

Nov. 9, 1954

G. T. LOMAN

2,694,050

THERMALLY SENSITIVE RESISTOR

Filed Sept. 1, 1949

3 Sheets-Sheet 1

FIG. 1

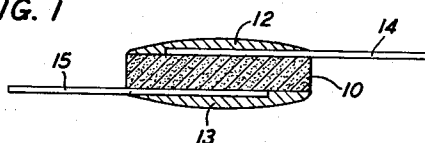


FIG. 2

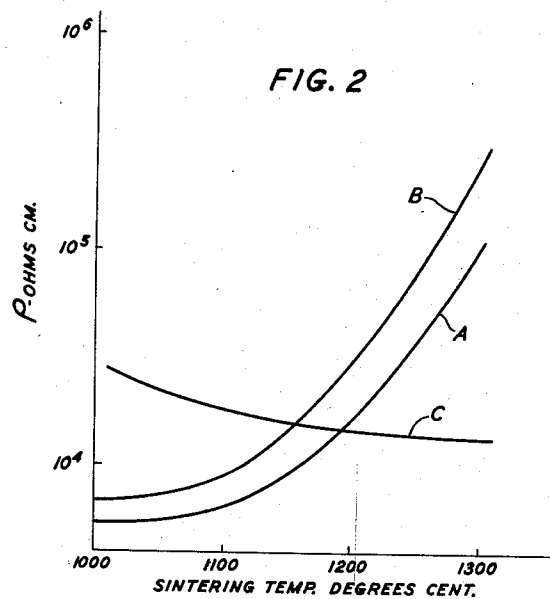
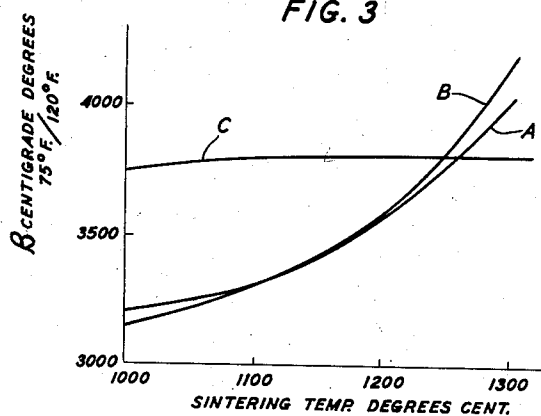


FIG. 3



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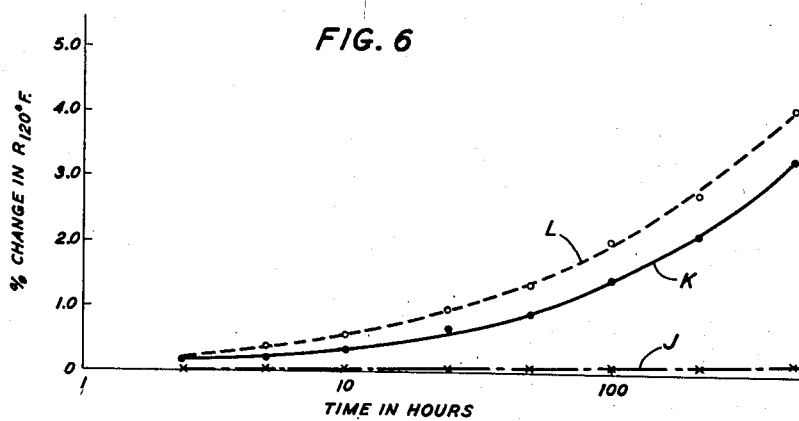
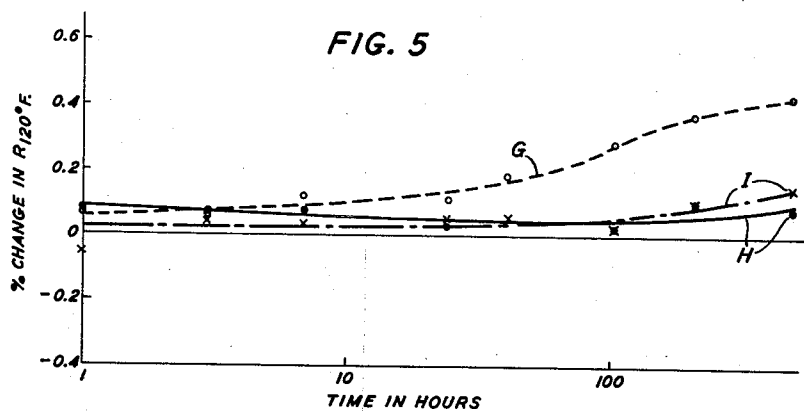
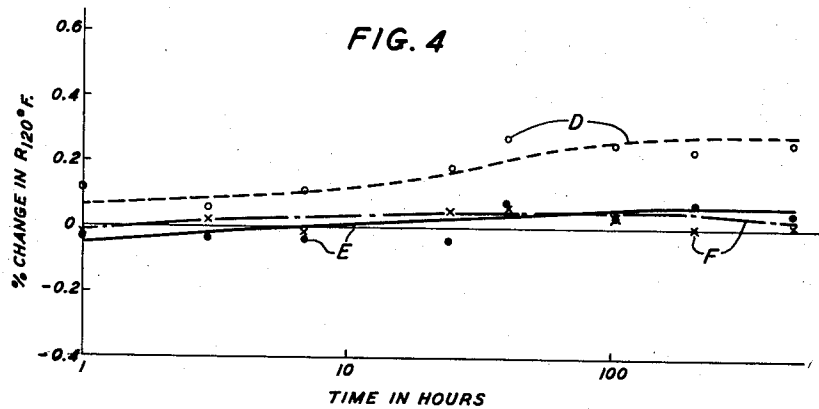
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3 Sheets-Sheet 2



