

Feb. 24, 1942.

E. F. DEARBORN

2,274,592

RESISTANCE MATERIAL AND METHOD OF MAKING THE SAME

Filed June 23, 1939

3 Sheets-Sheet 1

FIG. 1

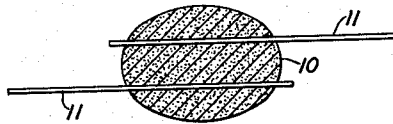


FIG. 2

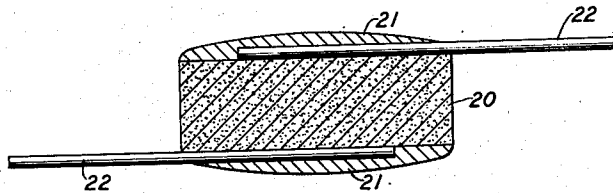
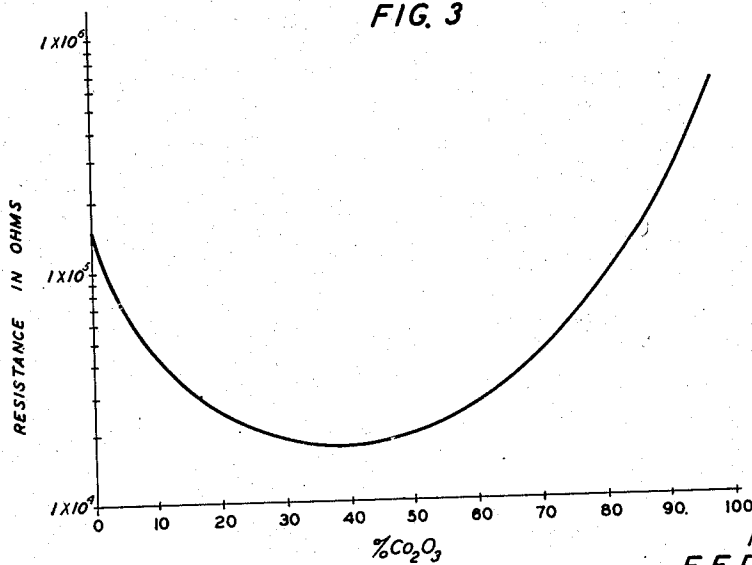


FIG. 3



INVENTOR
E. F. DEARBORN
BY

Halter C. Kiesel
ATTORNEY

Feb. 24, 1942.

