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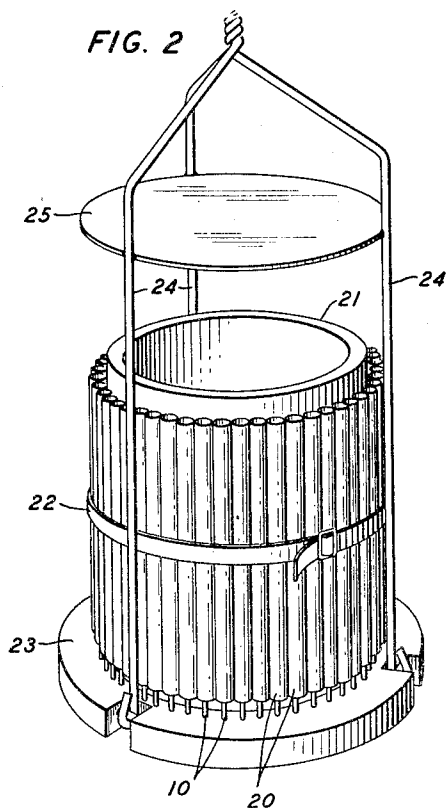
OXIDE RESISTORS AND METHOD OF MAKING THEM

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FIG. 1



FIG. 2



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OXIDE RESISTORS AND METHOD OF
MAKING THEM

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4 Claims. (Cl. 201—63)

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This invention relates to resistors and to methods of making them and more particularly to the type of resistors which are called "thermistors." A "thermistor" is a resistor, the resistance of which varies greatly with changes in temperature, and such a resistor is intended when the term "thermistor" is used in this specification or in the appended claims.

Thermistors have been made from various semiconductive materials including sintered mixtures of various oxides. One oxide combination which has been found useful is zinc ferrite composed of the combined oxides of zinc and iron. Since both the resistivity and the temperature dependence of resistivity of zinc ferrite are highly dependent upon oxygen content, considerable attention, during manufacture, must be paid to time, temperature and rate of cooling involved in the heat treatment.

An object of this invention is to make zinc ferrite resistors that are uniform in their resistance and their dependence of resistance upon temperature.

One feature of this invention resides in assuring a uniform temperature and uniform oxygen access among a plurality of thermistors during sintering.

Another feature of this invention lies in preventing distortion of relatively thin thermistor rods during heat treatment.

The foregoing and other objects and features of this invention will be more fully and clearly understood from the following description in connection with the appended drawing in which:

Fig. 1 shows in section a thermistor illustrative of one embodiment of this invention and;

Fig. 2 shows in perspective one form of apparatus that may be used in the heat treatment of rods of thermistor material.

The thermistor shown in Fig. 1 comprises a rod 10 of zinc ferrite to the ends of which are secured terminals 11 and 12. The thermistor rod and the terminals are secured together in abutting relation by wrappings of fine wire 13 and 14, respectively. The fine wires may be secured to the thermistor rod and terminals in any suitable manner. For example, attachment to the thermistor rod may be by means of a heat cured silver material, such as silver oxide and lavender oil which metallizes at about 500° C. The portions of wire wrapped on the terminals may be spot welded at several points. The wires 13 and 14 may be of platinum or other suitable material.

The thermistor rod is the enclosed in an en-

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velope such as the glass tube 15 which is fused around the rod and the terminals. The structure is such that the thermistor and the inner ends of the terminals are embedded in glass.

Zinc ferrite may be obtained by combining the oxides ZnO and Fe₂O₃ in the proportions called for by the equation $ZnO + Fe_2O_3 = ZnFe_2O_4$. The proportions are substantially two parts of iron oxide to one part of zinc oxide. With materials having an approximate purity of 99.5 per cent, 157.0 grams of Fe₂O₃ and 81.38 grams of ZnO have been used successfully.

Thermistor rods such as 10 may be made by mixing the iron and zinc oxides in the proportions to form zinc ferrite with water in a colloid mill until sufficiently blended. About ten minutes has been found suitable. The water is then removed and the dried material reduced to powder.

The powdered oxide mixture is mixed with a temporary binder such as isobutyl methacrylate and a suitable volatile solvent such as xylol or naphtha. Proportions which have been used successfully are 40 grams powdered oxide, 4 grams methacrylate and 60 cubic centimeters of volatile solvent. These combined materials are mixed while heat is applied to remove or reduce the amount of the solvent. The mixing and heating is carried on until the mass is relatively plastic.

