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ELECTRICAL RESISTANCE DEVICE AND METHOD OF MANUFACTURE THEREOF

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FIG. 1

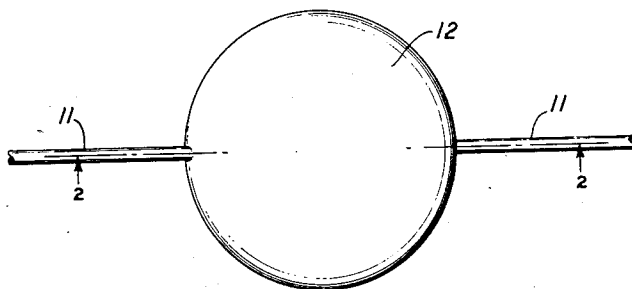
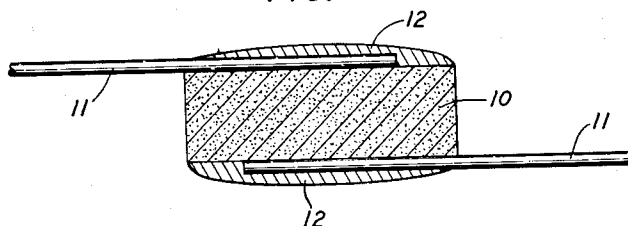


FIG. 2



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Application May 17, 1939, Serial No. 274,169

8 Claims. (Cl. 201-76)

This invention relates to electrical resistance devices and the manufacture thereof and more particularly to the fabrication of small resistor units having a negative temperature-resistance coefficient.

In the production of small resistor units having marked resistance-temperature coefficients, it has been found difficult to predict the ultimate resistance characteristics of the units upon the basis of the characteristics of the resistance materials employed. It has been found, for example, that resistor units including oxidic semiconductive materials may have specific resistance and resistance-temperature coefficients which are not predictable from a knowledge of these characteristics of the materials, and which are not logically correlated with the known characteristics of the materials.

One object of this invention is to enable the fabrication of resistor units including oxidic semiconductive materials which will have resistance and resistance-temperature characteristics corresponding to those of the materials employed.

Another object of this invention is to facilitate the manufacture in quantity of resistor units having similar desired resistance characteristics.

One feature of the invention resides in pressing finely divided oxidic materials into small uniformly dense resistance bodies.

In accordance with another feature of the invention, small amounts of waxy material are added to the oxidic material before pressing.

A further feature of the invention resides in the application of conductive leads to the resistor units after firing, thereby obviating the necessity of employing expensive highly refractory conductors and avoiding undesirable reaction between the conductors and the resistance material while firing.

The invention and the foregoing and other features will be understood more clearly and fully from the following detailed description with reference to the accompanying drawing in which:

Fig. 1 is a plan view of an illustrative form of resistor unit made in accordance with this invention; and

Fig. 2 is a sectional view taken on line 2-2 of Fig. 1.

An oxidic semiconductor of definite composition prepared under known conditions possesses a definite specific resistance and temperature coefficient of resistance. It is possible to duplicate these values repeatedly by reproducing the conditions under which it is prepared; but if altera-

tion is made in the process of production, it has been observed that the resistance and the temperature coefficient may assume new values. If the composition is intentionally changed prior to heat treatment or if the heat treatment is one giving rise to a different chemical equilibrium, then the observed values of resistance and resistance-temperature coefficient may be regarded as specific characteristics for a definite material; but if the change in process is simply one which results, for example, in a more porous material, then the observed properties are not necessarily those specific to a particular substance, but they may be spurious. A case in which the latter appears to be true arises when very small resistor units of semiconductive material are prepared by some of the known methods. As has been hereinbefore noted, difficulty has been experienced in obtaining a logical correlation between the resistance characteristics of the material and those of the small units made therefrom.

The differences in the resistances might be attributed, at least in part, to differences in porosity due to different methods of preparation. This, however, does not account for differences in temperature coefficients of resistance. In some types of units, the contact resistance may be a function of temperature, thus affecting the overall resistance-temperature coefficient of the unit. The method of preparation in accordance with this invention avoids several of the difficulties heretofore encountered and enables production of very small resistor units having expected resistance properties.

