United States Patent [19]

Tachibana et al.

[11] **3,795,048**

[45] **Mar. 5, 1974**

[54] **METHOD FOR MANUFACTURING NON-LINEAR RESISTORS**

[75] Inventors: **Kan-ichi Tachibana; Michihiro Nishioka; Mikiya Ono,** all of Kitakyushu, Japan

[73] Assignee: **Mitsubishi Mining & Cement Company, Ltd.,** Tokyo, Japan

[22] Filed: **Jan. 26, 1973**

[21] Appl. No.: **327,177**

[30] **Foreign Application Priority Data**

Feb. 16, 1972 Japan 47-16305

[52] **U.S. Cl.** **29/621,** 29/610, 338/204, 338/22

[51] **Int. Cl.** **H01c 1/14,** H01c 17/00

[58] **Field of Search** .. 29/621, 610, 612; 338/22, 20, 338/204, 333

[56] **References Cited**

UNITED STATES PATENTS

2,720,573	10/1955	Lundquist	338/22 R
3,124,772	3/1964	Newkirk	29/610 X
3,343,114	9/1967	Rice	338/22 R
3,503,029	3/1970	Matsuoka	29/612 X
3,689,863	9/1972	Matsuoka	338/20

FOREIGN PATENTS OR APPLICATIONS

1,446,249	6/1966	France	338/22 R

Primary Examiner—Charles W. Lanham
Assistant Examiner—Victor A. DiPalma
Attorney, Agent, or Firm—Brenner & Wray

[57] **ABSTRACT**

A method for manufacturing non-linear resistors comprising superposing several sintered wafers and applying silver electrodes to opposite surfaces of the sintered wafers superposed respectively is disclosed. The sintered wafer, consisting essentially of iron oxide and copper oxide has negative resistance and also possesses such thermister constant B°K and specific resistance R_0 KΩ at 273° K as satisfy the relation $B \times R_0 \leq 10^4$KΩ°K. The non-linear resistors manufactured by this method, based on utilization of the property of the contact surfaces between the sintered wafers superposed, have remarkably stable volt-ampere characteristics and are inexpensive in cost.

2 Claims, 3 Drawing Figures

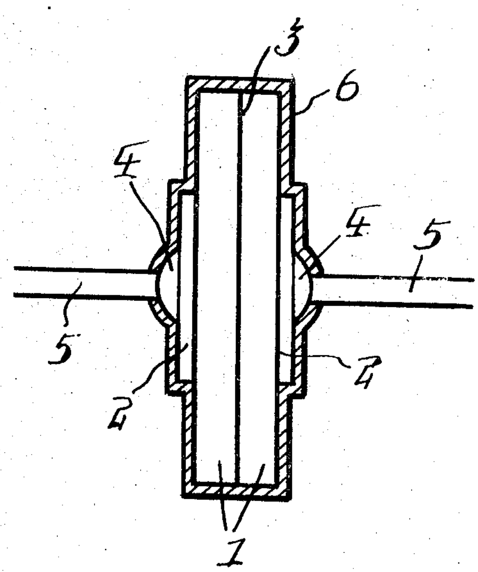


Fig. 1.

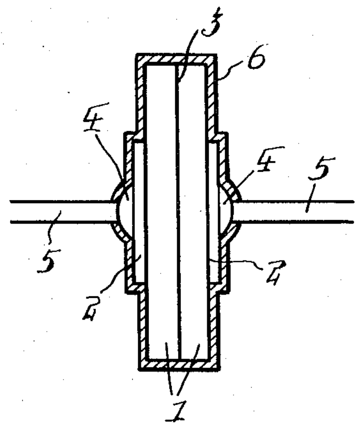


Fig. 2.

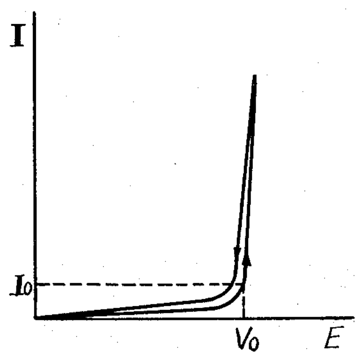
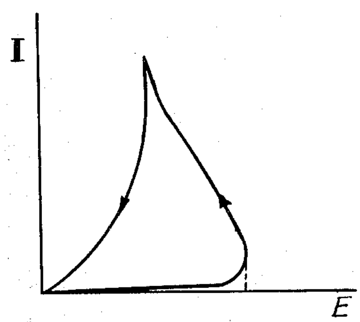


Fig. 3.



METHOD FOR MANUFACTURING NON-LINEAR RESISTORS

BACKGROUND OF THE INVENTION

This invention relates to a novel method for manufacturing non-linear resistors comprising superposing several sintered wafers, said sintered wafer having negative resistance and also possessing the thermistor constant B°K and the specific resistance R_0KΩ at 273° K that satisfy the following relation (1):

$$R_0 \times B \leqq 10{,}000 \text{K}\Omega\cdot{}^\circ\text{K} \ldots (1)$$

, and applying electrodes to opposite surfaces of said sintered wafers superposed respectively in a conventional manner.

