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RESISTANCE MATERIAL
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2,326,580

FIG. 1

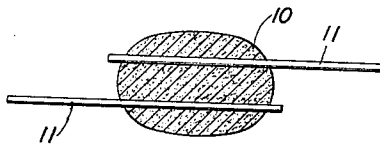
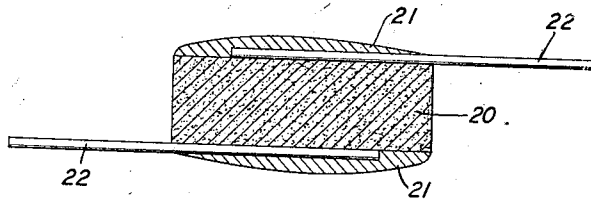


FIG. 2



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RESISTANCE MATERIAL

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8 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 these oxides for the resistance materials, 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. For example, the specific resistances of manganese oxide and nickel oxide are relatively high, but a heat treated combination of the two oxides in any proportion has a lower specific resistance than either of them. Furthermore, if these oxides are mixed in such proportions that the atomic ratio of manganese to nickel is in the order of from 2 to 1 to 4 to 1, a minimum specific resistance may be obtained. The resistance-temperature coefficient of each of these oxides is relatively high in absolute value and this value is not appreciably reduced for combinations of the two oxides. A further reduction in specific resistance may be obtained by adding to a minimum specific resistance composition of manganese and nickel oxides, an oxide of cobalt. A substantially minimum resistance for this ternary composition may be obtained when the cobalt atoms comprise from 30 to 40 per cent of the total metal atoms present.

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 oxides of manganese, nickel and cobalt.

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

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

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, nickel, cobalt and copper oxides.

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 this invention; and

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

It has been known, heretofore, that the addition of a suitable copper compound to manganese oxide or a combination of manganese and nickel oxides, would reduce the specific resistance thereof. However, it has also been found that in oxide combinations containing copper atoms, there have been undesired resistance variations due to factors forming a necessary part of the manufacturing processes following formation of the resistance material. For example, high sensitivity to heating and cooling rates. Although appreciable additions of copper would markedly reduce the specific resistance, lack of uniformity and reproducibility due to the other factors was a definite disadvantage. Given the problem of making an extremely small resistance body with relatively low resistance, the necessity of using a material of low specific resistance is apparent. In a situation where the manganese, nickel, copper oxide combination of minimum resistivity is too high in resistance for the size of body required, and the amount of copper necessary to obtain the required resistance with a combination of nickel, manganese and copper oxides is high enough to aggravate the above-noted difficulties, a different resistance material appears to be indicated. It has been discovered that by adding very small amounts of copper, to a minimum resistivity, manganese, nickel and cobalt oxide composition, that the desired low specific resistance can be obtained without the previously noted deleterious effects. For example, if to a composition of oxides in which the approximate atomic ratio of metals is 52Mn:16Ni:32Co there is added a small amount of a copper compound so that the resulting oxide mixture has an atomic ratio of metals of approximately 50Mn:16Ni:30Co:4Cu, a six fold reduction in specific resistance is attained. In such a composition the amount of copper with relation to the total metal present is about 4 per cent. The absence of difficulties with this composition previously ascribed to the presence of copper may be due to the relatively small amount of copper present therein. Whatever the reason may be, the fact remains that tests show that combina-

tions of this approximate composition have the required low specific resistance and are not subject to the previously noted handling difficulties.

In the preparation of a combined oxide resistance material, 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 purpose intended. The bodies are heat treated at temperatures ranging from 800° to 1450° C. For example, for a body in which the atomic ratio of metals is 50Mn:16Ni:30Co:4Cu 1200° C. is satisfactory. The temperature and atmosphere of heat treatment are regulated in accordance with the resistance desired. The resistance of the material, as previously indicated, 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 initial materials may be in the form of oxides, or other compounds of the required metallic elements which will produce a combined oxidic material upon proper treatment. For example, all or some of the materials may be combined in the form of finely powdered carbonates which mixture may be changed to a combination of oxides by suitable calcining. Where a relatively small amount of one of the metallic elements is required, such as the copper in the present composition, it may be added in the form of a soluble compound such as a nitrate dissolved in water.

