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2,329,511

METHOD OF MAKING RESISTORS

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FIG. 1

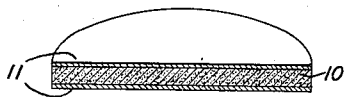
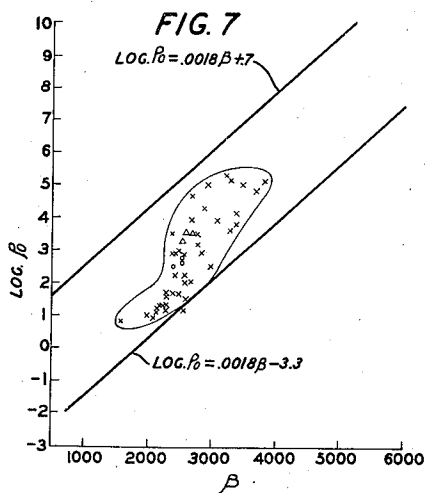
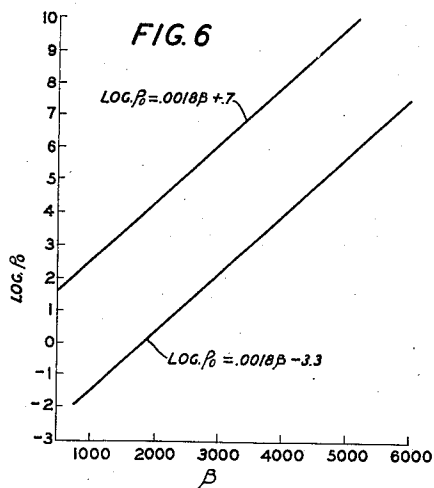
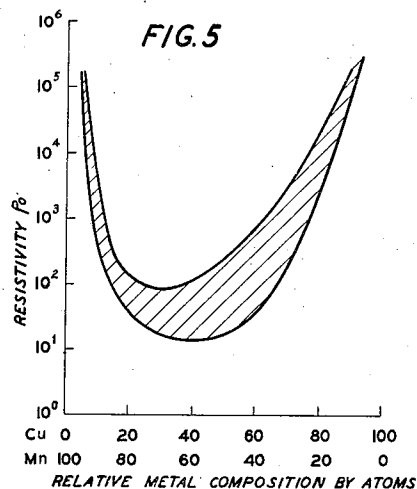
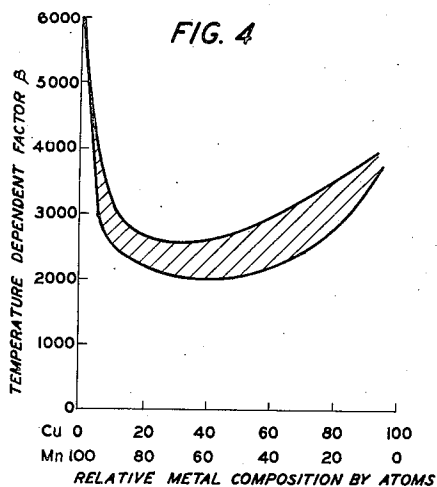
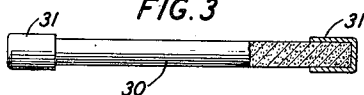


FIG. 2



FIG. 3



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METHOD OF MAKING RESISTORS

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9 Claims. (Cl. 201-76)

This invention relates to resistors and to methods of making them. In some of its more specific aspects it deals with particular ways of processing certain metal-oxygen compositions to obtain desired resistance characteristics therein. More particularly the invention is concerned with various temperature controls of some of the steps of combining the oxides of manganese and copper into resistors or resistance material.

The resistors particularly involved in this invention are those whose resistance varies greatly with changes in temperature and which have, for convenience of terminology been called "thermistors." Where this term is used it will be understood that such a resistor is intended.

