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HIGH TEMPERATURE COEFFICIENT RESISTORS
AND METHODS OF MAKING THEM
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2,674,583

FIG. 1

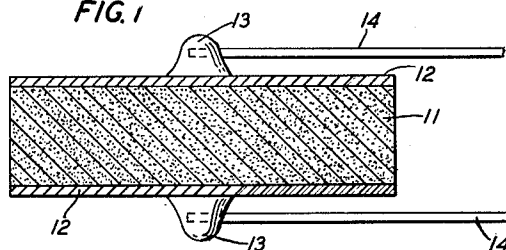


FIG. 2

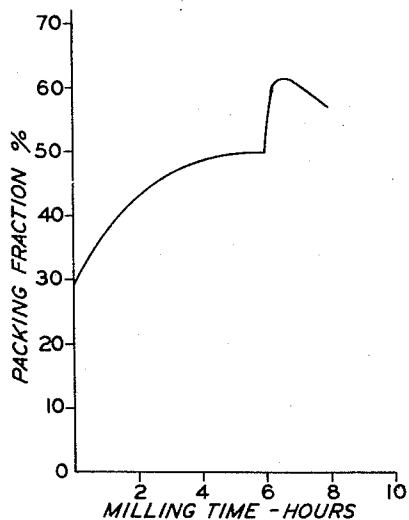


FIG. 3

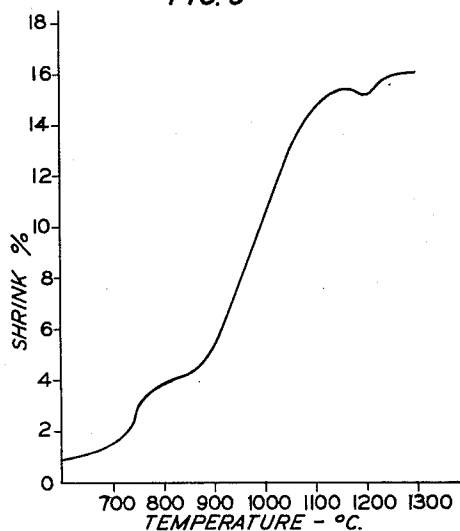
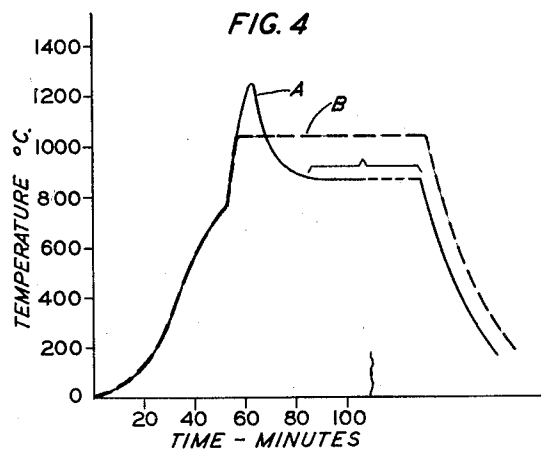


FIG. 4



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HIGH TEMPERATURE COEFFICIENT RESISTORS AND METHODS OF MAKING THEM

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6 Claims. (Cl. 252—490)

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

Thin-film resistors, particularly resistors of materials whose resistance varies greatly with temperature, often referred to as "thermistors," have been employed as bolometers for the detection of infra-red rays and as high speed thermally sensitive devices of the type disclosed in J. A. Becker Patent 2,414,792 issued January 28, 1947. The resistive films that are employed in such devices have heretofore been made up in accordance with the processes disclosed in Patent 2,414,793 issued January 28, 1947, to J. A. Becker and H. Christensen and application Serial No. 101,778 filed June 28, 1949, of the same inventors, now Patent No. 2,633,521, of a granular material having a maximum particle size about one-hundredth the desired thickness of the completed flake mixed with a temporary binder which is spread in a thin film on an optical flat and dried. The dried film is then taken from the flat and fired at from 1100° to 1450° centigrade depending on the material.