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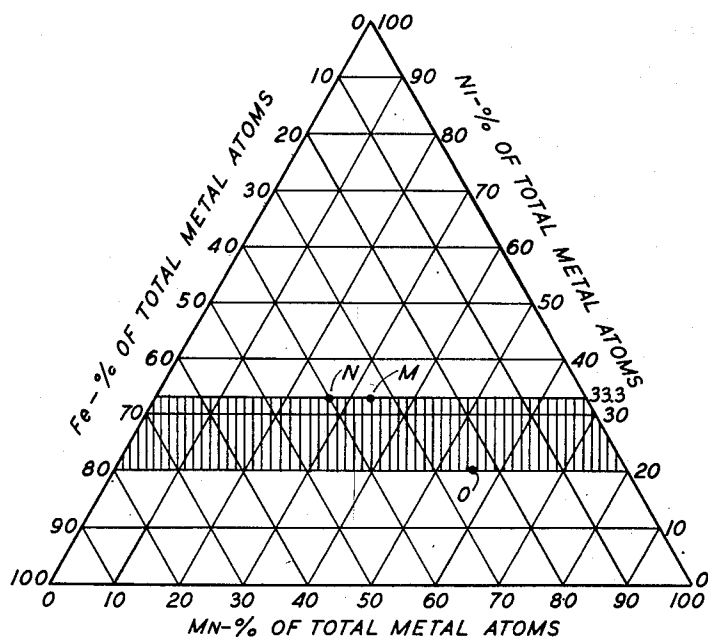
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THERMALLY SENSITIVE RESISTOR

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FIG. 7



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THERMALLY SENSITIVE RESISTOR

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Application September 1, 1949, Serial No. 113,590

1 Claim. (Cl. 252—490)

This invention relates to methods of making thermally sensitive resistors, particularly such resistors of the type disclosed in the application Serial No. 112,805, filed August 27, 1949, of Francis J. Morin, now Patent No. 2,645,700.

The resistors particularly involved in this invention are those whose resistance varies greatly with changes in temperature and which are 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 is usually obtained from the relationship

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

Applying this equation to (1) there is obtained

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

One object of this invention is to control the resistivity, resistance temperature coefficient, and stability of thermistors.

Another object of this invention is to facilitate the production of thermistors having prescribed electrical and operating characteristics.

One feature of this invention resides in fabricating resistors from a solid solution of manganese, nickel, iron and oxygen and controlling the sintering temperature to obtain desired values within a wide range of resistivity and resistance temperature coefficients with a given composition.