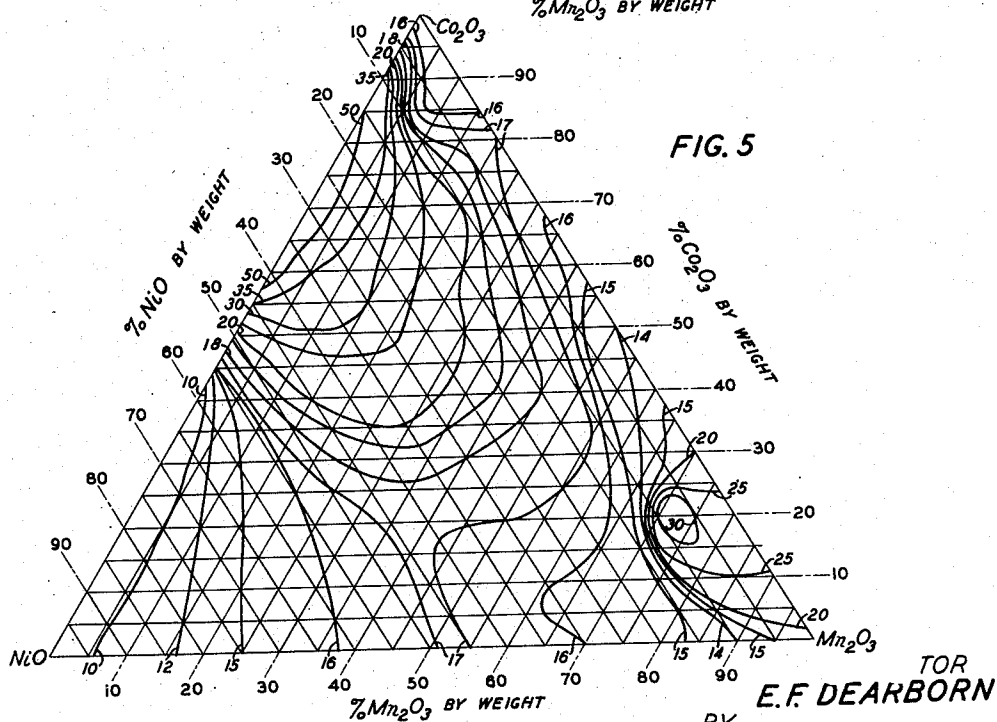
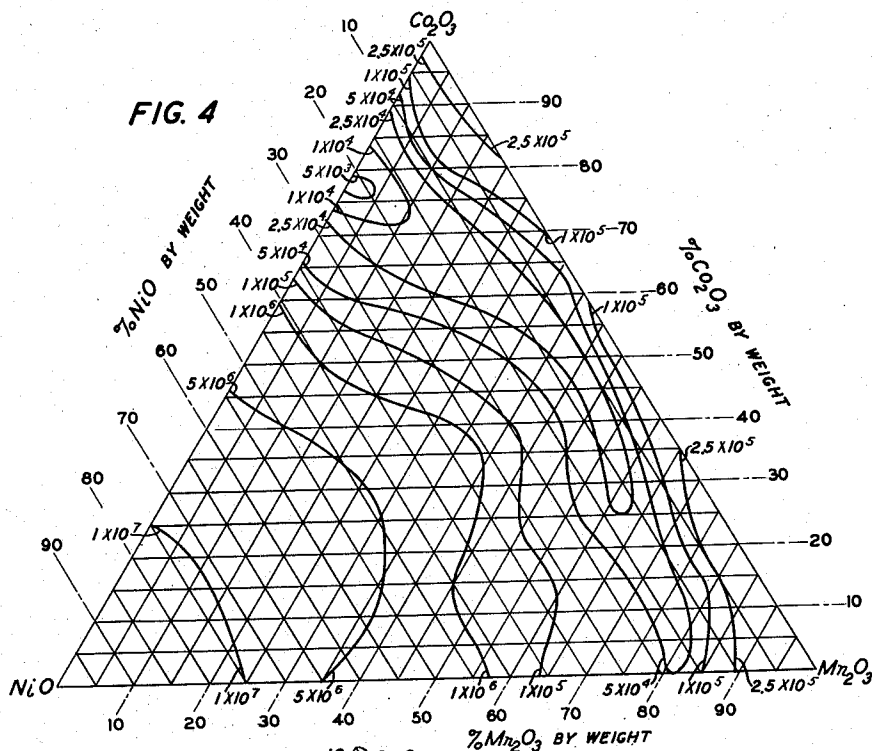
E. F. DEARBORN

2,274,592

RESISTANCE MATERIAL AND METHOD OF MAKING THE SAME

Filed June 23, 1939

3 Sheets-Sheet 2



FOR
E. F. DEARBORN
BY
Walter C. Kiesel
ATTORNEY

UNITED STATES PATENT OFFICE

2,274,592

RESISTANCE MATERIAL AND METHOD OF
MAKING THE SAMEErnest F. Dearborn, Yonkers, N. Y., assignor to
Bell Telephone Laboratories, Incorporated,
New York, N. Y., a corporation of New York

Application June 23, 1939, Serial No. 280,692

10 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 made from combinations of metal oxides.

As is pointed out in the application of Richard O. Grisdale, Serial No. 274,114, filed May 17, 1939, now Patent 2,258,646, issued October 14, 1941, resistance materials having particularly desirable characteristics may be made from combinations of metal oxides. By employing proper proportions of the oxides for the resistance material, 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. It has been found that mixtures of nickel and manganese oxides when properly heat treated combine to produce a resistance material having particularly desirable resistance characteristics.

One object of this invention is to improve resistors and resistance materials made from oxidic material.

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

One feature of this invention resides in the addition of cobalt oxide to the oxides of manganese and nickel in the formation of resistance materials.

In accordance with another feature of this invention, the ratio of the oxides is controlled to obtain a desired specific resistance.

In accordance with a further feature of this invention, a solution containing a compound of the metallic element of one of the oxides is employed as a binding material in the fabrication of resistance units.

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 drawings 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;

Fig. 3 is a curve showing the effect on the resistance of the addition of cobalt oxide to a mixture of nickel and manganese oxides;

Fig. 4 is a triangular diagram showing con-

stant resistance contours for different compositions of nickel, manganese and cobalt oxides;

Fig. 5 is a similar triangular diagram with constant half temperature contours; and

Figs. 6 and 7 are diagrams similar to those shown in Figs. 4 and 5 but for relative proportions of the metallic elements, Fig. 6 showing specific resistances and Fig. 7 half temperatures.

