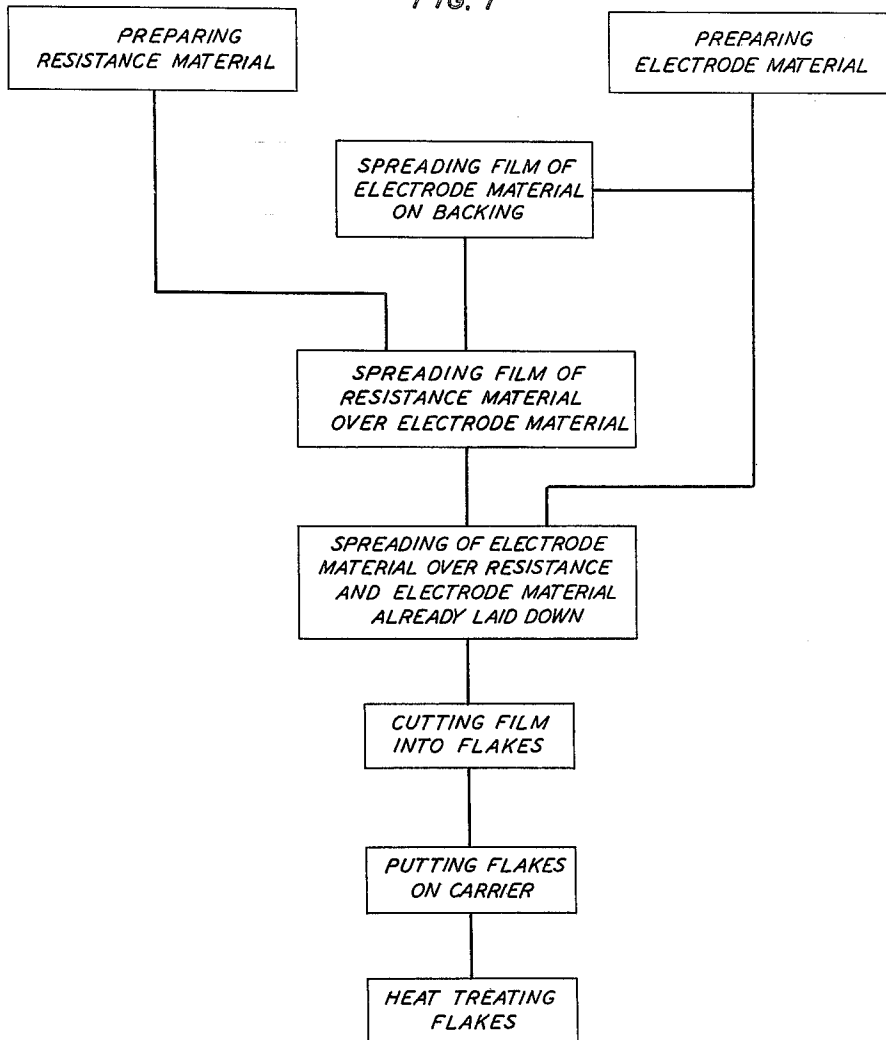
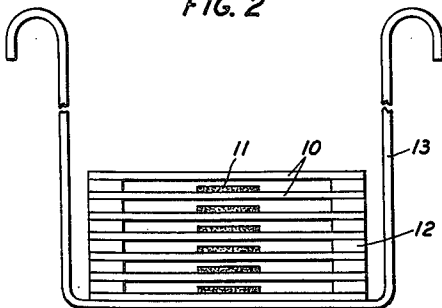