Referring now to the drawing, 10 is a plate or disc of pressed oxidic material having conductive leads 11 attached to opposite faces by a fused metallic medium 12, such as silver formed from a silver paste by heat treatment. Such a unit has a negative temperature-resistance coefficient and a non-linear current-voltage characteristic.

To prepare plate or disc-type resistors, such as shown in the drawing, a die of proper configuration may be employed for the forming operation. Where more than one metal oxide is employed, suitable quantities thereof, in a finely divided state, are intimately mixed. The oxides employed and the proportions thereof that are combined depend upon the characteristics desired in the completed unit or units. The mixed oxides are combined with a small quantity of a waxy material which is disseminated throughout the mixture. One suitable way of doing this is to dissolve the waxy material in a solvent such as carbon tetrachloride or petroleum ether and mix

it with the oxide. The solvent evaporates leaving the waxy material dispersed throughout the oxide. A preferred waxy material comprises a mixture of paraffin and carnauba wax.

- 5 A definite quantity of the mix is measured into the die cavity and a pressure of about 6,000 pounds per square inch is applied thereto. The pressed piece is removed from the die and fired at a temperature ranging from 450° C. to 1500° C., depending upon the materials employed and the resistance properties desired. A boat or receptacle of refractory material, such as Alundum (Al₂O₃) or platinum, may be employed to carry the piece or pieces during firing. After firing,
- 10 conductors, such as copper or nickel wire, are attached to the flat surfaces of the pieces. A paste of silver has been found particularly suitable for this purpose. The pieces are then heated to about 500° C. which firmly embeds the conductors
- 15 in a silver layer contiguous with and firmly adherent to the oxidic material. The completed unit may be mounted in a glass or other suitable envelope for its protection in use.

Units of various sizes may be made in accordance with the process of this invention; but, as indicated, it is particularly useful in the fabricating of very small units. For example, bodies, such as discs or short cylinders, having a volume as small as 1×10^{-5} cubic inches have been successfully fabricated. After contacts have been

- 20 added, these very small units exhibit the same resistance characteristics as relatively large bodies or portions of the same resistance material.
- Various oxidic materials may be employed in the making of resistor units in accordance with this invention. Two suitable materials comprise mixtures of iron and manganese oxides or manganese and nickel oxides, as disclosed in the application Serial No. 274,114, filed May 17, 1939, of
- 25 Richard O. Grisdale. As pointed out in that application, the above-noted materials form manganese-iron and nickel-manganese compounds under heat treatment.

The compound NiMn₂O₄ has a specific resistance at 0° C. of 25,000 ohm centimeters and a "half temperature" of 15° C. between 0° C. and 250° C. The term "half temperature" may be defined as the temperature interval over which the resistance is doubled or reduced by half. A plurality of small units about 0.035 inch in diameter and from 0.01 to 0.07 inch in thickness made from nickel and manganese in such proportions as to form the compound NiMn₂O₄ under heat treatment were each found to have a specific resistance of substantially 25,000 ohm centimeters at 0° C. and a "half temperature" of 15° C. between 0° C. and 25° C. Similar results were obtained with very small units made from manganese and iron. The resistance characteristics of these

- 30 units were substantially the same as for the compound, manganese ferrite.
- Because of the uniformity of the units made in the foregoing manner, the relation of resistance to thickness is linear. Moreover, if a curve of resistance vs. thickness at a given temperature be plotted and extrapolated, it passes through the origin, indicating that the effect of the contact resistance is negligible. Furthermore, measurements made at other temperatures exhibit the
- 35 same proportionality and, since all extrapolations of curves plotted from these measurements pass through the origin, the contact resistance is independent of temperature.

The high degree of reproducibility of resistance units made in accordance with the fore-

going process greatly increases the availability of such units for various uses in electrical circuits.

