RESISTANCE MATERIAL

Filed May 17, 1939

FIG. 1

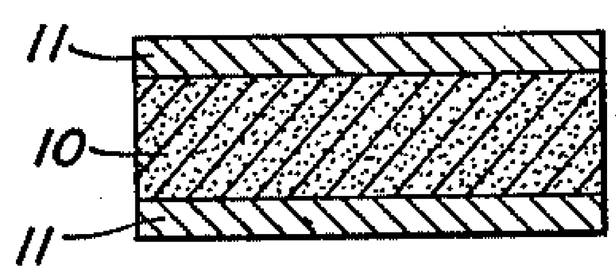


FIG. 2

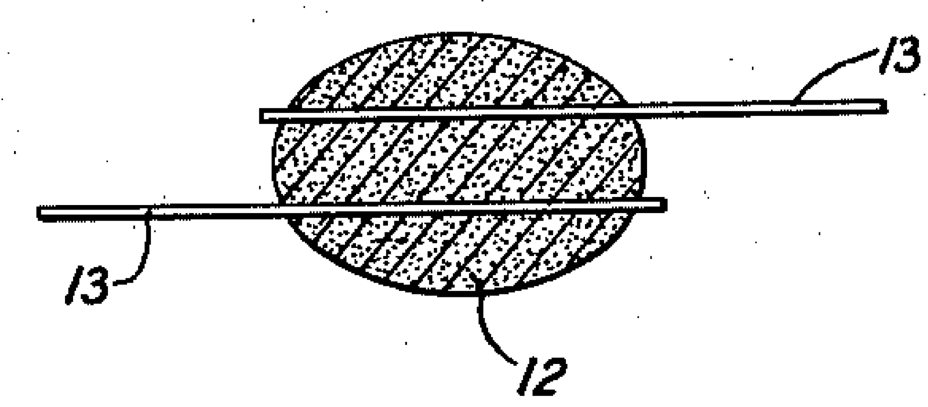
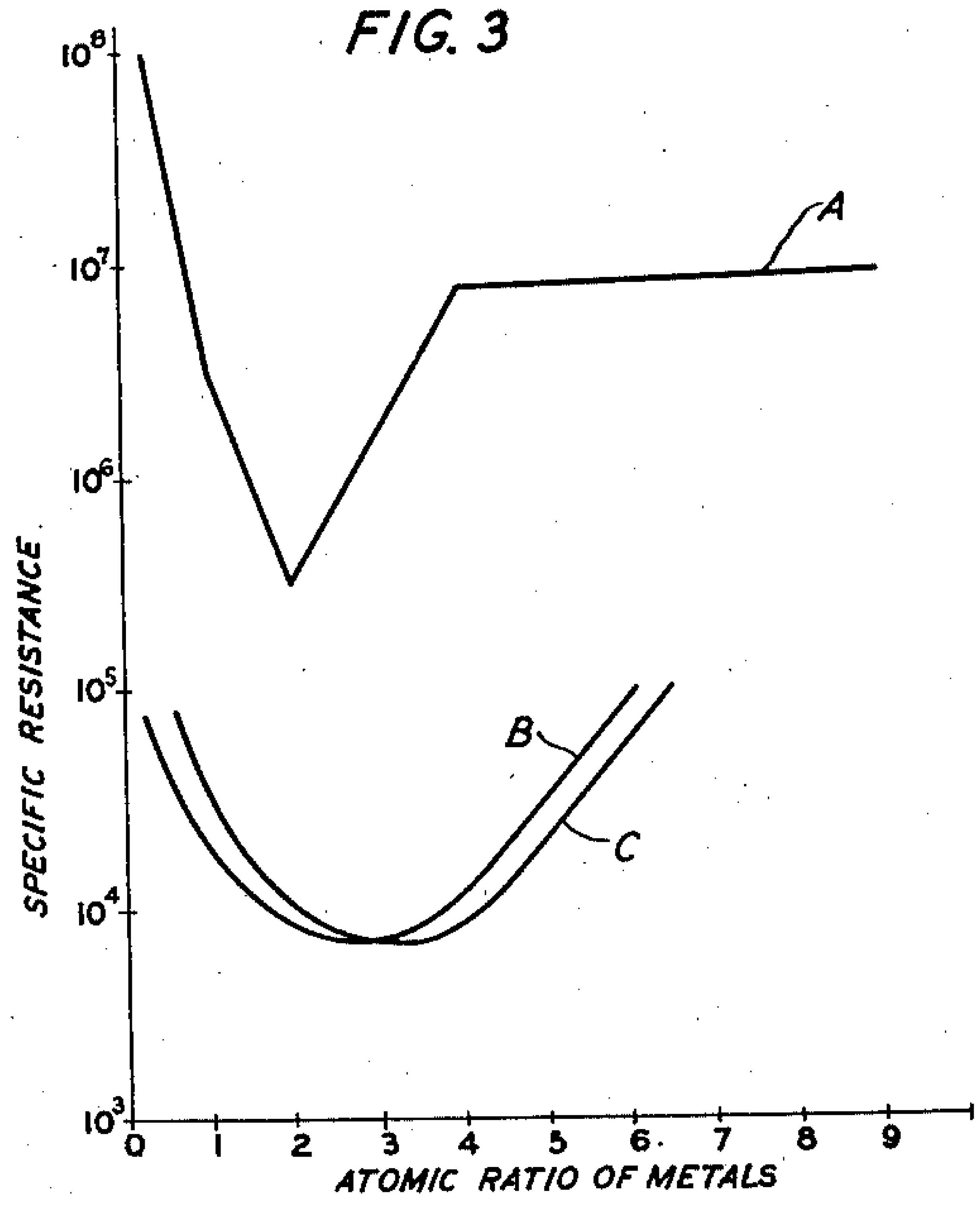