FIG. 2



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2 SHEETS—SHEET 2

FIG. 3

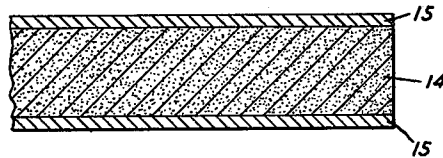


FIG. 4

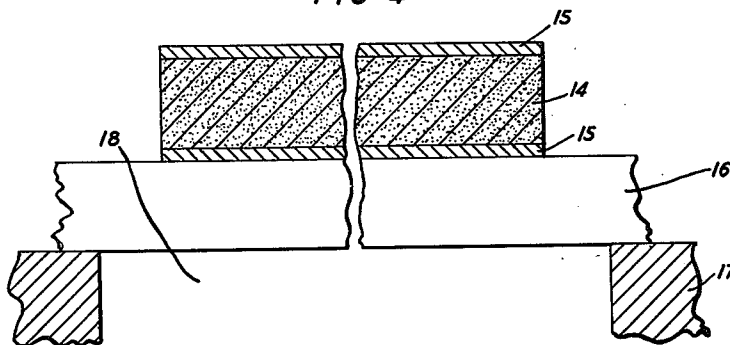
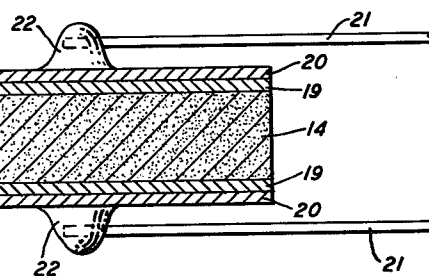


FIG. 5



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HIGH-TEMPERATURE COEFFICIENT RESISTOR AND METHOD OF MAKING IT

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12 Claims. (Cl. 201-73)

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This invention relates to resistors and more particularly to small thin film resistors and to methods of making them.

One general object of this invention is to improve the characteristics of and the production techniques for conductive devices having high temperature coefficients of resistance.

More specifically, objects of this invention are to lower the resistance, to increase the speed of thermal response, to eliminate noise, to increase the power capacity and to simplify the method of producing thermal sensitive resistance devices.

Conductive materials having high temperature coefficients of resistance have been called "thermistor materials" and devices employing such materials in their conductive paths have been identified as "thermistors" for convenience of terminology. Where these terms are employed hereinafter a material or device of the type indicated is intended.

Heretofore, resistors have been formed into thin films or flakes as disclosed, for example, in Patent 2,414,793 of January 28, 1947, issued to the present inventors. That device comprised a flake of resistance material produced by spreading a paste of a suitable material mixed in a fluid vehicle upon a drying surface, drying the paste to form a film, removing the dried film from the surface, cutting it into the desired shape and size, placing each bit or flake on a refractory surface and firing it to remove the binder to cure it so the material is completely sintered. The flake is supplied with electrodes.

This invention provides an improvement upon the method and devices discussed above. The electrodes are mounted on the flake in the steps of manufacture prior to the firing operation thereby effecting a considerable economy of labor.

Another feature is the application of electrodes which are in intimate association with the resistor material and therefore do not give rise to noise and modulation which often occur at the interface between semiconductive and conductive materials.

In accordance with this invention, green or uncured flake resistors are prepared with a green layer of electrode material on one or both of their major surfaces. The unit is fired to remove the binder in both the resistance and the electrode material and then both materials are sintered.

The above noted and other objects and features of this invention will be more fully understood from the following detailed description when read in conjunction with the accompanying drawings in which:

Fig. 1 represents a flow chart of the steps in the process of preparing resistor elements in accordance with this invention;

Fig. 2 shows one form of a carrier for support-

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ing resistor elements during the heat treatment;

Fig. 3 is an enlarged cross-section of a portion of a flake after heat treatment;

Fig. 4 is a sectional view showing a portion of the flake of Fig. 3 mounted on a conductive backing for use in one form of resistor; and

Fig. 5 is a sectional view of another form of flake resistor embodying features of this invention.

As indicated in the flow chart of Fig. 1, the initial step in producing flake thermistors in accordance with this invention comprises preparing the electrode and resistance material employed. The materials are made up of a mixture of granular particles of the material which forms the effective portions of the film, a binder which can be removed without leaving any detrimental residues and a solvent for the binder which gives it the fluid properties necessary to form a suitable vehicle for the finely divided particles of the effective portion.

