

July 14, 1953

F. J. MORIN

2,645,700

SEMICONDUCTOR OF MIXED NICKEL, MANGANESE, AND IRON OXIDES

Filed Aug. 27, 1949

2 Sheets-Sheet 1

FIG. 1

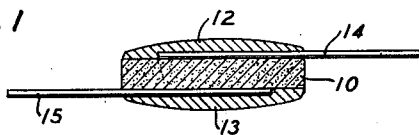


FIG. 2

SYSTEM $\text{NiMn}_2\text{Ox}-\text{NiFe}_2\text{Ox}$

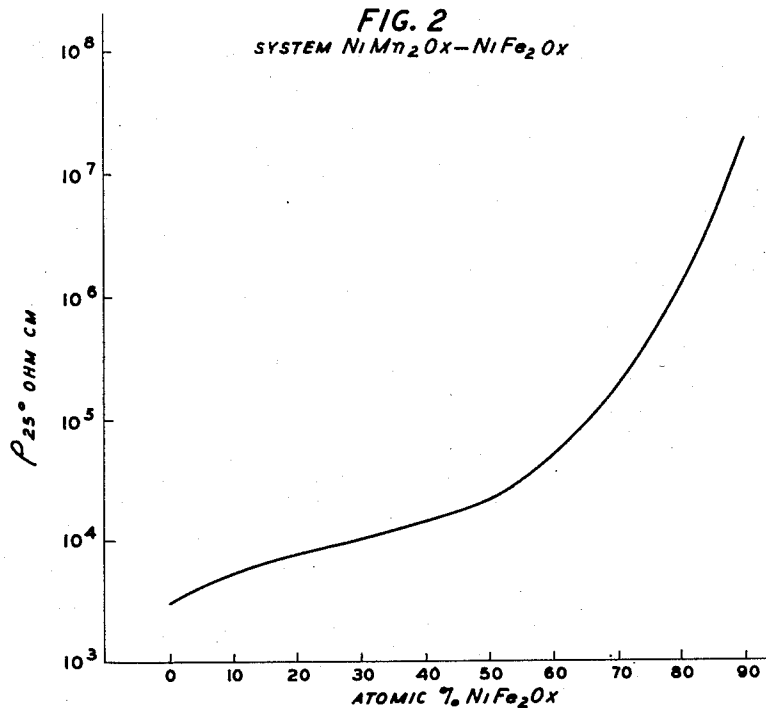
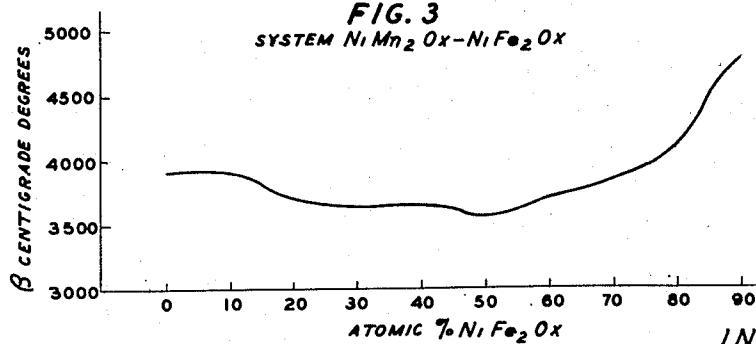