As disclosed in the previously mentioned application Serial No. 274,114 of Richard O. Grisdale, resistor units made from nickel and manganese oxides and containing the compound nickel-manganite, exhibit minimum specific resistance for an atomic ratio of Mn/Ni between 2 to 1 and 4 to 1. Moreover, in units having a higher specific resistance due to an excess of one of the constituents, the resistance-temperature coefficient or half temperature varies little from that of the minimum resistance material. The term "half temperature" may be defined as the temperature range over which the resistance is doubled or reduced by half. In specifying half temperatures the range over which the measurement is taken should be given. A convenient range is from 0° to 25° C. and will be understood in this application unless otherwise specified.

It has been found in accordance with this invention that the addition of cobalt oxide to the manganese-nickel oxide combination produces upon heat treatment a resistance material having a lower specific resistance, but with approximately the same half temperature as the manganese-nickel oxide resistance material. The mixed oxides when heat treated combine so that the resulting material is no longer a simple mixture thereof, but a new material. The term "combined oxides" or oxides in combination as employed in this specification and the appended claims is intended to define this new material.

In the preparation of the resistance material, the constituent oxides are usually employed in a finely divided state. Predetermined proportions of the three oxides 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. The temperature and the atmosphere of heat treatment are regulated in accordance with the resistance desired. For example, an oxidizing atmosphere reduces the resistance, if the cobalt oxide content is below about 70 per cent. If more than approximately 70 per cent cobalt oxide is used, the resistance is lowered by a reducing atmosphere. In general, for a given composition, the higher the temperature of heat treatment the

lower will be the resistance of the completed material or unit.

As will be pointed out more fully in subsequent paragraphs, the resistance of the material is a function of the relative amounts of the metallic elements present after the three oxides are combined. The atmosphere of heat treatment determines the amount of oxygen in the finished product, which also affects the resistance value. Consequently, different oxides of the three metals may be used and a suitable heat treatment employed for a given composition to give the desired resistance characteristics.

The amount of oxygen in, and consequently the resistance value of, the finished product, may be regulated both by the amount in the constituent oxides and in the atmosphere of heat treatment. For example, high oxides might be treated in a neutral atmosphere or low oxides in an oxidizing atmosphere with similar results as to final resistance. On the other hand, like resistance values can be attained by treating low oxides in a neutral atmosphere or high oxides in a reducing atmosphere. From the foregoing it will be evident that the atomic ratio of the metallic elements, the amount of oxygen and the temperature of heat treatment all play a part in the determination of the final resistance. However, the heat treatment has no marked effect upon the half temperature value of a given composition. The resistor units may be made up in several forms two of which are shown in Figs. 1 and 2.

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. A preferred binder comprises a nitrate solution of one of the metals involved, for example, cobalt nitrate. The powdered oxides may also be mixed with water. 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. Where a particular resistance material requires a low percentage of that oxide which has the same metallic constituent as the binder, account should be taken of the metallic content of the binder. For example, where a low cobalt content is desired and the binder is cobalt nitrate, the cobalt oxide should be adjusted so that the sum of the cobalt therein and the cobalt obtained from the nitrate during heat treatment will be in the proper amount.

A unit of the disc or plate type, such as shown in Fig. 2, may be made by intimately mixing the finely divided oxides and pressing them into a body 20. The heat treatment for this type of unit is similar to that employed for the bead unit. Contact electrodes may be applied to opposite faces of the disc or plate by any adequate means. A suitable connection can be made by applying metallic paste to the surfaces and embedding conductive leads 22 therein. The units are then heated to solidify the paste into electrodes 21 firmly bonding the leads 22 to the resistance body 20. The conductive leads 22 may also be applied as follows: Metallic paste is applied to the unit and heated to solidify it, a sprayed metallic layer, as from a Schoop spray, is applied over this and the leads soldered thereto. For many applications the body 20 is made relatively thin, so that the current path between the electrodes 21 is short compared to its cross-sectional dimensions.

The effect of the addition of a cobalt oxide, 75

such as Co_2O_3 , to the nickel-manganese oxide mixture is shown by the curve of Fig. 3. The atomic proportions of manganese and nickel are $\text{Mn/Ni}=2$, for example,



It will be noted that the addition of relatively small percentages of cobalt oxide has a marked effect in reducing the resistance. Beyond about 40 per cent cobalt oxide, a further addition increases the resistance to a considerable degree. The half temperature is only increased slightly above that of the binary mixture by the addition of cobalt oxide. A nickel-manganese-cobalt oxide unit in which Co_2O_3 up to about 40 per cent was added, has a half temperature of about 18°C . as compared to 16°C . for a corresponding nickel-manganese oxide unit.