This process, while having definite advantages, has been found to require rather rigid controls. One of the problems encountered is a tendency for the flakes, particularly the thinner ones, to curl during the sintering process. This may result from uneven shrink in the top and bottom portions of the flake during firing due to a slight dissimilarity in density between those portions in the unfired flake. The density variations are caused by the settling out of the particles in the fluid mixture when it is first spread in a film. Further difficulty has been experienced in that the results of some production runs may have characteristics which vary beyond close limits for the devices in which the resistors were to be used, these characteristics including the noise, specific resistivity and temperature coefficient of resistance of the unit and the stability thereof.

One object of this invention is to facilitate the manufacture of thin-film resistors.

Another object is to reduce the noise and improve the stability, reproducibility and uniformity of such film resistors.

A further object is to reduce the tendency of thin-film resistors to curl during firing.

One feature of this invention resides in producing a non-porous, homogenous resistor film from a mixture of two discrete ranges of particle sizes of resistor material.

Another feature of this invention pertains to

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forming the fluid mixture of resistance material from which the thin-films are produced by first mixing a long chain polymer temporary binder with particles of resistor material which are of such dimensions relative to the length of the polymer chain that a gel mixture forms, the gel resulting from the extension of a polymer chain from one particle to an adjacent one. To this mixture are added resistor particles of a larger size which are held in suspension during the production of the resistor film by the gel thereby providing a film of uniform density.

The above noted and other objects and features of this invention will be more clearly and fully understood from the following detailed description of an exemplary embodiment thereof taken in connection with the appended drawing in which:

Fig. 1 is a sectional view of one form of thin-film resistor constructed in accordance with this invention;

Fig. 2 shows a plot of the volume occupied by resistor particles in an unfired film as a function of the milling time in one method of producing these resistors;

Fig. 3 is a curve showing the relationship between the per cent shrink due to firing resistor flakes and the firing temperature, and

Fig. 4 is a curve of temperature plotted against time showing firing cycles employed for film resistors.

The curves and the specific process, the description of which follows, apply to a resistor flake composed of manganese and nickel oxide combined in the atomic ratio of manganese to nickel between 2.0 and 4.0 as disclosed in Patent 2,258,646 issued October 14, 1941, to R. O. Grisdale. It is to be understood, however, that other combinations of materials are to be included as within the scope of the invention and that the description pertains to this composition for illustrative purposes only. Such other materials include one or more of the oxides of manganese, nickel, cobalt, copper, iron, zinc and uranium.

In preparing a mixture for resistor flakes, 6 grams of thermistor material having a particle size of the order of 1 to one-half micron diameter (nickel and manganese oxide can be prepared in this size range by calcining their carbonates at 600° centigrade for 2 hours) are placed in a high speed ball mill with 6 grams of a temporary binder and 12 cubic centimeters of solvent and milled to the order of one-hundredth their original particle size, this requiring 6 hours of milling when nickel manganese oxide material is being

prepared. Seven grams more of the resistor material having a particle size of the order of 2 microns (nickel and manganese oxide of this size being conveniently prepared by calcining their carbonates at 900° centigrade for 16 hours) are then added to the mix which is then milled for an additional hour making a total milling time of 7 hours. A thin-film of this prepared mixture is then spread on a smooth surface such as an optical flat to a thickness of several microns. This may be done by spraying or preferably by spreading the mixture over a portion of the surface by means of a properly spaced straight edge. The film and supporting flat are then placed in a dust-free atmosphere and the volatile solvent allowed to evaporate.

The dried film is then removed from the optical flat, for example by soaking it with water at 25° centigrade, thus causing it to expand and shear loose from the glass surface. It is then dried and cut into the bits or flakes of suitable size and shape for incorporation into the electrical devices in which it is to be used by some suitable means such as a shear or by cutting with a thin knife or razor blade.

The resulting green or uncured flakes even when left in large area pieces are extremely tough and can be handled with no special precautions. Further these flakes may be made up in large batches and stored for long periods without detrimental effects thus greatly facilitating their manufacture. Another advantage of this toughness and stability is that the uncured flakes may be readily sold and shipped to the manufacturers of devices employing this type of electrical element leaving the firing and sintering process for them, since the particular firing conditions in some cases determine the electrical characteristics of the elements.