FIG. 3



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Patented Oct. 14, 1941

2,258,646

UNITED STATES PATENT OFFICE

2,258,646

RESISTANCE MATERIAL

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Application May 17, 1939, Serial No. 274,114

12 Claims. (Cl. 201—76)

This invention relates to electrical resistor materials and more particularly to such materials having large temperature coefficients of resistance.

Materials whose electrical resistances are highly dependent upon temperature are useful in many ways in electrical systems. A particular field of use is in regulating and protective systems. Usually the materials employed have relatively large negative resistance-temperature coefficients.

The specific resistance of metallic conductors is generally too low and that of insulators too high to make them of value as circuit elements for regulation and like purposes. The so-called semiconductors, which have intermediate resistance values, therefore, appear to comprise the useful field of materials having relatively high resistance-temperature coefficients.

Several of the semiconducting materials, including oxides of metallic elements, have been employed heretofore for negative resistance-temperature coefficient resistor units. Although such units have in some cases been reasonably satisfactory from a performance viewpoint, they are rather difficult and expensive to prepare and maintain.

One object of this invention is, therefore, to improve resistor materials whose resistances are highly dependent upon temperature.

Another object of this invention is to produce satisfactory resistor devices having high resistance-temperature coefficients from materials which are relatively inexpensive compared with those previously used with success.

In accordance with one feature of this invention, the resistor devices comprise combinations of oxides of metallic elements.

In accordance with another feature of the invention, the metal oxides employed are of such character that when intimately mixed and heated they combine to form a compound, solid solution, eutectic mixture, or some combination of these.

A further feature of this invention resides in the characteristic internal structure of the resistance material made in accordance therewith, in that it includes a crystal structure uniquely different from that of the materials from which it is made.

Another feature of this invention resides in the use, as resistance materials, of some combinations of metal oxides that exhibit a minimum resistance when the ratio of the numbers of the atoms of the metals present is that of integers and which have a higher resistance if there is an excess of one metal over the amount required by an integral atomic ratio.

Still another feature of this invention comprises the making of resistance units with negative temperature coefficients of resistance from oxides of manganese and iron or oxides of nickel and manganese, by heat treatment to form resistor units containing compounds of said oxides such as manganese ferrite and nickel manganite.

The invention and the foregoing and other features thereof will be understood more clearly and fully from the following detailed description with reference to the accompanying drawing in which:

Fig. 1 is a sectional view of a disc type resistor unit illustrative of one embodiment of this invention;

Fig. 2 is a sectional view of a bead type resistor unit illustrative of another embodiment of this invention; and

Fig. 3 is a graphical representation of data showing the relation between specific resistance and atomic ratio of the metallic elements, for a series of resistors made from different proportions of iron and manganese oxides and different proportions of nickel and manganese oxides.