Thermistors are generally made from semiconductive materials. Such materials are used because they have relatively high absolute values of temperature coefficient of resistance. These semiconductive materials as the name implies do not conduct current as well as the so-called conductors, since they have a relatively high resistance. One of the problems in making thermistors from semiconductive materials is that of maintaining a high resistance temperature coefficient and at the same time obtaining a resistivity sufficiently low to allow useful currents to flow.

It has been found that various metal-oxygen compositions comprise particularly suitable materials for making thermistors. One series of such compositions contains an oxide of manganese combined with one or more of the oxides of nickel, cobalt or copper. In the making of these thermistors the intimately mixed oxides are heat treated at some temperature in the range 600° to 1450° C. The resistivity of such thermistors may be controlled within certain limits during the manufacture thereof. A considerable difference in resistivity among thermistors may be obtained by variation of the constituent materials. This may comprise using combinations of different oxides and the proportioning of the relative amounts of the metallic element present. The terms "metallic elements," "metals," or like expressions as used in this application, are intended to refer to the metal atoms present in the compositions and not to actual metals.

The resistivity of the completed thermistor may also be controlled to some extent by the atmosphere and temperature of heat treatment. The amount of oxygen in the oxidic composition, even

though it departs from stoichiometric proportions by amounts too small to be detected by the usual methods of chemical analysis, affects its resistivity in a marked manner, and this in turn may be controlled by the atmosphere and temperature of the heat treatment. The temperature coefficient of resistance is also affected by the foregoing factors and there appears to be a relationship between the specific resistivity and the temperature coefficient of resistance.

An object of this invention is to control the ultimate resistivity and the temperature dependence of resistivity of thermistors made from various proportions of manganese and copper oxides.

Another object of this invention is to improve the stability of metal-oxygen compositions that include copper, i. e., copper atoms, as a constituent.

A feature of this invention resides in control of the heat treatment, and more particularly the temperature and cooling rate, of thermistors made from compositions of manganese and copper oxides.

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

Figs. 1, 2 and 3 show various forms, which a resistor made in accordance with this invention may take, the devices being respectively a disc, a short cylinder and a long cylinder or rod.

Figs. 4 and 5 are plots showing respectively the variation of the temperature dependence of resistivity (β) with composition, and the variation of the resistivity at 0° C. (ρ_0), with composition. The units of β are in degrees centigrade.

Fig. 6 is a plot showing the relation between the logarithm of the resistivity at 0° C. ($\log \rho_0$), and the factor β indicating the temperature dependence of the resistivity. The two curves shown are the envelope curves which include points representing these factors for practically all semiconductors that might be used for making resistance material; and

Fig. 7 is a plot of the values of $\log \rho_0$ vs. β which have been observed in studies of the manganese oxide-copper oxide systems of this invention.

As previously indicated there appears to be a relationship between the specific resistivity and the temperature coefficient of resistance of semiconductors. The mathematical expression re-

lating the specific resistivity ρ and the absolute temperature T is as follows:

$$\rho = \text{constant } e^{\theta/T} \quad (1)$$

The temperature coefficient of resistivity α is usually obtained from the relationship

$$\alpha = \frac{1}{\rho} \frac{d\rho}{dT}$$

Applying this equation to (1) there is obtained

$$\alpha = -\frac{\beta}{T^2}$$

In the study of semiconductors the value of β is much easier to use in discussing temperature dependence than α , for the reason that to the degree Equation 1 describes the behavior of the semiconductor, the value of β is a constant and independent of temperature, whereas α is highly dependent upon temperature as may be seen from the last equation above.

For each semiconductor specimen there may be obtained by measurement a specific value of ρ_0 and β , where ρ_0 is the specific resistivity at 0° C. From this pair of values there may be plotted a single point in a $\log \rho_0$ vs. β graph as shown on Fig. 6. If the points for practically all known semiconductors are thus plotted, it will be found that they all lie in a band on the $\log \rho_0$ vs. β graph. On Fig. 6 these various points are not actually shown, but the region in which they lie is indicated by the two envelope curves which are drawn on the graph. An equation for these envelope curves is as follows:

$$\log \rho_0 = .0018 \beta + b \quad (2)$$

where

b for the lower envelope curve is -3.3 and for the upper envelope curve is $+0.7$.