Each flake or bit of film is then placed on a flat surface of refractory material which may be a sintered slab of Alundum. Heretofore, uniform distribution of heat across the flake has been necessary to produce films of prescribed flatness, and for this purpose it has been specified that the supporting surface be of high heat conductivity and large area relative to the flake or film. While these conditions are desirable in the treatment of these flakes made of two particle sizes, acceptable flatness can be attained without the expensive equipment of the old processes, namely, platinum plates coated with Alundum which have to be recoated after each firing. For example, a solid plate of Alundum can be used for this purpose and lapped clean and flat after each firing.

After mounting the flakes a plurality of these carrier surfaces may be stacked with suitable intermediate spacers to prevent mechanical constraint of the flakes during firing and may then be placed in a furnace for removal of the temporary binder and sintering. Where the binder is polyvinyl butyral it can be driven off by depolymerization by gradually raising the temperature to about 400° centigrade. After the binder is removed the temperature may be raised according to the curve of Fig. 4 up to a temperature of from 1000° to 1300° centigrade in an interval of about an hour and then gradually cooled to a soak temperature of about 860° centigrade and held there for 16 hours after which it is permitted to cool in the furnace. Alternatively the temperature may be dropped from the peak temperature at the cooling rate of the furnace without a low temperature soak, or a lower peak

sintering temperature employed, for example 1030° centigrade with nickel-manganese oxide material, with a soak of from 16 to 64 hours at the peak temperature. The major factor which is to be considered in determining which heat treatment will be employed is the stability of the resulting device, this being greater for a long soak. This gives a stoichiometric composition of the material, higher temperatures decrease the oxygen in the material and thereby increase in the resistance of the material.

The flake 11 thus formed is supplied with electrodes 12 as shown in Fig. 1. These electrodes may be made by applying a metallic paste to the two surfaces of the flake and heat-treating the paste to solidify and bond it thereto. Another means of applying electrodes to flake resistors is disclosed in the application Serial No. 101,778 of J. A. Becker and H. Christensen filed June 28, 1949, now Patent No. 2,633,521, wherein a finely divided noble metal is mixed with a suitable temporary binder and solvent therefor, and a composite flake is built up by applying a thin layer of electrode material to a flat surface, drying this layer, applying a layer of resistor paste over the electrode layer, drying this layer, applying a second electrode layer and firing the resulting sandwich to produce a structure like that shown in Fig. 1. Leads 14 are then attached to the electrode layers by drops of a soft glass platinum powder mixture to complete the unit which may then be mounted in a suitable casing (not shown).

Referring now to the details of the preparation of the mixture, the one to one-half micron range of particle size is specified in view of the particular mill employed, namely a cubical steel container of inside dimensions of approximately one and one-half inch employing 130 grams of one-sixteenth inch diameter and 20 grams of three-thirty-seconds inch diameter chrome steel balls as the working media. The particles are thus crushed by an inertia milling, the container reciprocating through a two-inch amplitude at the rate of 500 strokes per minute.

The primary action of the mill is to crush the particles to small dimensions and to permit their surface to be wetted with the temporary binder before an adsorbed layer of air or other gap can form on their surface to decrease the density of the final mixture. Further action in regard to the surface gases is thought to be that of abrading the existing adsorbed layer off both the large and small particles in the mix. When the smaller particles are reduced to the order of 10⁻⁶ centimeters diameter, and the temporary binder is properly chosen, for example, one of a polyvinyl butyral syrup containing the following proportions by weight: 18.7 per cent polyvinyl butyral plastic, 65.3 per cent ethyl alcohol, 12 per cent isopropyl alcohol and 4 per cent amyl acetate, a suitable solvent for which may be made up in the following proportions by volume, 50 per cent amyl acetate and 50 per cent methyl alcohol, the polymeric chain structure in the binder is such that a single chain can wrap around adjacent particles and cause a gel structure to be set up. This gel has sufficiently high viscosity to allow comparatively large particles (those of 10⁻⁴ centimeters diameter being exemplary) to be held in suspension during the smearing and drying operation of the film.