In Figs. 4 and 5 are shown triangular diagrams indicating the relative amounts of the three oxides contained in any given unit. In Fig. 4, the contour lines pass through points of equal resistance and in Fig. 5 through points of equal half temperature. The resistance designations are in ohms and the half temperatures in degrees centigrade measured between 0° and 25°C . By referring to both diagrams a composition having a particular resistance and half temperature may be determined. The diagrams illustrated in these figures are for a bead unit, 0.03 inch in diameter, heat treated at 1300°C . in oxygen, the constituents being NiO , Mn_2O_3 and Co_2O_3 . Other similar diagrams may, for convenience, be made for other of the oxides of nickel, manganese and cobalt, other sizes of units and different heat treatments. Diagrams such as those illustrated in Figs. 6 and 7 showing proportions of the different metals and specific resistance values in ohm-centimeters are useful since they are more general in application. These diagrams are drawn for a temperature and atmosphere of heat treatment the same as for the diagrams of Figs. 4 and 5. As previously indicated the resistance values shown on the triangular diagrams may be varied to some extent by varying the heat treatment. However, this does not appreciably affect the half temperature of a given composition.

Illustrative of the use which may be made of these diagrams, suppose that a 0.03 inch bead unit having a resistance of 100,000 ohms and a half temperature of 16°C . is desired. By superposing the two diagrams of Figs. 4 and 5 it is found that the 1×10^5 resistance line intersects the 16°C . half temperature line at a composition of approximately 61 per cent manganese oxide, 29 per cent nickel oxide and 10 per cent cobalt oxide. In some cases there may be more than one intersection for a given set of resistance characteristics, so that more than one composition is available.

Reference to Figs. 4 and 5 indicates that the proportions of the constituents may be so adjusted that for a half temperature range between 10° and 20°C ., units may be obtained having resistances ranging from about 15,000 ohms to 10 megohms, which in terms of specific resistance is from about 3,000 to 2×10^6 ohm-centimeters.

The usefulness of resistors of the type disclosed, for many purposes, lies in their comparatively low half temperatures. A material in accordance with this invention, comprising any combination of the oxides of nickel, manganese and cobalt will produce resistors having a half temperature below 70°C . A very large por-

tion of the possible combinations gives a half temperature of 30° C. or lower and with a majority of the combinations a half temperature 20° or lower may be obtained. Moreover, a wide range of resistance values is obtainable for each half temperature. For example, the half temperature is 30° C. or lower for most compositions, the exception being for those in which manganese is less than 5 per cent for from about 4 to 30 per cent nickel, less than 10 per cent for from about 9 to 28 per cent nickel, less than 15 per cent for from about 12 to 25 per cent nickel and less than 18 per cent for from about 16 to 24 per cent nickel, the remainder in each case being cobalt. Referring to Fig. 7, it will be seen that the excepted compositions fall between the zero manganese line and the 30° C. half temperature contour. An inspection of Fig. 6 indicates that specific resistances from about 2,000 to over 2×10^6 ohm-centimeters can be obtained with these half temperatures.

Referring further to the diagrams of Figs. 6 and 7, it will be seen that the specific resistance is relatively high in the regions of high nickel, manganese or cobalt. This is particularly true for high nickel compositions for which the half temperatures are relatively low. Comparatively low half temperatures are also obtainable with fairly high percentages of either manganese or cobalt. With a Mn/Ni ratio ranging between 1 to 1 and 12 to 1, the cobalt percentage may be varied from a very small amount, about 2 per cent, up to over 95 per cent with a considerable difference in resistance values for the different compositions but with substantial retention of a low half temperature throughout the resistance range, namely 14 to 20° C.

As will be noted with reference to Fig. 7, a half temperature of 20° or less may be obtained for Mn/Ni ratios considerably above 12 to 1 if the cobalt content is kept above about 35 per cent or below about 3 per cent. For example, a unit having about 0.5 per cent nickel, 55 per cent manganese and 44.5 per cent cobalt has a half temperature of about 14° C. or one having percentages of 2, 95 and 3, respectively, for nickel, manganese and cobalt has a 20° C. half temperature. Moreover, for a combination in which the nickel is over about 33 per cent, a 20° C. or lower half temperature is obtainable for a wide range of ratios of manganese to cobalt. The specific resistance for these combinations is relatively high being of the order of 2×10^5 ohm-centimeters or higher.