Thus for a given value of β , the value of $\log \rho_0$ can have a variation of 4, which is a 10,000 fold variation in the value of ρ_0 . Otherwise stated, if we know the value of β for a given semiconductor, we can predict that its value of ρ_0 will lie within a band of values such that the highest value in the band divided by the lowest value in the band will be 10,000.

The usefulness of a semiconductor for making thermistors can, to some degree, be determined by the position of its $\log \rho_0$ vs. β point in the plot of Fig. 6. In general semiconductors are most useful for this purpose if they have a low ρ_0 and a high β . In relation to Fig. 6, these values will plot points near the lower envelope curve. The value of b for a given semiconductor, determined from Equation 2, is, in a sense a "figure of merit" for the semiconductor with respect to its usefulness as thermistor material. The best semiconductors will have values of $b=3.3$ and the poorest, values of $b=0.7$.

If a series of semiconducting oxide mixtures are made from two components, such as for example manganese oxide and nickel oxide and the $\log \rho_0$ vs. β points plotted on Fig. 6, the series of values will plot a more or less continuous curve. Thus it is seen that the value of β and ρ_0 is largely determined as soon as the composition is determined. On the other hand it has been found in accordance with this invention that with mixtures of manganese and copper oxides, an appreciable degree of control over the position of the $\log \rho_0$ vs. β point can be exercised by suitable heat treatment of the material. As previously indicated one of the objects of this invention is to affect this control.

Figs. 4 and 5 are plots showing respectively, the variation of the temperature dependence factor of resistivity (β) with composition, and the variation of the specific resistivity at 0° C. (ρ_0) with composition for a manganese oxide-copper oxide system. The bands of values shown represent the spread in such values which may be obtained by variations in heat treatment. As has already been discussed there is a certain dependence between the values of β and ρ_0 , so that one cannot in general arbitrarily select both the value of β and ρ_0 from those shown in the plot of Figs. 4 and 5.

On Fig. 7 is shown a plot of values of $\log \rho_0$ vs. β which have been observed in a study of the manganese oxide-copper oxide system. The region in which all of the observed values lie is approximately outlined. A semiconductor with properties represented by any point within this region can be made by suitable choice of the ratio of manganese to copper atoms and suitable control of the heat treatment. Fig. 7 also shows the envelope curves for practically all semiconductors as discussed in connection with Fig. 6. It is seen that a large portion of the semiconductors made from the combined oxides of manganese and copper have a high "figure of merit" since they lie near the lower envelope curve of Fig. 7.

In making resistors in accordance with this invention, finely divided resistance material may be intimately mixed in any suitable manner and formed into bodies such as discs, cylinders, rods, sheets, tubes or other suitable shapes by pressing, extruding or similar operations.

The bodies may then be heat treated by sintering at a suitable temperature between 600° and 1450° C. and then cooling at a controlled rate. After heat treatment, the bodies may be furnished with electrodes.

Resistors such as 10 and 20 of Figs. 1 and 2, respectively, may be supplied with adherent electrodes 11 and 22, respectively, as follows: A metallic paste, for example, one containing silver or a silver compound, a fusible glass and an organic vehicle, is spread over the flat surfaces and the organic vehicle removed by drying. The resistors are then baked to fuse the glass and bind the silver to the resistor as an adherent metal coating. Silver paste can be made up, in which the glass will fuse and the paste cure at temperatures as low as 475° C.

A rod or stick resistor, such as 30, shown in Fig. 3, may be similarly supplied with electrodes, or metal caps 31 may be employed. The caps may be attached by friction or by means of a suitable conductive cement.

An investigation of resistors of different relative compositions and heat treated at different temperatures within the range 600° to 1450° C. reveals that a relatively high temperature is needed to properly prepare resistors rich in manganese and a lower temperature is needed for those rich in copper. If the temperature is somewhat lower than 1000° C. for manganese rich compositions, the sintering is poor. For copper rich resistors a temperature not much above 1000° C. tends to fuse the material, which is undesirable. Therefore, a temperature of approximately 1000° C. is indicated where the proportions are nearly equal with higher temperatures for more manganese and lower temperatures for more copper.