Other suitable binders include isobutyl methacrylate, cellulose acetate butyrate and the like type of long chain carbon to carbon valence

bond polymers which are soluble in an organic solvent and are non-halogenated. The essential characteristics of these binders are that they have long polymer chains, do not chemically affect the resistor material, leave no residue after heating to a temperature below that at which the material sinters, have a high mechanical strength, and can be removed from the flat surface on which the resistor films are dried.

The larger particles in the mixture serve as "seeds" into which some of the smaller particles pass during the sintering process. Their uniform distribution throughout the flake greatly increases the uniformity of shrink in the firing process. Another effect of the use of large particles in conjunction with the smaller ones is that they also produce a somewhat higher unfired density in the mixture which is reflected in less shrink and consequently less chance for distortion in the firing process.

The aforementioned tendency toward warping due to uneven distribution of the larger particles and hence uneven densities throughout the thickness of resistor flake is materially reduced by the production of small particles by milling for 6 hours as outlined above. When the particles are of the order of 10^{-6} centimeters or less in size and a binder having a polymer chain of the order of 500 to 1500 angstroms length is employed, the extension of the polymer chain from one particle to another adjacent one occurs readily while such a structure does not form when the particles are somewhat larger, say tenfold.

The addition of the larger particles and their subsequent milling for about one hour to uniformly distribute them throughout the mixture and to remove the adsorbed surface layer of gas from them increases the density of the uncured material considerably as is disclosed by the hump in the curve in Fig. 2 which shows the portion of the unfired flake volume occupied by thermistor material as a function of the milling time. When one particle size range is used, previous measurements show that the packing fraction does not exceed a value of 52 per cent and this is obtained only after 15 hours of milling. The addition of the larger particles therefore produces about a 10 per cent increase in the packing fraction and consequently a material increase in the density of the over-all mixture.

Other effects of using two particle sizes in the resistor material mix are apparent in the firing cycle of the material. The plot of per cent shrink, given by

$$100 \times \frac{L_0 - L}{L_0}$$

against firing temperature is shown in Fig. 3. L_0 is the length of a unit edge before firing and L is the length of that edge after firing. The manganese-nickel oxide plates employed to obtain this data were approximately 11.5 microns thick in the unfired state so that they shrank on complete firing to about 10 microns thick. The curve of Fig. 3 shows the shrink resulting from heating a test sample in accordance with the firing cycle curve shown on Fig. 4 to the desired temperature and then rapidly cooling to the ambient temperature.

Micrographic studies of the samples employed in obtaining the curve of Fig. 3, which were immediately cooled on reaching the temperature in question and therefore represent a transient state, have been made to aid in interpreting that curve. Shrink in the temperature range of 700

to 850° C. is attributable to the incorporation of the smaller size particles in their neighbors and to a lesser extent to the adsorption of the smaller particles in the larger particles. Pores or voids are evident in samples fired to the temperatures however these disappear to a large extent when the material is taken further along the curve into the range of 850 to 1100° C. Up to about 1000° C. only a small change in size occurs in the larger particles but they do develop crystallographic surfaces as the temperature increases. The smaller particles, which also tend to develop crystallographic surfaces, grow rapidly in this range until they are indistinguishable from the large particles. Voids, created in part by the adsorption of the small particles in larger ones, are reduced to a large extent thus resulting in a large shrink at these higher temperatures. The effects observed above about 1100° C. are attributable to grain growth, which is rapid at those temperatures, and to recrystallization processes neither of which are associated with the original particle size of the green material.

Heat treatments employed in producing flakes used in resistors, rather than for the crystal studies discussed above, include soak periods at elevated temperatures which result in a further reduction of the voids and therefore a better contact between the particles and better electrical characteristics. In view of this reduction of voids a greater shrink occurs in these bodies and thus the characteristic of shrink against temperature for any treatment including a soak will fall to the left of the curve in Fig. 3. Two firing cycles including soak periods are shown in Fig. 4. That cycle represented by curve B is of particular interest in the production of flake resistors of nickel-manganese oxide having 10^{-6} cm. and 10^{-4} cm. diameter particle ranges since it has been found that a heat treatment of that material to a temperature of about 1030° C. and a soak of 16 hours at that temperature results in a body having substantially no pores when examined under conditions providing a resolution of points that are closer than 5×10^{-7} cm.