Other features and objects will be understood from the following detailed description when read with reference to the accompanying drawings in which:

Fig. 1 shows a resistor representative of the type to which this invention relates;

Fig. 2 is a curve of specific resistivity plotted against sintering temperature for several illustrative mixtures of nickel, manganese, iron and oxygen;

Fig. 3 shows the temperature dependence factor, β , of the illustrative mixtures plotted against sintering temperature;

Figs. 4, 5 and 6 disclose the aging characteristics plotted as per cent change in resistance versus time for resistors of the type shown in Fig. 1 composed of the illustrative mixtures, the several curves representing the characteristics of resistors sintered at selected temperatures; and

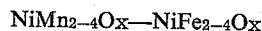
Fig. 7 is a ternary diagram of the metallic constituents present in the metallic oxide semiconductor under consideration, the shaded portion indicating the range of proportions of metallic constituents to which this invention is applicable.

Various mixtures of a system composed of nickel, manganese, iron and oxygen which when sintered at 1200° C. produce resistor bodies having a wide range of resistivity and temperature coefficient of resistance depending upon the ratio of the metal atoms present, within

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such limits that the ratio of the number of Mn atoms plus Fe atoms to the number of Ni atoms is between 2 and 4 inclusive, are disclosed in the above-noted application of Francis J. Morin.

In accordance with a feature of this invention, further control of the resistivity and temperature characteristics of such mixture of the oxides of nickel, manganese and iron is obtained by controlling the sintering temperature of the mixture. This may be attributed to the variations from the stoichiometric compositions which are produced at the various sintering temperatures. The oxygen content of the various combinations of nickel, manganese and iron oxides in the oxide system



which form solid solutions in all proportions varies with the sintering temperature. More specifically, the specific resistance and β , the temperature dependence factor, of the resistors in this system have been found to be extremely sensitive to the sintering temperature employed. For the compounds lying within the limits of this system which are disclosed for illustrative purposes, namely NiMnFeO_x , $\text{Ni}_{1.0}\text{Mn}_{0.8}\text{Fe}_{1.2}\text{O}_x$, and $\text{Ni}_{1.0}\text{Mn}_{2.8}\text{Fe}_{1.2}\text{O}_x$, the subscripts representing the ratio of the number of atoms of each element present, the specific resistance varies from 6000 to 300,000-ohm centimeters at 75° F. over the sintering temperature range of 1000° to 1400° C. These illustrative compounds are represented in Fig. 7 by the points M, N and O respectively. Temperature dependence, β , which is used as an index for the temperature coefficient α and is related thereto in accordance with the formula

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

where T is the absolute temperature, in this sintering range extends from 3150 to 4150° C.

The oxide system $\text{NiMn}_{2-4}\text{O}_x\text{—NiFe}_{2-4}\text{O}_x$ making up the resistor body can be prepared in a number of ways starting either with the oxides or the carbonates of the metals and proportioning the components with the nickel as the reference quantity. In terms of the metal atoms, the mixtures which are herein employed as illustrative, consist of ten atoms of Ni, ten atoms of Mn and ten atoms of Fe; ten atoms of Ni, eight atoms of Mn and twelve atoms of Fe; and ten atoms of Ni, twenty-eight atoms of Mn and twelve atoms of Fe. When the mixtures are made directly from the oxides of nickel, manganese and iron, for example, the NiMnFeO_x mixture having a ratio of the metals of 1:1:1 is made up as follows:

	Grams
NiO	14.94
Fe ₂ O ₃	15.97
Mn ₂ O ₃	15.79

These oxides are mixed in a colloid mill with distilled water and acidified with acetic acid to obtain better wetting of the oxide particles. The liquid is filtered off after mixing and the resulting cake is dried and screened. A binder is mixed with the screened oxides, for example, isobutyl methacrylate in the proportions of 5 grams to 100 grams of the oxides and a solvent for the isobutyl methacrylate which may be xylene in the proportion of one gram per gram of the oxides. The consistency of the mixture can be further controlled by adding a plasticizer such as dimethyl phthalate mixed in the proportion of 5 cubic centimeters to 100 grams of the oxides. The mixture is then screened a second time to prepare it for pressing.

While the resistor bodies may take any convenient form, for example, rods, beads or discs, the latter is the only type illustrated. Fig. 1 discloses a disc resistor having a body 10 composed of a mixture of the oxide system $\text{NiMn}_{2-4}\text{O}_x\text{—NiFe}_{2-4}\text{O}_x$ on the opposite faces of which are mounted electrodes 12 and 13 providing the means for making electrical and mechanical connections of the leads 14 and 15 thereto.