Referring again to Figs. 6 and 7, it will be seen that a minimum specific resistance of the order of 5×10^3 ohm-centimeters may be obtained with a half temperature within the range 14° to 20° C. with compositions containing from approximately 3 to 10 per cent nickel, 25 to 70 per cent manganese and 25 to 75 per cent cobalt. For applications in which a higher half temperature is suitable, a material having a minimum specific resistance of about 1,000 ohm-centimeters is obtainable with compositions of the order of 12 per cent nickel, 3 per cent manganese and 85 per cent cobalt. The half temperature of such a material would be around 50° C.

Because of the wide range of resistance values available within a fairly narrow range of low half temperatures, (10° to 20° C.) resistance units for many different applications may be made with the resistance material of this invention.

The conduction of resistor units made from

the combined oxides of nickel, manganese and cobalt in accordance with this invention is predominantly electronic, allowing their use for both alternating and direct current applications. Since units of this type, for many applications, must be very small, they are preferably mounted in an enclosing vessel, such as a glass envelope, for protection. The units may also be kept stable over long periods by enclosing them in an evacuated envelope. A vacuum of 10^{-3} millimeters of mercury or better is suitable. Exemplary of such units is a small bead type of about 0.03 inch diameter. This unit has a resistance of 30,000 ohms at 25° C. and a half temperature of about 18° C. measured between 0° and 25° C. and comprises 23 per cent NiO, 47 per cent Mn_2O_4 and 30 per cent Co_2O_3 .

Although specific embodiments of this invention have been shown and described, it will be understood that various 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 negative resistance-temperature coefficient resistance material consisting of oxides of nickel, manganese and cobalt, heat treated between 800° and 1450° C., the major portion of said material comprising said oxides in combination, the metals being in the approximate proportions corresponding respectively to 23 percent NiO, 47 per cent Mn_2O_4 and 30 per cent Co_2O_3 .

2. The method of making a negative resistance-temperature coefficient resistance material that comprises mixing finely divided oxides of nickel, manganese and cobalt, and combining the oxides by heat treating the mixture at a temperature between 800° and 1450° C. in a controlled atmosphere.

3. The method of making a negative resistance-temperature coefficient resistance unit that comprises intimately mixing finely divided oxides of nickel, manganese and cobalt, forming the mixture into a body, and combining the oxides by heat treating the body in an atmosphere free from reducing agents at a temperature between 800° and 1450° C.

4. The method of making a resistor unit that comprises mixing finely divided oxides of the metals nickel, manganese and cobalt with a concentrated nitrate solution of one of said metals, forming the resultant paste into a bead on parallel conductors, drying the bead, and heat treating it at a temperature between 800° and 1450° C. in a controlled atmosphere.

5. A negative resistance-temperature coefficient material consisting of oxides of nickel, manganese and cobalt intimately mixed and heat treated between 800° and 1450° C., the constituents being in the proportion of more than about 45 per cent of the oxide of manganese, up to about 30 per cent of the oxide of cobalt, and the remainder the oxide of nickel, the major portion of said material comprising the oxides in combination.

6. A negative resistance-temperature coefficient material consisting of oxides of nickel, manganese and cobalt intimately mixed and heat treated between 800° and 1450° C., the major part of said material comprising the oxides in combination.

7. The method of controlling the resistance of a nickel and manganese oxide negative resistance-temperature coefficient material that comprises adding thereto a cobalt compound con-

taining a selected amount of cobalt and heat treating the constituents together at a temperature between 800° and 1450° C. in a controlled atmosphere.

8. A negative resistance-temperature coefficient resistance material consisting of oxides of nickel, manganese and cobalt, heat treated between 800° and 1450° C., the major portion of said material comprising said oxides in combination, the metals being in the approximate proportion corresponding respectively to 14 per cent NiO, 56 per cent Mn_2O_3 and 30 per cent Co_2O_3 .

9. A negative resistance-temperature coefficient resistance material consisting of oxides of nickel, manganese and cobalt, heat treated be-

tween 800° and 1450° C., the major portion of said material comprising said oxides in combination, the metals being in the approximate proportion corresponding to 17 per cent NiO, 61 per cent Mn_2O_3 and 22 per cent CoO.

10. A negative resistance-temperature coefficient material consisting of oxides of nickel, manganese and cobalt intimately mixed and heat treated between 800° and 1450° C., the constituents being in the proportion of up to 30 per cent of the oxide of cobalt with the oxides of manganese and nickel in the approximate ratio of 4 to 1 to 2 to 1, the major portion of said material comprising the oxides in combination.

ERNEST F. DEARBORN.