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RESISTANCE COMPOSITION AND METHOD OF MAKING IT

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FIG. 1

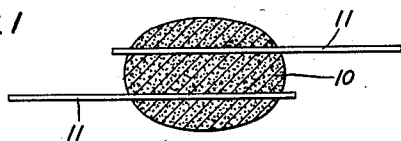
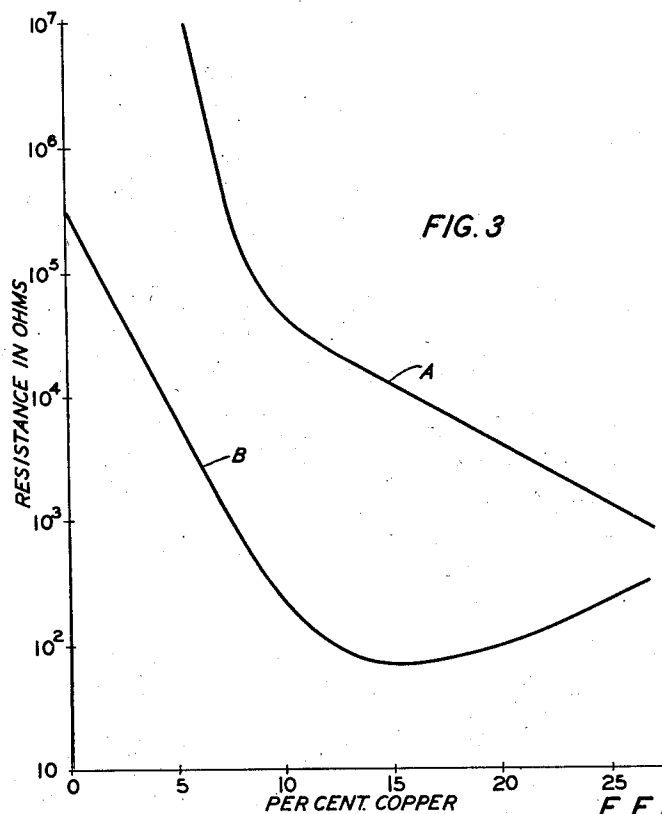
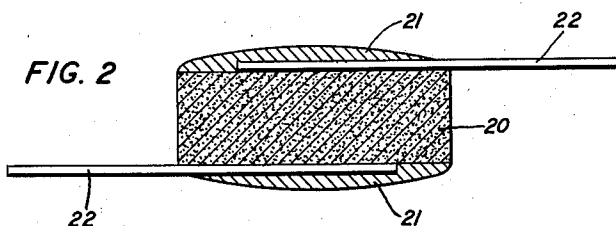


FIG. 2



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RESISTANCE COMPOSITION AND METHOD
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14 Claims. (Cl. 201-76)

This invention relates to resistors and resistance materials which have high negative temperature coefficients of resistance, and to methods of making such resistors and resistance materials. More specifically, it relates to resistance materials containing combinations of metal oxides.

It is known that resistance materials having certain desirable characteristics may be made from heat-treated combinations of metal oxides. By employing the proper proportions of certain oxides for the resistance materials, a series of units may be made having a wide range of specific resistance but all within a comparatively narrow range of high resistance-temperature coefficients. If small amounts of nickel oxide are added to manganese oxide the resistance material which may be produced therefrom has a lower specific resistance than a resistance material made from manganese oxide alone. In oxide combinations of this type there is an approximate minimum composition beyond which the addition of further nickel increases the resistance. For example, with approximately 80 per cent Mn_2O_3 and 20 per cent NiO the minimum resistance is obtained upon proper heat treatment.

One object of this invention is to further improve resistors and resistance materials made from oxides of metal.

Another object of this invention is to improve the resistance characteristics of resistors and resistance material containing manganese oxide or manganese and nickel oxides.

A further object of this invention is to control the specific resistance of resistance materials without appreciably affecting their resistance-temperature coefficients.