Reference in this specification and the appended claims to total metal present, metallic elements, metals generally or to the specific metals manganese, nickel, cobalt or copper is not intended to refer to metals as such, but to the metallic elements in the resistance combination or a constituent thereof, the atomic viewpoint being intended. The resistor units may be made in several forms, two of which are shown in Figs. 1 and 2, respectively.

A bead type unit, such as that shown in Fig. 1, may be made by mixing the finely divided constituents and forming a paste with a suitable binder. The binder may be water or preferably comprises a solution of a compound of the metal appearing in the smallest proportions, in this case copper. For example, having obtained a mixture of the oxides of manganese, nickel and cobalt in proper proportions, these may be mixed with water to which has been added a sufficient amount of copper nitrate to give the desired amount of copper in the resistance composition. The resulting paste is formed into bodies, such as bead 10, on parallel wires 11 of refractory conductive material, such as platinum or an alloy of platinum and iridium. The bodies or beads are then dried and heat treated.

A unit of the disc or plate type, such as is shown in Fig. 2 may be made by intimately mixing the finely divided oxides, pressing them into a body 20 and heat treating said body. Contact electrodes may be applied to opposite faces of the heat treated disc by any adequate means. A suitable connection can be made by applying metallic paste to the surfaces and imbedding conductive leads 22 therein. The units may then be heated to solidify the paste into electrodes 21 firmly bonding the leads 22 to the resistance body 20. The electrodes may also be applied to

opposite faces of the disc and the leads soldered thereto.

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 intimately mixed, collectively heat treated oxides of manganese, cobalt, nickel and copper in which the metallic elements are present in amounts according to the order given, the amount of manganese being the greatest and of the order of more than about one-half and the amount of copper being less than approximately one-sixth of the total metallic elements present.

2. A resistance material consisting of intimately mixed, collectively heat treated oxides of manganese, nickel, cobalt and copper in which of the total metal present, manganese comprises about 50 per cent, copper about 5 per cent, the remainder cobalt and nickel of which remainder cobalt exceeds nickel and the sum of cobalt and nickel is less than the manganese.

3. A thermally sensitive resistance material consisting of intimately mixed, collectively heat treated oxides of manganese, nickel, cobalt and copper, the major portion of the material comprising the oxides of manganese, cobalt and nickel among which the manganese exceeds the sum of the cobalt and nickel and the cobalt exceeds the nickel, and a small remainder of copper oxide, the copper oxide content being less than about 5 per cent of the whole.

4. A resistance material consisting of intimately mixed, collectively heat treated oxides of manganese, nickel, cobalt and copper in which the manganese to nickel ratio ranges between 2 to 1 and 4 to 1, the cobalt is in the order of 30 per cent, and the copper in the order of 5 per cent of the total metal present.

5. A resistance material consisting of the combined oxides of manganese, nickel, cobalt and copper sintered at about 1200° C. and in which the atomic ratio of metals is approximately 50 manganese:16 nickel:30 cobalt:4 copper.

6. A resistance material consisting of the combined oxides of manganese, nickel, cobalt, and copper heat treated at a temperature between 800° and 1450° C. in which the percentage range of metals with respect to the total metal present is 50 to 60 per cent manganese, 13 to 18 per cent nickel, 25 to 40 per cent cobalt and 1 to 5 per cent copper.

7. 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, nickel to the extent of $\frac{1}{2}$ to $\frac{1}{4}$ of the manganese and the remainder of cobalt and copper, said copper not to exceed approximately 5 per cent of said metallic elements.

8. A resistance material consisting of intimately mixed, collectively heat treated oxides of manganese, nickel, cobalt and copper in which manganese exceeds about one-half of and copper is less than about one-quarter of the total metal present.

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