Sintering of this type of mixture has been found to take place at lower temperatures than for similar materials produced by the old calcining processes. This lowering of the sintering temperature is explained by the higher free energy associated with the large surface area of the fine particles in the mix and in the heating cycle used. Milling produces an increase in the free energy of the powder by virtue of the fact that it exposes more area as a given weight of the powder is subdivided. The area and hence the surface-free energy increases with a decrease in particle size so that in the case of the fine particles of resistance material of the order of 10^{-6} centimeters diameter which is of the order of 50 to 100 atom diameters the free energy of these particles is of the order of 1 or 2 per cent of the heat of sublimation. This amount of energy is larger than is normally available to commercially sintering processes. One advantage of being able to sinter resistor materials at these lower temperatures is that the final product is more easily controlled since the higher sintering temperature formerly necessary were often sufficient to cause an unwanted departure from the stoichiometric composition of the resistor material, which in turn causes a change in the resistance. Another advantage of this lower sintering temperature is the elimination of any tendency for the resistor

bodies to stick to their supporting members and the losses that result therefrom.

What is claimed is:

1. In the method of making a conducting device of metallic oxide material, the step in preparing the uncured material which comprises mixing metallic oxide particles of the order of 10^{-6} centimeters diameter with about an equal quantity by weight of metallic oxide particles of the order of 10^{-4} centimeters diameter and a binder comprising a carbon-to-carbon valence bond polymer which is soluble in an organic solvent, is non-halogenated and has a polymer chain length of at least 500 Angstrom units.

2. In the method of making a thermally sensitive conductive device of a metallic oxide material, the steps in preparing the uncured material comprising mixing metallic oxide particles of the order of 10^{-4} centimeters diameter with about an equal quantity by weight of metallic oxide particles of the order of 10^{-6} centimeters diameter and a binder comprising a carbon-to-carbon valence bond polymer which is soluble in an organic solvent, is non-halogenated and has a polymer chain length of at least 500 Angstrom units, and mechanically working the oxide particles in the liquid binder.

3. In the method of making a thermally sensitive conductive device the steps in preparing the uncured conductive material comprising mixing metallic oxide particles of the order of 10^{-6} centimeters diameter with about an equal quantity by weight of metallic oxide particles of the order of 10^{-4} centimeters diameter and mechanically working the metallic oxide particles in a polyvinyl butyryl syrup having a polymer chain length of at least 500 Angstrom units.

4. A mixture for a thermally sensitive conductive device consisting essentially of metallic oxide particles of the order of 10^{-6} centimeters diameter, metallic oxide particles of 10^{-4} centimeters diameter, each range of particle size being present in about equal quantities by weight, and a binder comprising a carbon-to-carbon valence

bond polymer which is soluble in an organic solvent, is non-halogenated and has a polymer chain length of at least 500 Angstrom units.

5. An uncured metallic oxide material for thermally sensitive conductive devices consisting essentially of metallic oxide particles of the order of 10^{-6} centimeters diameter, a binder of polyvinyl butyryl having a polymer chain length of at least 500 Angstrom units mixed with said particles and metallic oxide particles of the order of 10^{-4} centimeters diameter uniformly dispersed throughout the mixture, each range of particle size in the mixture being present in about equal quantities by weight.

6. The method of preparing semiconductive material which comprises mixing manganese and nickel oxide particles of about 10^{-6} centimeters diameter with about an equal quantity of manganese and nickel particles of about 10^{-4} centimeters diameter and mechanically working the particles in a liquid binder comprising a carbon-to-carbon valence bond polymer which is soluble in an organic solvent, is non-halogenated and has a polymer chain length of at least 500 Angstrom units.

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