In general, the relation between the resistance RKΩ at T°K and the above mentioned R_0KΩ, B°K of an oxide semiconductor is expressed by the following equation (2):

$$R = R_0 \exp\,[B(1/T - 1/273)] \ldots\ldots\ldots \quad (2)$$

The equation (2), however, is not necessarily applicable in any temperature range, but this invention relates to R_0, B in the temperature range in which the equation (2) is applicable.

Among conventionally used non-linear resistors (the term "non-linear resistor" is referred to as "varistor" hereinafter) are silicon carbide varistors, silicon varistors, barium titanate varistors and the like.

The volt-ampere characteristic of such a varistor is given by the following equation (3):

$$I = I_0(V/V_0)\alpha \ldots\ldots\ldots \quad (3)$$

where I is the current flowing through the varistor, V is the voltage across the varistor, V_0 is the voltage applied to the opposite surfaces of the varistor at $I=I_0$mA, that is, a threshhold voltage, and exponent α, an index representing non-linearity is a numerical value greater than 1, usually $3 \sim 5$.

Silicon carbide varistors, when made to be smaller in size, deteriorate the characteristics and exhibit α values less than 3.

Silicon varistors and barium titanate varistors are both able to be small-sized, but are limited in uses because V_0 value is only 0.5 ~1.2V. Moreover, in such a varistor which is based on utilization of the mutual contact between internal particles of a sintered body as silicon carbide varistors, it is difficult to completely control the state of said mutual contact between the internal particles even under the same manufacturing condition, consequently the product is inevitably variable in the characteristic.

We have found that the defects of the conventional varistors as described hereinabove is able to be overcome by processing conventional thermister materials (the term "sintered oxide material" is hereinafter referred to as "thermister") so as to limit the product of the thermister constant B° K and the specific resistance R_0KΩ at 273° K thereof within a certain range.

SUMMARY OF THE INVENTION

A primary object of this invention is to provide a method for manufacturing a varistor which has a remarkably stable volt-ampere characteristic.

Another object of this invention is to provide a method for manufacturing a varistor which is able to be small-sized.

Still another object of this invention is to provide a method for manufacturing a varistor which is inexpensive in cost.

According to this invention, there is provided a method for manufacturing a non-linear resister comprising superposing several sintered wafers, said sintered wafer having negative resistance and also possessing the thermister constant B°K and the specific resistance R_0KΩ at 273°K that satisfy the relation $B\times R_0 \leqq 10{,}000$ KΩ· ° K, and applying electrodes to opposite surfaces of said sintered wafers superposed respectively.

This invention is now explained in detail with reference to the attached drawings.

BRIEF DESCRIPTION OF THE ATTACHED DRAWINGS

FIG. 1 is a sectional view of a varistor manufactured by the method of this invention.

FIG. 2 shows a volt-ampere characteristic suitable for a varistor.

FIG. 3 shows a volt-ampere characteristic unsuitable for a varistor.

In FIG. 2 and FIg. 3, voltage E is plotted as abscissa and current as ordinate.

DETAILED DESCRIPTION OF THE INVENTION

This invention, as described hereinabove, is based on the new information obtained from our studies that in case a thermister material possesses the thermister constant B°K and the specific resistance R_0KΩ at 273° K that satisfy the relation $B\times R_0 \leqq 10{,}000$ KΩ · ° K, a resistor manufactured by superposing several plates of such thermister material shows a stable volt-ampere characteristic as shown in FIG. 2, thus proviing to have an aptitude for a varistor, whereas in case a thermistor material possesses the thermistor constant B°K and the specific resistance R_0KΩ at 273° K that satisfy $B\times R_0 > 10{,}000$KΩ· ° K, a resistor manufactured by superposing several plates of such thermistor material shows a unstable voltampere characteristic as shown in FIG. 3, thus providing to have no aptitude for a varistor.

Therefore, this invention provides a method for manufacturing a varistor comprising, for example, superposing two sintered wafers 1, 1, each sintered wafer obtained by processing and sintering a thermister material so as to make the product of B°K and R_0KΩ and thereof be not more than 10,000KΩ·° K, applying electrodes, for example silver electrodes 2, 2 to opposite surfaces of the sintered wafers 1, 1 superposed respectively in a conventional manner, attaching lead wires 5, 5 to the silver electrodes 2, 2 respectively by using solder 4 and coating over the whole with suitable insulating coating material 6.

The wafer 1 is a sintered plate having any one of various shapes such as circular, square, rectangular, etc.

In this case, no surface barrier exists at the surface of the sintered wafer 1, which the electrode 2 is applied to, but at the contact surface 3, which no electrode is applied to, exists a surface barrier. Therefore, when such sintered wafer 1 is superposed upon the other, there generates a high resistance R_2KΩ at a low voltage. Thus, a desired varistor having a remarkably stable volt-ampere characteristic as shown in FIG. 2 is obtained.