Flake thermistors in accordance with this invention are preferably very thin, the thermistor layer being of a few microns to several tens of microns thickness and the electrode layers on top and bottom surfaces of the flake being of the order of from .5 to 2 microns. In order that the electrode and thermistor films are sufficiently homogeneous to give the necessary uniformity of operation, the size of the particles which are used in making these films is of considerable importance. It has been found desirable in the preparation of the resistance and electrode material to employ a granular material having a maximum particle size about $\frac{1}{16}$ the desired thickness of the complete layer.

The effective thermistor material employed may be of various materials having relatively high temperature coefficients of resistance. For example, one or more of the oxides of manganese, nickel, cobalt, copper, iron, or zinc may be used. This material is employed in finely divided granular form. The mixture employed in forming the resistor is made up in the form of a paste comprising a quantity of the prepared resistance material thoroughly mixed, as in a ball mill, with a temporary binder such as polymerized methacrylates (e. g., isobutyl methacrylate), polyvinyl butyral, polyvinyl chloride, or cellulose acetate butyrate and a volatile solvent. While a plasticizer such as dimethyl phthalate may be added in the case of a polymerized methacrylate where desirable it is generally found unnecessary, the plasticity of the binder being controlled by the degree of its polymerization.

The electrode material is prepared in paste form by milling finely divided metal such as platinum black or palladium black or other noble metal with a binder in a solvent in the manner described for preparing the thermistor material.

For some applications the quality of the final thermistor is improved by employing an electrode mixture composed of thermistor material and a noble metal. The thermistor material used in this mixture is the same as that used for the thermistor flake, and its range of volumetric percentage in the mixture extends up to 50 per cent. By using a noble metal-thermistor material mixture for the electrode, the formation of the usual barrier layer at the electrode-thermistor interface is reduced since there is a graduating of the conductivity from that of the thermistor to the high conductivity portion of the circuit thereby reducing the noise and modulation associated with the barrier layer. In either type of contact mixture, the metal used must sinter at the thermistor material firing temperature and yet not evaporate, diffuse into the thermistor body, nor act as a surface catalyst for breaking down atmospheric oxygen which might pass through the electrode material to the body of the flake and change its resistance.

While the binder and solvent of the thermistor and electrode material may be identical, it is often desirable to employ a binder and solvent for one which is mutually insoluble with that of the other so that the one will not soften the other when they come into contact prior to the drying and sintering operation. Examples of such binders, suitable for use with the electrode material in combination with those binders previously mentioned, are "carbawax" (poloxyethylene) with water as a solvent and a copolymer butadiene-styrene with a solvent of cyclohexane.

In forming a thermistor, a very thin film of electrode paste, prepared in accordance with one of the alternatives heretofore set forth, is spread out on an optical flat of glass. This may be done by means of a properly spaced straight edge or by spraying so that upon drying the film will be of the order of $\frac{1}{2}$ to 2 microns in thickness. This film is then dried in a dust free atmosphere by passing air at room temperature over it to evaporate the volatile binder solvent. A film of the thermistor material is then spread on top of the electrode film so that on drying its thickness will be on the order of tens of microns. When this film is dry, a third thin film of electrode material is smeared over it and dried.

The composite film is then removed from the flat in the form of a sheet. This may be done by applying an agent which causes a swelling of the temporary binder of the film. A bath of water has been found satisfactory for removing those films made with the binders heretofore set forth which are not water soluble while some other swelling agent must be employed for those having the water soluble binder suggested. The film can then be lifted away from the flat by means of some thin member such as a razor blade. Another way of removing the film is to place a sheet of lint-free paper moistened with a suitable swelling agent over the film for a short time to wet it, then to remove the paper and lift the film with a thin member as before.

After the swelling agent evaporates the sheet is found to be quite flexible and can be handled readily. It is cut into the desired shape and size of flakes, for example, by a sharp blade and then fired. At this point one of the advantages of a metal-thermistor material mixture for the electrode material becomes evident. In the cutting of the flexible composite film it is sometimes found that small amounts of electrode material

spread across the edges of the flakes thereby shunting the thermistor layers. While the metal-thermistor mixture material provides an excellent contact of low resistance over the face of the flake, when in small area paths such as would be formed across the edge of the thermistor material in this cutting operation its resistance is high enough to avoid having any material effect upon the electrical characteristics of the flake. The dilution of the metal with thermistor material actually serves to prevent a continuous path of electrical flow through contiguous metal particles.