It has been found that, where there is a tendency towards reaction or solid solution of two or more metallic oxides, semiconduction, which is predominantly electronic, can be expected, the conductivity being dependent upon the composition of the reaction product. In those cases in which definite compounds are formed from the oxides under the influence of heat, satisfactory semiconductors frequently result.

The specific resistance of an oxidic system, in addition to its dependence, upon the composition of the reaction mixture, is also a function of the temperature to which it is heated and of the nature of the atmosphere in which the heat treatment is carried out. Actually, alterations in heat treatment and atmosphere displace the chemical equilibrium between the components and hence change the composition of the reaction product. There are, however, two types of alteration in composition, each of which has a large effect on the specific resistance of an oxidic material. It has been shown theoretically and demonstrated experimentally that very slight departures from the stoichiometrical composition in an oxide system can produce very large changes in its conductivity. Thus, an excess of oxygen or metal over that required by the chemical formula can bring about changes in conductivity which are dependent on the concentration of the overabundant element.

The stability or constancy of composition of an oxide indicates that the element in excess is firmly bound, either by secondary valence forces or in solid solution and, because of this, is not to be considered as "free" in the sense that it is mobile or chemically reactive. Thus, the dependence of the conductivity on the ambient oxygen concentration is determined by preparing the samples at high temperatures in various atmospheres and subsequently measuring their conductivities at low temperatures where they are stable over long periods of time regardless of the atmosphere. It is only after these specimens are again heated at high temperatures that the resistances are altered. This type of change is dependent upon the mobility of the constituent atoms at high temperatures and since their mobilities are very small at normal temperatures the excess atoms are "frozen" firmly in place. For an oxidic material given suitable heat treatment, the ratio of combined to uncombined elements is therefore constant at normal temperatures. There is for each temperature and each atmosphere a definite composition and any change in environment results in a tendency for the system to alter its composition. However, for most oxides at normal temperature the rate of approach to a new equilibrium is so small that apparent constancy of composition is observed.

While the ratio of combined to uncombined atoms for an oxidic system is a constant for a specific heat treatment, it has been determined that in some systems the specific resistance is further dependent upon the ratio of the number of atoms of one metal to that of another. When this ratio has a value equal to the ratio of two integers, the two metals will be present in the proper proportions to form a compound. When no oxygen is lost from or taken up by the oxides during heat treatment the compound is simply the addition product of the two. This need not be the case, however, and the same compounds may be formed from oxides in other valence states with subsequent loss or absorption of oxygen. Thus, the fact that the specific resistance of the reaction product is dependent only upon the atomic ratio of the two metals and not on their valences in the original oxides, indicates that for the heat treatment employed only one oxide of each metal is stable, or that the compound formed is more stable than any oxide of either metal. It has been found that in certain oxide systems the specific resistance is a minimum when the atomic ratio has a value that is the ratio of two integers or very nearly so.

In some cases, the minimum in resistance as a function of the atomic ratio of the metals is pronounced, occurring at a value of this ratio corresponding to a definite oxidic compound characteristically different from either of the original oxides. In other cases, the minima are less sharply defined, although they are associated with atomic ratios nearly the same as those corresponding to compound formation. In either case, it has been found by chemical and X-ray analysis that there is present in the material of lower specific resistance a solid phase having a crystal structure uniquely different from that of any of the initial ingredients. In those cases where the minima in resistance are sharply defined it is probable that there is no extensive solid solution. However, where a new crystal phase is present and where the minimum does not occur at an integral atomic ratio there are solid solutions present. These solutions may be of two natures. They may consist of a solution of the new compound in one or more of the intial ingredients or they may be solutions of these initial ingredients in the new crystalline phase resulting from the heat treatment.

The curves of Fig. 3 illustrate the foregoing statement with respect to minimum resistance. Curve A, which is for a series of units having different proportions of iron and manganese oxides, exhibits a pronounced minimum for an atomic ratio Fe/Mn=2. The minima in curves B and C, which are for combinations of manganese and nickel oxides, are not so sharply defined, occurring between Mn/Ni=2 and Mn/Ni=4. The differences between curves B and C are due to differences in heat treatment.