This invention also provides a method for manufacturing a non-linear resistor comprising superposing more than three plates of said sintered wafers and applying electrodes to opposite surfaces of said sintered wafers superposed in the same manner. The thus manufactured resistors have remarkably stable volt-ampere characteristics as shown in FIG. 2, thus providing to be suitable for a varistor.

As the varistors of this invention have, as Example shows, remarkably stable volt-ampere characteristics, their yield rate is much higher, as compared with the conventional methods. Moreover, as the varistors of this invention utilize iron oxide, copper oxide, etc. as the main raw materials, they are also advantageous in cost. This invention, as described hereinabove, provides a method for manufacturing varistors having remarkably stable characteristics at much higher yield rate and at quite lower cost, therefore it is industrially of great value.

The invention will be understood more readily with reference to the following example. However, the example is intended to illustrate the invention and is not to be construed to limit the scope of the invention.

EXAMPLE

The sintered body is prepared by a conventional technique. The starting material in the composite defined in Table 1 is respectively mixed in a pot mill so as to produce a homogeneous mixture. The mixture is dried in a dryer, pressed in a mold at a pressure of about 1000kg/cm^2 into a disc of 15mm in diameter and 2mm in thickness. The pressed disc is sintered in air at about 1,000° C, thus the sintered disc **1** is obtained. A varistor is manufactured by superposing the sintered disc **1** upon the other, applying silver electrodes **2, 2** to opposite surfaces of the sintered discs **1, 1** superposed, asttaching lead wires **5, 5** to the silver electrodes **2, 2** by using solder **4** and coating over the whole with epoxy resin **6**. As described hereinabove, a surface barrier exists at the contact surface between the sintered discs **1, 1** which no silver electrode is applied to. Therefore, when the sintered disc **1** is superposed upon the other, there generates a high resistance R_2KΩ. The measured values of R_2, V_0, α of the thus manufactured varistor is respectively shown in Table 1. In Table 1, the V_0-value is a voltage at $I=1mA$. Further, the resistance R_0KΩ and the thermister constant B° K of the sintered disc **1** are measured in a conventional manner, and the values of R_0, B and $B \times R_0$ are also shown in Table 1.

TABLE 1

		Composition of Sintered Body			
Fe_2O_3	(mol%)	66	50	40	34
CuO	(mol%)	34	50	60	66
R_0	(KΩ)	0.5	0.1	0.04	0.01
B	(°K)	2100	1900	1100	1500
R_2	(KΩ)	130	125	125	125
V_0	(V)	19	19	19	19
α	(—)	5	5	5	5
$B \times R_0$	(KΩ·°K)	1050	190	44	15

As Table 1 shows, the values of $B \times R_0$ of the sintered bodies are all not more than 10,000KΩ·°K. The varistor manufactured by superposing two plates of each of these sintered bodies shows respectively a remarkably stable volt-ampere characteristic as shown in FIG. 2, thus proving to have an aptitude for varistor. The measured values of the varistors manufactured by superposing two~four plates of the sintered body consisting of Fe_2O_3 (50mol percent) and CuO(50mol percent) as shown in Table 1 are shown in Table 2.

Table 2

Number of plates	2	3	4
R_2 (KΩ)	125	250	376
$V_{(0)}$	19.5	38.5	48.0
α(—)	5	4	4

Table 2 shows that varistors of good quality having different V_0 values can be manufactured by superposing more than three plates of such sintered bodies having the product of B and R_0 not more than 10,000KΩ·°K as shown in Table 1.

Next, comparison with Example, the sintered bodies are prepared in the same manner as Example from the starting materials in the compositions defined in Table 3. The values of R_0, B, R_2, $B \times R_0$ are also shown in Table 3.

TABLE 3

		Composition of Sintered Body			
Fe_2O_3	(mol%)	70	0	0	50
MnO_2	(mol%)	0	70	66	0
CoO	(mol%)	30	30	34	50
R_0	(KΩ)	20	20	10	6
B	(°K)	4,500	4,500	6,000	3,500
R_2	(KΩ)	140	140	30	50
$R_0 \times B$	(KΩ·°K)	90,000	90,000	60,000	21,000

As Table 3 shows, the values of $B \times R_0$ of the sintered bodies are all larger than 10,000KΩ·°K. The resistor manufactured by superposing two plates of each of these sintered bodies shows respectively a unstable volt-ampere characteristic as shown in FIG. 3, thus proving to be unsuitable for a varistor.

We claim:

1. A method for manufacturing a non-linear resistor comprising superposing several sintered wafers, said sintered wafers having negative resistance and also possessig the thermister constant B° K and the specific resistance value R_0KΩ at 273° K that satisfy the relation $B \times R_0 \leq 10{,}000$KΩ·°K, and applying electrodes to opposite surfaces of said sintered wafers superposed respectively.

2. A method for manufacturing a non-linear resistor as described in claim **1**, wherein said sintered wafers comprise 66~34 percent of iron oxide (Fe_2O_3) and 34~66 mol percent of copper oxide (CuO).

* * * * *