The rate at which the resistors are cooled after heat treatment also affects the final electrical

characteristics. For manganese rich compositions rapid cooling results in lower values of ρ_0 , β and b than are obtained with slow cooling. A few examples to illustrate this are shown in the following table:

Metal ratio ¹	Heat treating temperature	Cooling rate	ρ_0	β	b
	°C.				
Mn/cu=90/10.	1,100	Rapid....	300	2,400	-1.84
Mn/cu=90/10.	1,100	Slow....	1,900	2,550	-1.32
Mn/cu=90/10.	1,150	Rapid....	600	2,550	-1.82
Mn/cu=90/10.	1,150	Slow....	3,300	2,700	-1.34
Mn/cu=90/10.	1,200	Rapid....	400	2,550	-2.00
Mn/cu=90/10.	1,200	Slow....	3,400	2,600	-1.15
Mn/cu=70/30.	1,100	Rapid....	21	2,300	-2.82
Mn/cu=70/30.	1,100	Slow....	50	2,400	-2.62

¹ This specifies the composition of the semi-conductor. Thus Mn/Cu=90/10 means that the composition of the mixed oxides is such that for every 90 atoms of manganese there are 10 atoms of copper.

In all cases shown in the table above, where the manganese atoms are in excess of the copper atoms, the values of ρ_0 are lower for samples rapidly cooled. The figure of merit (b) is also most favorable for the rapidly cooled samples. For manganese oxide-copper oxide semiconductors which are rich in copper, the reverse characteristics obtain. Thus the slow cooled samples possess the lower values of ρ_0 and more favorable values of b . This is indicated below for one composition.

Metal ratio	Heat treating temperature	Cooling rate	ρ_0	β	b
	°C.				
Mn/Cu=20/80.	1,000	Rapid....	850	2,850	-2.20
Mn/Cu=20/80.	1,000	Slow....	15	2,300	-2.96

Since for the production of thermistors there is usually sought a semiconductive material whose value of ρ_0 is low and which has the most favorable (lowest) value of b , i. e., one whose value of β is high for the specified value of ρ_0 , a desirable end is obtained by utilizing semiconductive material made by mixing manganese oxide and copper oxide and heat treating the material in such a manner that manganese rich mixtures are rapidly cooled from the sintering temperature and copper rich mixtures are slowly cooled from the sintering temperature.

There is a tendency for resistors made from mixtures of oxides to increase their resistance with time. This increase usually becomes less and less as time goes on until the device becomes relatively stabilized in resistance value. This increase in resistance may, however, go on for a relatively long time, that is a matter of years. Substantial stabilization may, however, be obtained by what is known as accelerated ageing. This is accomplished by maintaining resistors at a temperature higher than normal operating temperatures for a period of several days or possibly several weeks. Since the increase in resistance is a function of both time and temperature, the use of the higher temperature shortens the time considerably. Of course, care must be taken not to have the temperature so high that the resistor will be damaged.

It has been found in accordance with this invention that rapidly cooled manganese rich resistors and slowly cooled copper rich resistors

are substantially free from changes in resistance with time. In other words, the resistance is relatively stable from the time of manufacture on. Thus no accelerated ageing treatment is necessary with these resistors.

Although this invention has been disclosed by reference to specific embodiments thereof, it is to be understood that said invention is not limited thereby; but by the scope of the appended claims only.

What is claimed is:

1. The method of controlling the resistivity of resistors made from combined, heat treated oxides of manganese and copper that comprises intimately mixing measured amounts of the two oxides in a finely divided condition, forming the mixture into a body and heat treating the body at a temperature between 600° C. and 1450° C., and cooling said body at a controlled rate, the heat treating temperature being about 1000° C. for compositions in which the atomic ratio of manganese to copper is approximately 1, this temperature being increased above about 1000° C. for mixtures containing more manganese atoms than copper atoms, and being decreased below about 1000° C. for mixtures containing more copper atoms than manganese atoms, the resistivity being dependent upon both the cooling rate and the ratio of manganese to copper, whereby the resistivity of manganese rich mixtures is relatively low and that of copper rich mixtures is relatively high for rapid cooling and the opposite for slow cooling.