These flakes are fired to remove the temporary binder and sinter the respective layer. Each flake is placed on a flat surface of refractory material, which may be of platinum coated with aluminum oxide or aluminum oxide alone to avoid any tendency of the flakes to stick thereto during the firing operation. These plates are of relatively large area with respect to that of the flakes in order to insure uniform temperature distribution across the plate, thereby inhibiting any tendency of the flake to warp due to uneven heating. A plurality of the carrier plates are stacked with spacers between them in preparation for firing. The spacers are slightly thicker than the resistor flakes so that the flakes will be allowed to shrink during firing without mechanical constraint.

The stacks of loaded carrier plates may be placed in a suitable support for suspension in a furnace. For example, as illustrated in Fig. 2, a plurality of supporting plates 10 each loaded with one or more flakes 11 and separated from adjacent plates by spacers 12 may be mounted on the support or hanger 13. The support may be simple U-shaped elements of wire having overturned upper ends, two or more of which may be used to support a stack, the front one only being shown in Fig. 2. If desired cross bars may be employed to connect two or more hangers together into a rack.

A rack of loaded plates may then be placed in a suitable furnace for removal of the temporary binder and sintering. Where the binder is polyvinyl butyral, the temperature may be gradually raised to about 600 degrees C. to depolymerize and drive off the binder. Other techniques may be employed for removing the temporary binder, depending on its characteristics. Usually they will include gentle heating.

After the binder is removed the temperature may be raised rapidly to about 1100 degrees C. Most of the sintering of the flakes takes place in this range. This temperature may be further raised to some point between 1100 and 1450 degrees C. to complete the sintering depending on the material from which the flakes are made. The flakes and their support are then allowed to cool and the flakes are removed from the supporting plate.

The completed flake will then appear as disclosed in Fig. 3 and will comprise a layer of thermistor material 14 and a layer of electrode material 15 intimately joined to both its major surfaces. For some applications it may be desirable to employ a thermistor of this type with a thermal sink. In such a case it is difficult to find a material of permissive cost having the necessary thermal properties and expansion characteristics such that the thermistor can be attached directly thereto without either destroying the thermistor or breaking it away from the surface of the sink as it is subjected to large temperature changes. A

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mounting which is not subject to such expansion limitations is disclosed in Fig. 4. It comprises a strip of metal 16, having a similar coefficient of expansion to that of the thermistor layer 14 and its electrode 15, to which the flake electrode 15 is directly secured, as by welding. This strip, which may conveniently be of platinum ribbon where the electrode is of platinum, is then secured to a sink, which may comprise a block 17 of some material having a high thermal diffusivity such as copper, so that the portion of the platinum ribbon supporting the thermistor is spaced therefrom. A slot 18 in the face of the block under the thermistor will achieve this result. Thus the platinum ribbon, being in intimate contact with a large area of both the block and the thermistor, and having a high thermal conductivity, readily transmits the heat of the thermistor to the sink while providing one conductive path to the lower electrode 15. The conductive path may be completed through the thermistor and upper electrode 15 by securing a contact to the upper electrode as by welding another platinum ribbon thereto or by employing a method hereinafter set forth in regard to the construction of the thermistor of Fig. 5.

Fig. 5 illustrates a flake thermistor with wire leads attached. Difficulty has been encountered in attaching leads to semiconductive material as there is a tendency for a change in composition to occur and thereby change the electrical characteristics of the device when heat is applied thereto. These difficulties, which might also occur in some metal-thermistor mixture electrodes, can be avoided in the case of flake thermistors manufactured according to this invention by modifying the production techniques set forth above so that where a metal-thermistor material electrode layer 19 is employed an additional layer 20 substantially entirely of metal is applied in the formation of the film. This is done by first applying a thin layer of the all-metal paste to the optical flat, then the metal-thermistor material, thermistor material, and metal-thermistor material layers, and finally applying a final layer of the all-metal paste and heat treating in the usual manner to drive off the binder and sinter the layers. Leads 21 can be attached to the resulting flake by soldering them directly to the outer all-metal layers. This eliminates the problems which are involved when leads are secured directly to thermistor material or a mixture containing such material while requiring no further heat treatment and retaining the reduction of barrier layer effects which are obtained when the metal-thermistor electrode mixture is used.