FIG. 3

SYSTEM $\text{NiMn}_2\text{Ox}-\text{NiFe}_2\text{Ox}$



INVENTOR
F. J. MORIN
BY *[Signature]*
ATTORNEY

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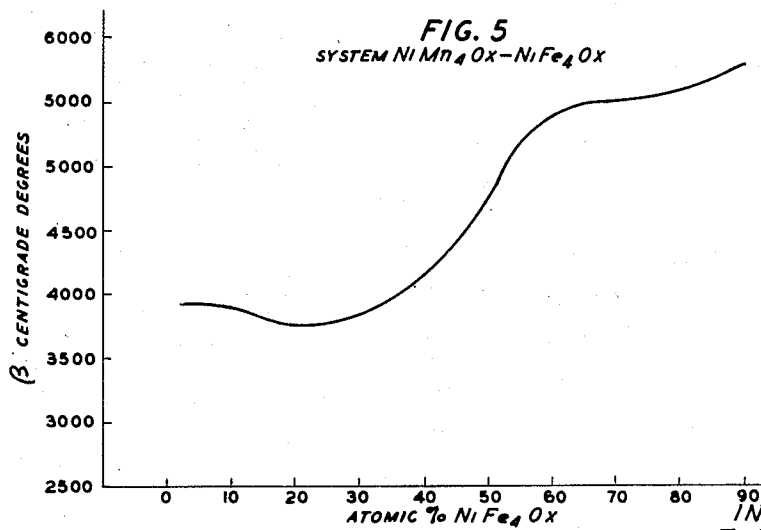
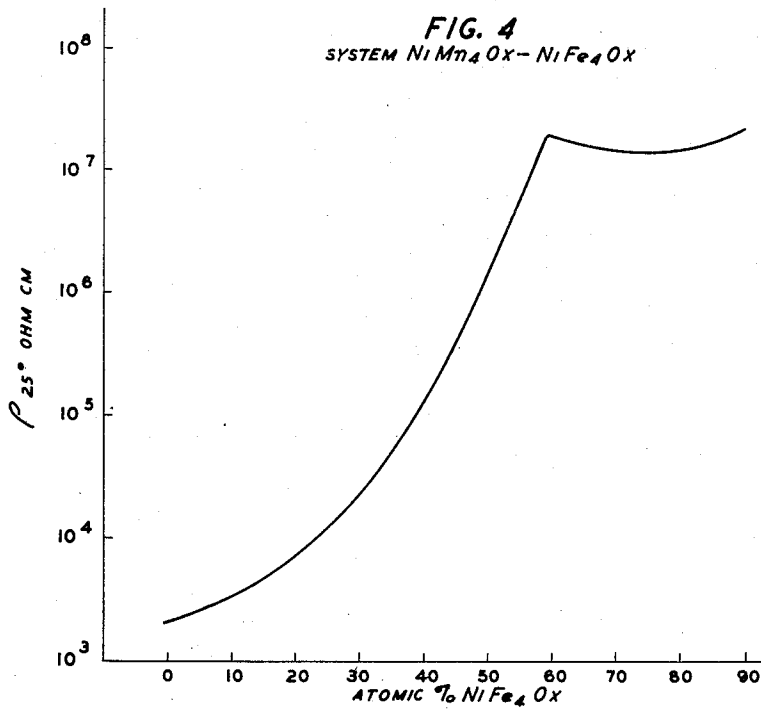
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SEMICONDUCTOR OF MIXED NICKEL, MANGANESE, AND IRON OXIDES

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2 Sheets-Sheet 2



INVENTOR
F. J. MORIN

BY

J. Hunter

ATTORNEY

UNITED STATES PATENT OFFICE

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SEMICONDUCTOR OF MIXED NICKEL,
MANGANESE, AND IRON OXIDESFrancis J. Morin, Berkeley Heights, N. J., assignor
to Bell Telephone Laboratories, Incorporated,
New York, N. Y., a corporation of New York

Application August 27, 1949, Serial No. 112,805

3 Claims. (Cl. 201—63)

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This invention relates to thermally sensitive semiconductors and to methods of making them. In some of its more specific aspects it relates to resistors comprising certain metal-oxygen compositions and to methods of combining such compositions to obtain particular resistance characteristics.

The semiconductor resistors particularly involved in this invention are those whose resistance varies greatly with changes in temperature and which are commonly known as "thermistors." Where this term is employed, it is to be understood that resistors of this nature are intended. The principal characteristics of such devices are the specific resistance, commonly designated ρ , the temperature coefficient of resistance α , and the temperature dependence factor β which unlike α is a constant and is independent of temperature. The mathematical expression relating the specific resistance ρ , temperature dependence factor β and the absolute temperature T is as follows:

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

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

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

Applying this equation to (1) there is obtained

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

Thermistors having particular temperature coefficients of resistance are sometimes necessary in the proper operation of a circuit. While a wide range of coefficients are disclosed in the materials of the art, these materials are compounded from a large variety of constituents some of which are required only rarely and therefore not generally kept in stock.