One feature of this invention resides in the addition of a copper compound to manganese oxide or to combined oxides of manganese and nickel, in the formation of resistance materials.

In accordance with another feature of this invention large variations in resistance are obtained by small changes in the copper content of resistance materials containing manganese and copper or nickel, manganese and copper oxides.

In accordance with a further feature of the invention exact control of the amount of copper in the combination is obtained by adding the copper in the form of a compound in solution in a liquid.

Other and further objects and features of this invention will be understood more fully and

clearly from the following detailed description with reference to the accompanying drawing in which:

Fig. 1 is a sectional view of a resistor illustrating one embodiment of the invention;

Fig. 2 is a sectional view of a different resistor illustrating another embodiment of the invention; and

Fig. 3 is a curve showing the effect on the specific resistance, of the addition of copper to manganese oxide or to a mixture of nickel and manganese oxides.

It has been found in accordance with this invention that the addition to manganese oxide of copper in a form to produce a combined oxide upon heat treatment has a much greater reducing effect on the specific resistance than the addition of nickel oxide thereto. For example, a given bead type resistor of Mn_2O_3 has a resistance considerably higher than 1×10^7 ohms. A resistor of the same dimensions but containing the combined oxides of manganese and copper in which the copper content is in the order of 10 per cent has a resistance of about 6×10^4 ohms. When the copper content of such a resistor is 25 per cent the resistance is down to 1×10^3 ohms. Curve A of Fig. 3 graphically shows the effect of the addition of copper to manganese oxide resistance material.

Copper oxide may also be employed to reduce the resistance of a combined manganese-nickel oxide resistance material. The copper oxide not only has a more marked effect on manganese oxide than the nickel oxide has, but if copper oxide be added to a minimum resistance manganese-nickel oxide combination the resistance will be further reduced. Curve B of Fig. 3 illustrates the effect of the addition of copper to a manganese-nickel oxide combination containing 80 parts Mn_2O_3 and 20 parts NiO . As will be seen from an inspection of this curve a minimum resistance is obtained when the copper content is in the order of 15 per cent. The very marked effect of copper can be seen when a comparison is made between a manganese-nickel oxide resistor which has a resistance of approximately 3.6×10^5 ohms, as compared with a similar resistor containing 15 per cent copper for which the resistance is about 70 ohms.

In the preparation of resistance material of the type contemplated by this invention, the constituents are usually employed in a finely divided state. Predetermined portions of the materials are intimately mixed and formed into bodies of suitable size and shape for the pur-

pose intended. The bodies are heat treated at temperatures ranging from 800° to 1450° C. The temperature and the atmosphere of heat treatment are regulated in accordance with the resistance desired. The resistance of the material is a function of the relative amounts of the metallic elements present after the materials are combined. The atmosphere of heat treatment determines the amount of oxygen in the finished product which also affects the resistance value. The materials usually employed are in the oxide form although other compounds may be used provided a combined oxidic material is produced by heat treatment. The expressions "metallic elements present" or "metal present" in this specification and the appended claims do not refer to metals as such, but to the metallic elements in the combination, the atomic viewpoint being intended. The resistor units may be made up in several forms, two of which are shown in Figs. 1 and 2, respectively.

A bead type unit, such as is shown in Fig. 1, may be made by mixing the finely divided oxides and forming a paste with a suitable binder. The binder may be water or preferably comprises a solution of a compound of one of the metals involved. Where such a solution is employed, account must be taken of the amount of metallic element introduced by said solution, since this has an effect on the final resistance. In view of the marked effect of copper on the specific resistance of the material, it is necessary to carefully regulate the amount of copper entering into the composition. This may conveniently be done by adding the copper in solution in the binder liquid. If this procedure is followed a mixture of finely divided manganese oxide or nickel and manganese oxides and a water solution of a copper compound, such as copper nitrate, are used to form a paste from which the beads are made. The paste is formed into small beads 10 on parallel wires 11 of refractory conductive material, such as platinum. The beads are then dried and heat treated.