The plastic mass of oxides and methacrylate is extruded into thin rods. The consistency of the material should be such that a rod of uniform diameter is made. Six to eight inch rods of 0.016 inch diameter have been made. These are dried at about 110° C. and may be broken into lengths of about 1½ inches for sintering.

The sintering is carried out in an apparatus such as shown in Fig. 2. The rods 10 are supported in tubes or rod holders 20 of a refractory material, such as aluminum oxide. The rod holders 20 are secured around a supporting body such as the cylinder 21 which also may be of aluminum oxide as by a band 22 which may be of platinum.

The cylinder 21 is placed on the base member 23, which may be of refractory material such as zirconium silicate. For convenience of handling, the plate 23 may be provided with supports 24 of platinum or like suitable material. A reflector 25 also of platinum or like material may be secured to supports 24 above cylinder 21 to aid in concentrating heat on the work.

The tubes 20 are secured to the cylinder 21 in such positions that their lower ends are spaced from the plate 23, the spacing between tubes 20

and plate 23 allowing the ambient atmosphere to flow through the tubes during firing, thereby providing a uniform atmosphere along the length of each rod 10. The tubes and cylinder, due to their storage and distribution of heat, also assure a substantially uniform temperature both along and among the rods. During the early stages of heat treatment the rods tend to soften, but distortion and bending are prevented by the supporting tubes.

The loaded fixture is placed in a furnace and the rods sintered in air. With a thermistor material consisting of about two-thirds iron oxide and one-third zinc oxide, complete sintering has been obtained in about 30 minutes at 1300° C. The methacrylate binder is driven off during the early stages of heating. The rods being so thin, no particular precautions appear necessary in removing the temporary binder, as may be necessary with more massive elements.

Zinc ferrite is an excess semiconductor in which the conductivity increases with decrease in oxygen content. Since oxygen tends to diffuse out at high temperature, the conductivity may be too high after sintering. This may be remedied by a heat treatment at a lower temperature allowing some oxygen to return to the material. In order to keep the oxygen content constant the thermistor is sealed in glass. A glass tube is sealed over the thermistor for its whole length, so that it is essentially a glass coating. The sealing takes place at a temperature higher than normal operating temperature, but lower than the sintering temperature, and oxygen is taken up, thereby decreasing the conductivity. This necessary heating may bring the conductivity down to the required value. If it does not, an intermediate heat treatment may be used to bring the conductivity to such a value that a further change during sealing will make it correct.

Although this invention has been disclosed by means of an exemplary embodiment thereof, it is not intended as limiting the invention, the scope of which is defined by the appended claims only.

What is claimed is:

1. The method of making resistor elements from semiconductive material, the resistance of which is highly dependent upon oxygen content that comprises preparing a plastic mixture of such material, forming elongated rods from this mixture, mounting the rods in a vertical position, supported at their lower ends, providing lateral constraint for the vertical rods to prevent their bending while plastic, and heat treating the rods while permitting free circulation of ambient atmosphere around said rods.

2. The method of making a long, zinc ferrite resistor rod of the order of 16 mils diameter, that comprises mixing oxides of iron and of zinc in the approximate proportions of two parts iron oxide to one part of zinc oxide with a temporary

binder and a volatile solvent, removing sufficient solvent to render the mixture relatively plastic, forming long rods from this plastic mixture, separating the rods into shorter resistor length portions, placing these portions in a vertical position supported at their lower ends, providing lateral constraint for the vertical rods to prevent bending while plastic, subjecting the rods to a temperature of about 1300° C. for approximately 30 minutes in a freely circulating ambient atmosphere to drive out the temporary binder and to sinter the rod portions, and supplying each rod portion with terminal means.

3. The method of making resistor elements of oxidic semiconductive material, the resistance of which is highly dependent upon oxygen content, that comprises preparing an oxide mixture, forming long slim rods from the mixture, supporting the rods axially in open end vertical refractory tubes having diameters sufficiently greater than those of the rods to permit the free circulation of ambient atmosphere around said rods while preventing them from bending while plastic, and heat treating the rods in an ambient atmosphere containing oxygen.

4. The method of making resistor elements from semiconductive material, the resistance of which is highly dependent upon oxygen content, that comprises preparing a plastic mixture of such material with a temporary binder, forming slim, elongated rods from this mixture, inserting said rods in individual rod-supporting cylinders of a fixture that prevents bending of the rods while they are plastic, allows free circulation of ambient atmosphere around and induces uniform heat distribution over said rods, and subjecting the rods and fixture to heat to remove the temporary binder from and to uniformly sinter the rods.

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