As an example of a thermistor made up in the form disclosed in Fig. 5, the contact layers 20 might be formed from a paste of platinum black, isobutyl methacrylate and a volatile solvent, the electrode layers 19 might be formed from a paste comprising a mixture of 75 per cent by volume of platinum black and 25 per cent by volume of a thermistor material mixed with a copolymer butadiene styrene and cyclohexane as a solvent, and the thermistor layer formed from a paste of thermistor material, isobutyl methacrylate and a volatile solvent. Thus the adjacent layers in the unfired thermistor have binders and solvents which are mutually insoluble and therefore there is no tendency to disrupt the desired organization thereof. The thermistor is completed by securing leads 21 to the substantially pure platinum contact layer 20 by beads 22 of silver solder.

While the preceding disclosures have included

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composite films and resistor flakes having both major surfaces of the resistance material layer coated with an electrode layer, and while specific materials have been suggested for this resistor and its method of production, it is to be understood that this invention is not to be so limited and that one surface or only portions of one or both surfaces of the resistor layer may be coated with an electrode material of a variety of compositions.

What is claimed is:

1. The method of making a rapid response resistor having a high factor of resistance dependence upon temperature which comprises mixing finely divided metal with a temporary binder, spreading a film of the mixture on a surface, mixing finely divided high resistance-temperature coefficient semiconductive material with a temporary binder, spreading a thin film of this mixture on the metallic mixture film, removing the sheet comprising the superposed films from the surface, and heat treating the sheet to remove the temporary binder from the layers and to consolidate the finely divided material into a self-sustaining resistor.

2. The method of making a rapid response resistor having a high factor of resistance dependence upon temperature which comprises mixing finely divided metal with a temporary binder, spreading a film of the mixture on a surface, mixing finely divided high resistance-temperature coefficient semiconductive material with a temporary binder, spreading a thin film of this mixture on the metallic mixture film, spreading another metallic mixture film on the semiconductive mixture film, removing the sheet comprising the superposed films from the surface, and heat treating the sheet to remove the temporary binder from the layers and to consolidate the finely divided material into a self-sustaining resistor.

3. The method of making a rapid response resistor having a high factor of resistance dependence upon temperature which comprises mixing finely divided platinum black with a temporary binder, spreading a thin film of the mixture on a smooth surface, mixing finely divided high resistance-temperature coefficient semiconductive material with a temporary binder, spreading a thin film of this mixture on the platinum mixture film, spreading another platinum mixture film on the semiconductive mixture film, drying the sheet comprising the superposed films, removing the sheet from the surface, dividing the sheet into flakes, and heat treating the flakes first at a moderate temperature to remove the temporary binder and then at a higher temperature to consolidate the finely divided material into a self-sustaining resistor.

4. The method of making a rapid response resistor having a high factor of resistance dependence upon temperature which comprises mixing finely divided high resistance-temperature coefficient semiconductive material and finely divided metal with a temporary binder, spreading a film of the mixture on a surface, mixing finely divided high resistance-temperature coefficient semiconductive material with a temporary binder, spreading a thin film of this mixture on the semiconductive material-metal mixture film, spreading another semiconductive material-metal mixture film on said semiconductive mixture film, removing the sheet comprising the superposed films from the surface, and heat treating the sheet to remove the temporary binder from the layers and to consolidate the

finely divided material into a self-sustaining resistor.