A unit of the disc or plate type, such as shown in Fig. 2, may be made by intimately mixing finely divided oxides and pressing them into a body 20. Units of the disc or plate type may be heat treated in a manner similar to that employed for the bead type units. Contact electrodes may be applied to opposite faces of the disc by any adequate means. A suitable connection can be made by applying metallic paste to two surfaces and embedding conductive leads 22 therein. The units are then heat treated to solidify the paste into electrodes 21 firmly bonding the leads 22 to the resistance body 20.

Although specific embodiments of this invention have been shown and described, it will be understood that 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. A resistance material consisting of a composition of metal-oxygen compounds, the metallic elements thereof consisting of manganese in excess of approximately 50 per cent and a remainder including copper, said copper not to exceed approximately 25 per cent of said metallic elements.

2. A resistance material consisting of a composition of metal-oxygen compounds, the metallic elements thereof consisting of manganese

in excess of approximately 73 per cent and a remainder of copper.

3. A high negative resistance-temperature coefficient resistance material consisting of the oxides of manganese, nickel and copper, the metallic elements being in the proportions of 73 per cent manganese, 21 per cent nickel and 6 per cent copper.

4. A resistance material consisting of a composition of metal-oxygen compounds in which on the basis of total metal present, manganese exceeds approximately 50 per cent and copper is present to the extent of not more than approximately 25 per cent, the remaining metallic element being nickel.

5. A resistance material consisting of intimately mixed, collectively heat-treated oxides of manganese, nickel and copper in which the manganese is equal to or greater than the nickel, and the copper ranges from a trace up to about 25 per cent of the total metal present.

6. A resistance material consisting of intimately mixed, collectively heat-treated oxides of manganese, nickel and copper in which the manganese to nickel ratio is approximately 4 to 1 and the copper is present up to about 15 per cent of the total metal present.

7. A thermally sensitive resistance material consisting of intimately mixed, collectively heat-treated oxides of manganese, nickel and copper, the major portion of the material comprising the oxides of manganese and nickel with a small amount of copper oxide whereby the copper content is less than 25 per cent of the whole.

8. A thermally sensitive oxidic resistance material having a high negative resistance-temperature coefficient and consisting of intimately mixed, collectively heat-treated oxides of manganese, nickel and copper, the manganese and nickel oxides being in a ratio of about 4 to 1 and the remainder copper oxide in an amount sufficient to include in the combination from approximately 1 to 15 per cent of the total metal present as copper, the resistance of said material being a minimum for about 15 per cent copper and doubling for each 1 per cent decrease in copper.

9. A high negative resistance-temperature coefficient resistor comprising a heat-treated body of intimately mixed manganese, nickel and copper oxides, and electrodes embedded therein, the metallic elements of the body consisting of approximately 75 per cent manganese, 7 per cent copper, and the remainder nickel.

10. The method of controlling the resistance of a thermally sensitive resistance composition including oxides of manganese and nickel as its primary constituents, the manganese exceeding the nickel in amount, that comprises adding small amounts of a copper compound to said oxides before heat treatment, and heat-treating at 800° to 1450° C.

11. The method of making a thermally sensitive resistance material that comprises mixing oxides of manganese and nickel with a solution containing a small amount of a copper compound, drying the mixture and heat treating it at 800° to 1450° C.

12. The method of making a resistor that comprises mixing selected amounts of finely divided, heat-treated oxides of manganese and nickel, forming the mix into a paste by the addition of a solution of a copper compound thereto, forming the paste into a body on spaced electrodes, drying

the body and heat treating it between 800° and 1450° C.

13. The method of reducing the resistance of an oxidic resistance material which includes manganese oxide as its primary constituent that comprises adding small amounts of copper to the material and thereafter heat treating the mixture at 800° to 1450° C. to form a combined oxide material including copper oxide.

14. The method of controlling the resistance of a resistance material comprising oxygen compounds of metals in which of the total metal present manganese exceeds approximately 50 per cent, that comprises adding to such material small amounts of copper and thereafter heat treating the mixture at 800° to 1450° C.

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