Resistor bodies of the disc type are prepared from the screen cake by pressing approximately one gram of material in a half inch diameter die at about 12,700 pounds

per square inch. The pressed discs are then heat treated first to remove the binder and all its residue and then to sinter them so that the body material forms a solid solution. In preparing the discs for firing, they are mounted in a receptacle of refractory material which may be a fused silica boat, and are individually buried in finely divided refractory material, for example, 120-mesh Alundum. The boat and contents are then heated to 300° C., for example in air, and held at that temperature for about four hours until all the binder is evaporated.

The sintering of the discs is effected at a variety of temperatures depending upon the desired resistivity ρ and temperature dependence factor β as disclosed in Figs. 2 and 3. These characteristics for the nickel, manganese, iron and oxygen mixtures having the metallic ratios of 1:1:1 for curve A, 5:4:6 for curve B and 5:14:6 for curve C are plotted against sintering temperature in those figures. These sintering treatments were effected on units of the three representative mixtures at temperatures ranging from 1000° C. to 1400° C. for sixteen hours in air at atmospheric pressure, the temperature depending upon the characteristics desired. After sintering the units may be cooled in any convenient manner, the cooling rate having no apparent effect upon the resistivity or temperature dependence factor of the sintered body.

Leads are then secured to the unit. In the case of the discs disclosed in Fig. 1 they are secured to each face by a layer of conductive material which also serves as an electrode, this material generally being applied in the form of finely divided metal in a temporary binder, the binder evaporating and the metal being cured at a relatively low temperature. Specific examples of suitable electrodes are those composed of a paste of finely divided silver mixed with a temporary binder such as isobutyl methacrylate and cured at 600° C., or those made up of a paste of finely divided platinum as disclosed in Patent 2,418,461 issued April 8, 1947, to Joseph A. Becker et al.

In the preceding discussion of the materials making up the body of the thermistors, the amount of oxygen present has been indicated as an indefinite quantity represented by the subscript X in the formulas. The sintering temperature controls the oxygen content of the resulting solid solution and thus the resistivity ρ and the temperature dependence factor β , the quantity of oxygen decreasing with higher sintering temperatures.

A further effect of the sintering temperatures disclosed in Figs. 4, 5 and 6 showing per cent change in resistance at 120° F. plotted against age is that the unit sintered

at the higher temperatures exhibited a more stable characteristic than did those sintered at the lower temperatures. In making the test to obtain the plotted results an accelerated aging was attained by holding the units at 105° C. during the periods intermediate the resistance test. These results indicate that with higher sintering temperatures the resistance is substantially constant. Figs. 4 and 5 show the aging characteristics of the NiMnFeO_x and $\text{Ni}_{1.0}\text{Mn}_{0.8}\text{Fe}_{1.2}\text{O}_x$ mixtures, respectively, when sintered at 1000° C., curves D and G, 1175° C., curves E and H, and 1300° C., curves F and I, for the respective mixture show a change of resistance of the order of ± 0.5 per cent at sintering temperatures of 1175° C. and 1300° C. At the lower sintering temperatures the stability of the NiMnFeO_x unit showed a resistance change of 0.3 per cent and the $\text{Ni}_{1.0}\text{Mn}_{0.8}\text{Fe}_{1.2}\text{O}_x$ units changed about 0.5 per cent.

The $\text{Ni}_{1.0}\text{Mn}_{0.8}\text{Fe}_{1.2}\text{O}_x$ discs of Fig. 6 when sintered at 1300° C., curve J, changed 0.3 per cent but at the lower sintering temperatures of 1175° C., curve K, and 1000° C., curve L, the resistance changed 3.2 and 4.0 per cent, respectively.

Thus this process provides a system of thermistor materials composed of the oxides of nickel, manganese and iron which when compounded in various proportions and sintered at accurately controlled temperatures produces thermistors having prescribed characteristics within an extremely wide range of temperature coefficient and resistivity with stable aging properties.

I claim:

The method of producing a high stability resistance material having a large temperature coefficient of resistance that comprises heating a combination of the oxides of nickel, manganese, and iron in the proportion of 5 atoms of nickel, 14 atoms of manganese, and 6 atoms of iron in air at a temperature of about 1300° C. for about 16 hours.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
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2,274,592	Dearborn	Feb. 24, 1942
2,326,580	Trenkle	Aug. 10, 1943
2,414,793	Becker et al.	Jan. 28, 1947
2,645,700	Morin	July 14, 1953

OTHER REFERENCES

Physica, v. 3, No. 6, June 1936, pp. 463-483.