One object of this invention is to enable the manufacture of resistor bodies from a mixture of a limited number of constituent oxides whose temperature coefficient of resistance is reproducible and can be varied over a wide range, and whose structure is that of a stable compound.

Another object of this invention is to improve methods of forming resistor bodies from finely divided particles.

In accordance with one feature of this invention, the resistor materials comprise combinations of the oxides of nickel, manganese and iron.

Another feature of this invention resides in controlling the relative amounts of the con-

stituent oxides of nickel, manganese and iron in the material to obtain a desired resistance-temperature coefficient and specific resistance.

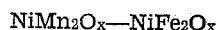
A further feature of this invention resides in a method of applying a coating of a wax binder to the individual particles making up the resistor body by precipitating the wax out of a suspension and onto the particles.

In one of its more specific aspects, this invention involves the compounding of two stable compounds, which may be of the spinel-type, which are mutually soluble in all proportions to produce a system having a single phase throughout the composition range. The resulting mixture thus has stable electrical characteristics which depend upon relative proportions of the component metals.

Further objects and features of this invention will be understood from the following detailed description with reference to the accompanying drawings in which:

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

Fig. 2 is a curve showing the specific resistance of one mixture of the material at 25° C. as a function of the NiFe_2O_x present in a



composition;

Fig. 3 shows the relationship between the temperature dependence factor β and the composition of the $\text{NiMn}_2\text{O}_x - \text{NiFe}_2\text{O}_x$ mixture;

Fig. 4 is a curve showing the specific resistance of a $\text{NiMn}_4\text{O}_x - \text{NiFe}_4\text{O}_x$ mixture at 25° C. as a function of the NiFe_4O_x content; and

Fig. 5 is a curve showing the relationship between the temperature dependence factor β and the composition of the $\text{NiMn}_4\text{O}_x - \text{NiFe}_4\text{O}_x$ mixture.

Resistors having particularly desirable temperature-resistance characteristics compounded from combinations of the oxides of nickel and manganese have been disclosed in Patent 2,258,646 issued October 14, 1941 to Richard O. Grisdale. These oxides were compounded in various ratios of the metal atoms to produce materials having varying specific resistances. However, the temperature coefficient of resistance was essentially independent of the atomic ratios of the metals. In accordance with a feature of this invention, it has been found that mixtures of nickel, manganese and iron oxides in varying proportions show great stability and have very desirable electrical properties including a tem-

perature coefficient which can be varied by controlling the proportions of the components.

Thermistor materials composed of three oxide mixtures of nickel, manganese and iron can be produced with the extremely stable spinel-type cubic structure and with a variety of temperature dependence factors by maintaining the ratio of the constituent oxides of the final product such that the number of Mn atoms plus Fe atoms to the number of Ni atoms will be in the range from 2 to 4 inclusive. The specific resistance and temperature dependence factors of compounds at these limits are disclosed in the curves of Figs. 2 to 5, the resultant mixtures having a constant ratio of nickel atoms to the combined iron and manganese atoms, the iron atoms being varied from zero to 90 per cent of the total of the two. These mixtures in effect are compounded of the combination of two mutually soluble spinel-type compounds in all proportions from zero to 90 per cent of NiFe_2O_x in the mixture of NiMn_2O_x and NiFe_2O_x and from zero to 90 percent of NiFe_4O_x in the mixture of NiMn_4O_x and NiFe_4O_x .

The end products of the mixtures have been characterized as having an indefinite quantity of oxygen represented by the symbol O_x . This has been done since the quantity of oxygen varies with the partial pressure of oxygen and temperature conditions under which the mixture of the oxides is sintered to form the solid solution. The materials disclosed here have all been sintered at 1200°C . in air at atmospheric pressure. Further temperature treatments and their effects upon the characteristics of thermistors produced from these compounds are disclosed in the application of George T. Loman, Serial No. 113,590, filed September 1, 1949.

As disclosed in the curves of Figs. 2 and 3, by proportioning the atomic per cent of the NiFe_2O_x in the system of NiMn_2O_x and NiFe_2O_x the value of the temperature dependence factor β can be varied from the order of 3500°C . to the order of 4600°C . while the specific resistance at 25°C . varies between 3×10^3 and 2×10^7 ohm centimeters.