The specific resistance of a dense oxidic material is then dependent upon the ratio of combined to free elements and, in systems of two or more oxides, upon relative amounts of the various metals present. In general, the resistance of a semiconductor is dependent also upon its porosity, upon the size of the individual crystallites, and upon its homogeneity. As the porosity of an oxidic material decreases, its resistance also generally decreases and in the limit approaches that of a completely dense mass. The stability of oxidic semiconduction increases with decrease in porosity because in a porous material the current is concentrated in small areas which in some cases are raised to temperatures sufficient to alter the equilibrium composition. The effect of heating a porous semiconductor by a current flowing through it may then be a permanent change in its resistance. In general, the porosity of an oxidic system in which compounds, eutectoids and/or solid solutions are formed by heat treatment is less than for systems where compactness is achieved simply by sintering and recrystallization.

As has been stated, the specific resistance and the mechanical properties of oxidic materials are highly dependent upon their composition. For qualitative purposes the specific resistance ρ of such materials may be given by the expression $\rho=\rho_0 e^{-\alpha(T-T_0)}$ where ρ_0 is the specific resistance at temperature T_0, α the temperature coefficient of resistance and T the temperature, and where ρ_0 and α are constant. Actually α is a decreasing function of increasing temperature but for purposes of comparison it can be considered as constant over small temperature ranges. It has been observed in the study of some metallic oxides, where the resistance was varied by heat treatment, that α measured over a given range, increased as the resistance increased. It appears however, that this is not a universally valid rule, for certain oxide systems have been found for which α within the temperature range used for comparison is substantially independent of the specific resistance ρ_0 at the reference temperature T_0, even though ρ_0 is highly dependent upon the atomic ratio of the metals involved. It has been observed that ρ may be essentially independent of α for those systems whose specific resistances show minima as functions of the atomic ratios of the metals.

In the manufacture of resistance units from oxidic materials in accordance with this invention, the constituent oxides are so selected that mixtures thereof upon heat treatment take on characteristics other than those associated with a simple mixture. When the oxides are properly chosen and heat treated the resulting material partakes of the nature of a compound, a solid solution, a eutectic mixture, or some combination of these. Moreover, as has been previously stated, the combined material includes a crystal structure that is characteristic and not like that of any of the constituents. The new material may for purposes of this specification and the appended claims be called a homogeneous combination as distinguished from a simple mixture.

Certain oxide mixtures upon heat treatment form definite compounds. For example, a mixture of iron and manganese oxides heat treated at a temperature ranging from 1000° to 1450° C. will produce manganese ferrite. When the proportions of the two oxides are such that there are two atoms of iron for each atom of manganese, that is, for an atomic ratio $Fe/Mn=2.0$, the specific resistance is a minimum as illustrated by the curve A in Fig. 3.

A resistance unit comprising nickel manganite made from nickel and manganese oxides heat treated at a temperature ranging from 1000° to 1450° C. shows like characteristics. As may be seen from curves B and C Fig. 3 the specific resistance is minimum between atomic ratios $Mn/Ni=2.0$ and 4.0.

Although in either case the variation in the specific resistance ρ for small changes in composition is large over a considerable range, the resistance-temperature coefficient α remains substantially constant. Other oxide combinations such as zinc and uranium or manganese and uranium also show a minimum of specific resistance where the metals are present in such quantities that their atomic ratio is nearly that of two integers.

Other metal oxides which tend to combine in the presence of heat may be used for resistance materials of the type described. Among these are noted the oxides of aluminum, magnesium, copper, zirconium, tin, chromium, cobalt, titanium and zinc.

Practical embodiments of oxidic resistance units may be made in several forms, two of which are illustrated in the drawing. The unit shown in Fig. 1 is of the disc or plate type. The semiconducting material is denoted by 10 and the terminals or electrodes by 11. Units of this type may be made by grinding and intimately mixing predetermined amounts of the constituent oxides. A die of proper dimensions may then be charged with the mixed oxides and pressure applied. A pressure of the order of ten tons per square inch is suitable for producing satisfactory discs or plates. The pressed discs are then heat treated to bring about the necessary combination of elements. Firing temperatures of from 450° to 1500° C. have been found suitable. The electrodes 11 may be formed by applying silver paste to appropriate surfaces of material 10 and heating to solidify the paste.