2. In the manufacture of resistors from combined heat treated oxides of manganese and copper, the step of controlling the resistance of the final product, that comprises controlling the rate of cooling after heat treatment whereby said rate is high for resistance material low in copper, and low for resistance material high in copper.

3. The method of controlling the resistivity of a resistor comprising a mixture of the combined oxides of manganese and copper, during the making of said resistor, that comprises heat treating a body of said mixture and then cooling the body at a rate determined by the ratio of manganese to copper and by the resistivity desired, low resistivity resulting from rapid cooling with high manganese and slow cooling with high copper.

4. In a method of making resistors that comprises forming a body from mixed oxides of manganese and copper, heating the body to a temperature between approximately 600° and 1450° C. to sinter the mixture and then cooling said body, the step of insuring a well sintered body of substantially uniform density, that comprises controlling the temperature of heat treatment as a function of the relative amounts of each oxide present in the mixture, said temperature being high for manganese rich mixtures and low for copper rich mixtures, the temperature for a mixture containing approximately equal atomic portions of each metal being about 1000° C.

5. In the method of making resistors from combined heat treated oxides of manganese and copper, wherein the finished resistor has a much higher resistance for combinations, rich in either metallic element than for combinations containing more nearly equal amounts of each element, the step of obtaining a relatively low resistance with said rich combinations that comprises cool-

ing after heat treatment, the manganese rich combinations rapidly and the copper rich combinations slowly.

6. The method of controlling, during processing, the ultimate resistivity and resistance temperature coefficient of resistors made from the combined oxides of manganese and copper, that comprises preparing an intimate mixture of said oxides, forming a body of said mixture, heat treating the body between 600° and 1450° C. and cooling said body at a controlled rate, the cooling rate being rapid for manganese rich mixtures and decreasing with reduction in the relative amount of manganese present to a slow cooling rate for low manganese content.

7. The method of making a stable semiconductor of relatively low resistivity that comprises preparing an intimate mixture of the oxides of manganese and copper, forming a body from said oxide mixture, heat treating said body between 600° and 1450° C. and cooling the body at a controlled rate, the heat treating temperature being high and the rate of cooling rapid for mixtures wherein manganese is the predominating metal atom and the heat treating temperature being lower and the rate of cooling slow where copper is the predominating metal atom.

8. The method of making a resistor that comprises intimately mixing finely divided oxides of manganese and copper, forming a body therefrom, heat treating the body between 600° and 1450° C. to sinter it, the heat treating temperature being below 1000° C. for copper rich mix-

tures and above 1000° C. for manganese rich mixtures, and cooling the body at a controlled rate to determine the resistivity and resistance temperature coefficient characteristics thereof, these characteristics having relatively high values for slow cooling of manganese rich mixtures and rapid cooling of copper rich mixtures and relatively low values for slow cooling of copper rich mixtures and rapid cooling of manganese rich mixtures.

9. The method of making resistors having a value of approximately -3.0 for a factor b , where b is defined by the equation

$$\log \rho_0 = .0018\beta + b$$

in which ρ_0 is the specific resistivity at 0° C. and β is a temperature dependent factor given by the equation

$$\rho_0 = \text{constant } e^{\beta/T}$$

in which T is absolute temperature in degrees Kelvin; from a semiconductive material consisting of a mixture of manganese oxide and copper oxide, wherein the ratio of manganese atoms to copper atoms lies between 3 to 1 and 1 to 3; that comprises sintering the mixed oxides at a temperature in the range 950° to 1250° C., and then cooling them at a controlled rate, the lower sintering temperature and a slow cooling rate being used for copper rich mixtures and the higher sintering temperatures and a rapid cooling rate being used for manganese rich mixtures.

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