At the other extreme of the mixtures, i. e., in the NiMn_4O_x and NiFe_4O_x system, the temperature dependence factor β as disclosed in Fig. 5 and the specific resistance at 25°C . as shown in Fig. 4 plotted against the atomic per cent of NiFe_4O_x varies between 3700°C . and 5800°C . and between 2×10^3 and 2×10^7 ohm centimeters.

Resistors of these materials may be made in the forms of beads, rods, or as disclosed in Fig. 1, discs 10 having electrodes 12 and 13 securing leads 14 and 15 to the body portion.

The basic elements employed in the mixing of the body material are NiO , Mn_2O_3 and Fe_2O_3 particles of the order of one micron in diameter which are mixed in a colloid mill with a solution which may be either slightly acidic or basic, for example distilled water slightly acidified with acetic acid, in order to improve the wetting of the oxide particles and therefore the intimacy of mixing. Considering a 50 per cent NiFe_2O_x mixture in the NiMn_2O_x and NiFe_2O_x system as exemplary, the following quantities of oxides are mixed:

18.67 grams of NiO
19.73 grams of Mn_2O_3
19.96 grams of Fe_2O_3

The quantities of oxides which must be mixed to obtain the desired ratio of the number of metal atoms in any other mixture may be determined

in the well-known manner by considering the atomic weight of the elements.

After the oxides are thoroughly mixed, a binder in a liquid suspension is added, the liquid being of such a nature and concentration as to be neutralized by the solution originally employed in mixing and produce a water soluble salt. In the case of an acetic acid solution, for example, a petroleum wax in an amine, such as triethanolamine, emulsifying agent is added to the mixture in the mill. The acid in the original mixture neutralizes the emulsifying agent in the binder causing the wax to precipitate from the emulsion and to coagulate on the oxide particles. The resulting mixture is then removed from the mill and the salt solution filtered off. After the solution is removed the resulting cake is in condition for pressing to the desired resistor form.

The resistor of Fig. 1 is constructed by pressing the dried cake into discs, for example discs of one-half inch diameter containing about 1 gram of material. High densities are attainable in this pressing operation since the wax not only acts as a binder but also lubricates the particles so they readily slide over each other to reduce the voids in the pressed body. Then the pressed body is mounted in a holder buried in 120 mesh alundum and heated to about 300°C . until the wax binder is evaporated and all binder residue is removed. Next the body is sintered in air for 16 hours at 1200°C . and is allowed to cool in air to room temperature.

To complete the unit, electrodes 12 and 13 are applied to the sintered body 10, for example by coating the surfaces with a metallic paste comprising finely divided metal particles, a binder and a solvent and then curing the paste at an elevated temperature to form a stable and tough layer on the body faces. Contact to the electrodes can be made in several ways, including soldering, by mechanical pressure, or as disclosed in the drawing by embedding leads 14 and 15 in the electrode paste prior to curing it.

What is claimed is:

1. A conductive device consisting essentially of a sintered body of the combined oxides of nickel, manganese and iron having a specific resistance and temperature coefficient of resistance dependent upon the atomic ratio of the constituent metals, said atomic ratio falling between the limits of

$$\frac{\text{Mn} + \text{Fe}}{\text{Ni}} \text{ of } 2.0 \text{ and } 4.0$$

and spaced electrodes connected to the body.

2. A conductive device comprising a sintered body consisting essentially of combined oxides of nickel, manganese and iron in the proportions of one atom of nickel, one atom of manganese, and one atom of iron, and spaced electrodes connected to said body.

3. A conductive device comprising a sintered body consisting essentially of a first spinel type compound consisting essentially of the oxides of nickel and manganese in solid solution with a second spinel type compound consisting essentially of the oxides of nickel and iron, the atomic ratio of the nickel to the manganese in said first compound falling between the limits of 1:2 and 1:4, the atomic ratio of nickel to iron in the second compound falling between the limits of 1:2 and 1:4, and spaced electrodes connected to said body.

FRANCIS J. MORIN.

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