The atmosphere in which the units are heated may be adjusted in accordance with the oxides employed in order to obtain a desired final resistance. For example, with mixture of Fe_2O_3 and Mn_3O_4 or NiO and Mn_3O_4 the resistance of the resulting unit is least for a pure oxygen atmosphere and greatest for pure nitrogen. Air gives results intermediate these two extremes and atmospheres containing water vapor, illuminating gas or hydrogen give low resistances. When the metals are present in an atomic ratio of two integers the atmosphere generally has less effect on the final resistance than for other atomic ratios. In general, the changes in resistance due to changes in atmosphere are completely reversible.

The unit shown in Fig. 2 is of the bead type comprising a bead 12 of a selected semiconducting material with conducting leads 13 embedded therein. The leads 13 should be of some refractory conducting material such as platinum. In the manufacture of these units, the constituent oxides are ground and mixed as for the disc type devices. The mixed oxides are made into a paste by the addition of a suitable liquid such as distilled water or a solution of a metal salt. The paste is formed into small beads on platinum or other suitable wires and dried. The units are then heat treated in a manner similar to that employed for disc units.

The conduction of oxide resistors, that are made in accordance with this invention, is predominately electronic, making them available for use with direct as well as alternating current. The devices are very stable at normal operating temperatures and the resistance-temperature cycle is completely reversible.

By employing the materials and following the procedure of the foregoing disclosure, resistances may be produced having a sufficiently high temperature coefficient of resistance to make them useful as circuit elements. By varying the heat treatment and composition of the oxide mixture, resistances may be prepared which have a wide range of values of specific resistance but all having essentially the same resistance-temperature coefficient.

Although specific embodiments of this invention have been shown and described, it will be understood, of course, that they are but illustrative and 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 unit consisting of a compound of manganese oxide and an oxide from the group consisting of iron oxide and nickel oxide and an excess of one constituent oxide, there being solid solution between the compound and the excess oxide.

2. A resistance material consisting of a homogeneous combination of manganese oxide and an oxide from the group consisting of iron oxide and nickel oxide, and having a specific resistance dependent upon the atomic ratio of the constituent metals and a temperature coefficient of resistance substantially independent of said ratio.

3. A resistance material consisting of a homogeneous combination of manganese oxide and an oxide from the group consisting of iron oxide and nickel oxide, and having a specific resistance dependent upon the atomic ratio of the metals.

4. A resistance material consisting of a homogeneous combination of manganese oxide and an oxide from the group consisting of iron oxide and nickel oxide and having a specific resistance dependent upon the atomic ratio of the metals in the combination, said specific resistance having a minimum value for an atomic ratio approximating that necessary for a compound between the oxides.

5. A resistance unit consisting of a compound of iron oxide and manganese oxide.

6. A resistance unit consisting of a compound of manganese oxide and nickel oxide.

7. A resistance material consisting of a combination of iron oxide and manganese oxide and

having a specific resistance dependent upon the atomic ratio of the iron and manganese in the combination, said specific resistance being a minimum for an atomic ratio of Fe/Mn=2.0.

8. A resistance material consisting of a combination of manganese oxide and nickel oxide and having a specific resistance dependent upon the atomic ratio of the manganese and nickel in the combination, said specific resistance being a minimum for atomic ratios between Mn/Ni=2.0 and Mn/Ni=4.0.

9. The method of making a resistance unit that comprises intimately mixing finely divided oxides of iron and manganese, forming said mixture into a body, and heat treating said body at a temperature ranging from 1000° to 1450° C.

10. The method of making a resistance unit that comprises intimately mixing finely divided oxides of manganese and nickel, forming said mixture into a body, and heat treating said body at a temperature ranging from 1000° to 1450° C.

11. The method of making a resistance unit that comprises intimately mixing finely divided manganese oxide and a finely divided oxide from the group consisting of iron oxide and nickel oxide, forming the mixture into a body and heat treating said body at a temperature ranging from 1000° C. to 1450° C.

12. A resistance unit consisting of manganese oxide and an oxide from the group consisting of iron oxide and nickel oxide, and a compound of the constituent oxides having a specific resistance lower than that of either constituent oxide.

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