5. The method of making a rapid response resistor having a high factor of resistance dependence upon temperature which comprises mixing finely divided high resistance-temperature coefficient semiconductive material and finely divided platinum black with a temporary binder, spreading the film of the mixture on a surface, mixing finely divided high resistance-temperature coefficient semiconductive material with a temporary binder, spreading a thin film of this mixture on the semiconductive material-platinum mixture film, spreading a semiconductive material-platinum mixture film on the semiconductive mixture film, removing the sheet comprising the superposed films from the surface, and heat treating the sheet to remove the temporary binder from the layers and to consolidate the finely divided material into a self-sustaining resistor.

6. The method of making a rapid response resistor having a high factor of resistance dependence upon temperature which comprises mixing finely divided high resistance-temperature coefficient semiconductive material and finely divided metal with a temporary binder, spreading a film of the mixture on a smooth, plane surface, mixing finely divided high resistance-temperature coefficient semiconductive material with a temporary binder, spreading a thin film of this mixture on the semiconductive material-metal mixture film, removing the sheet comprising the superposed films from the plane surface, and heat treating the sheet to remove the temporary binder from the layers and to consolidate the finely divided material into a self-sustaining resistor.

7. The method of making a rapid response resistor having a high factor of resistance dependence upon temperature which comprises mixing finely divided platinum black with a temporary binder, spreading a thin film of the mixture on a smooth, plane surface, mixing finely divided high resistance-temperature coefficient semiconductive material and finely divided platinum black with a temporary binder, spreading a thin film of this mixture on the platinum mixture film, mixing finely divided high resistance-temperature coefficient semiconductive material with a temporary binder, spreading a thin film of this mixture on the platinum-semiconductive material mixture film, spreading another platinum-semiconductive material mixture film on the semiconductive film, spreading another platinum film on the platinum-semiconductive material mixture film, drying the sheet comprising the superposed films, removing the sheet from the plane surface, dividing the sheet into small pieces, and heat treating the pieces first at a moderate temperature to remove the temporary binder and then at a high temperature to consolidate the finely divided material into a self-sustaining resistor.

8. The method of making resistor elements that comprises mixing finely divided metal particles with a temporary binder, applying a thin film of the mixture to a smooth, flat plate, mixing finely divided resistance material with a temporary binder, spreading a film of the resistance material on said metal mixture film, removing the sheet comprising the superposed films from the plane surface, and heat treating the sheet to remove the temporary binder and consolidate

the finely divided material into a self-sustaining resistor.

9. The method of making resistor elements that comprises mixing finely divided resistance material and finely divided metal particles with a temporary binder, applying a thin film of the mixture to a smooth, flat plate, mixing finely divided resistance material with a temporary binder, spreading a film of the resistance material on the resistance-metal mixture film, removing the sheet comprising the superposed films from the plane surface, and heat treating the sheet to remove the temporary binder from the layers and to consolidate the finely divided material into a self-sustaining resistor.

10. The method of making resistor elements that comprises mixing finely divided metal with a temporary binder, spreading a film of the mixture on a smooth, plane surface, mixing a finely divided resistor material with a temporary binder, said binders being mutually insoluble, spreading a film of the resistor material on said metal mixture film, drying the sheet comprising the superposed films, removing the sheet from the plane surface, and heat treating the sheet to remove the temporary binder and to consolidate the finely divided material into a self-sustaining resistor.

11. The method of making resistor elements that comprises mixing a finely divided metal with a temporary binder, spreading a film of the mixture on a smooth plane surface, mixing a finely divided mixture of metal and resistor material with a temporary binder, said binder being mutually insoluble with that binder of the metal mixture, spreading a film of the metal-resistor mixture material on said metal mixture film, mixing a finely divided resistor material with a temporary binder, said binder being mutually insoluble with that of the metal-resistor mixture material, spreading a film of the resistor material on said metal-resistor mixture film, drying the sheet comprising the superposed films, removing the sheet from the plane surface, and heat treating the sheet to remove the temporary binder and to consolidate the finely divided material into a self-sustaining resistor.

12. The method of making thin flake resistor elements which comprises laying down a plurality of superposed fluid films including an electrode film and an adjacent resistor film on a surface, drying each film prior to laying the next film on it, dividing the flake composed of the dried superposed films into sections of the desired shape and area, and heat treating the sections to form them into self-sustaining resistor elements.

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