Although an illustrative embodiment of the invention has been disclosed in the foregoing, it will be understood that it is but illustrative and that various modifications may be made therein without departing from the scope and spirit of this invention as defined in the appended claims.

What is claimed is:

1. The method of making an oxidic resistor unit, having a volume in the order of 1×10^{-5} cubic inches and a specific resistance and resistance-temperature coefficient substantially the same as that of the resistance material employed that comprises mixing at least one of the oxides of metals with a small amount of waxy material, placing a measured quantity of the mixture in a die cavity, applying pressure to the mixture to solidify it into a self-sustaining body, removing the body from the die, heat treating said body at a temperature from 450° C. to 1500° C., attaching conductive leads to the body with a metal paste, and heating to bond the leads to the body.

2. The method of making an oxidic resistor unit, having a volume in the order of 1×10^{-5} cubic inches and a specific resistance and resistance-temperature coefficient substantially the same as that of the resistance material employed that comprises mixing at least one of the oxides of metals with a small amount of waxy material, placing a measured quantity of the mixture in a die, applying a pressure of about 6,000 pounds per square inch to the mixture to solidify it into a self-sustaining body, removing the body from the die, heat treating said body at a temperature from 450° C. to 1500° C., attaching conductive leads to the body with a metal paste, and heating to bond the leads to the body.

3. The method of making an oxidic resistor unit, having a volume in the order of 1×10^{-5} cubic inches and a specific resistance and resistance-temperature coefficient substantially the same as that of the resistance material employed that comprises mixing at least one finely divided oxide of metal with a waxy material, placing a measured amount of the mixture in a die, applying a pressure of about 6,000 pounds per square inch to the mixture to solidify it into a self-sustaining body, removing the body from the die, heat treating it in air at about 1250° C., attaching conductive leads to the body with silver paste, and heating to about 500° C. to bond the leads to the body.

4. The method of forming an oxidic resistor unit, having a volume in the order of 1×10^{-5} cubic inches and a specific resistance and resistance-temperature coefficient substantially the same as that of the resistance material employed that comprises mixing finely divided oxides of metallic elements with a small amount of wax, charging a die with the mixture, applying a pressure of about 6,000 pounds per square inch to the mixture to form it into a dense body, removing the body from the die, heat treating said body at about 1250° C., attaching conductive leads thereto with a metallic paste, and heating to bond the leads to the body.

5. The method of making an oxidic resistor unit, having a volume in the order of 1×10^{-5} cubic inches and a specific resistance and resistance-temperature coefficient substantially the same as that of the resistance material employed that comprises mixing finely divided oxides of metal with a small amount of paraffin and car-

nauba wax, charging a die with a measured quantity of the mixture, pressing the mixture at about 6,000 pounds per square inch into a dense body, removing the body from the die, firing it in air up to about 1250° C., attaching conductive leads to appropriate surfaces of the body with silver paste, and heating to about 500° C. to bond the leads to the body.

- 5 6. The method of making a resistor unit that
10 comprises dissolving a waxy material in a highly
volatile solvent, thoroughly mixing the dissolved
waxy material with finely divided oxidic material
15 having known resistance characteristics, allowing
the solvent to evaporate until the mixture is
dry, charging a die with a measured quantity of
the dry mixture, applying pressure to form a
compact body, removing the body from the die,
and heat treating it at a temperature ranging
20 from 450° C. to 1500° C., depending upon the

oxidic material used and the final resistance desired.

7. The method of making a resistor unit that
comprises dissolving paraffin and carnauba wax
in carbon tetrachloride, thoroughly mixing the
dissolved material with finely divided oxidic material, allowing the solvent to evaporate until the
mixture is dry, pressing a measured quantity of
the mixture to form a compact body, and heat
treating said body at a temperature of about
1250° C.

8. The method of making a resistor unit that
comprises dissolving paraffin and carnauba wax
in petroleum ether, thoroughly mixing the dissolved material with finely divided oxidic material, drying the mixture, pressing a measured
quantity of the mixture to form a compact body,
and heat treating said body at a temperature of
about 1250° C.

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