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(54) VOLTAGE DEPENDENT RESISTOR AND ITS MANUFACTURING PROCESS

(71) We, MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD., a corporation organized and existing under the laws of Japan, of 1006, Oaza Kadoma, Kadoma-shi, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a non-linear voltage dependent resistor, and to methods of manufacturing the same.

A non-linear voltage dependent resistor element is generally called a varistor and it has been widely used for the purpose of voltage stabilization and surge absorption. A typical example is a silicon carbide (SiC) varistor which makes use of the high sensitivity of the contact resistance of silicon carbide particles, and it has been used as a spark quencher for contacts or in other applications. The voltage (V) — current (I) characteristic of the varistor can be generally approximated by the relation,

$$I = \frac{V^\alpha}{C}$$

where C is a constant corresponding to the voltage a given current, and the exponent α is a number greater than 1, and called non-linear exponent. The characteristic of the varistor is conveniently represented, in general, by a voltage at a given current and the α -value.

The SiC varistor is inexpensive in cost and has been widely used, but because the α -value is small such as 3—7, the effect of the use of the SiC varistor for voltage stabilization or surge absorption has not been sufficient and hence the realization of an element having a high α -value has been strongly desired.

As one approach to the above desire, a zinc

oxide varistor has been recently developed. It is manufactured by adding small amounts of bismuth oxide, lead oxide, barium oxide or the like to zinc oxide, mixing them together, molding the mixture and sintering it in air at 800°C—1,500°C to produce a sintered body, on which electrodes are provided. The non-linear voltage dependent properties thereof depend on a sedimentation layer which surrounds zinc oxide fine particles and mainly consists of the additives, and the value of the exponent α reaches as high as 50 or higher. Therefore, the zinc oxide varistor has been finding broad usage in various applications.

While the zinc oxide varistor has many advantages as described above, it also includes problems to be resolved owing to its high performance. One of the problems lies in that the resistance of the varistor element is reduced in a moist atmosphere, resulting in substantial decrease in the α -value. This tendency is particularly remarkable when a D.C. voltage is applied in the moist atmosphere. Such deterioration in the characteristic is due to the increase in a leakage current owing to the decrease in the resistance value of the surface portion varistor element.

In order to prevent the above deterioration in the characteristic, it has been tried to coat the side of the element with epoxy resin or or like. However, the effect of this moisture-proofing approach has not been satisfactory because the adhesion between the sintered body mainly consisting of zinc oxide and the epoxy resin was not sufficient. To overcome the above drawback, it has been recently tried to apply bismuth oxide (Bi₂O₃), silicon dioxide (SiO₂), antimony oxide (Sb₂O₃) or the like, either singly or in combination, on a side of a molded body mainly consisting of zinc oxide, and sinter the body to form a high resistance layer on the side. This approach has overcome the above difficulty to a certain extent. It has been effective in

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improving the moisture-proofing property and preventing the occurrence of a creeping discharge path for a high voltage applied across the element. However the element manufactured by the above method also includes a drawback. Namely, the thickness of the high resistance layer formed on the element is very thin, e.g. not less than of the order of several tens of microns. Consequently, if the side is contaminated, not only the moisture-proofing property but also the stability of the side against high voltage tend to be lost and hence it has been required to continuously keep the side clean. Accordingly, the treatment after the sintering step was critical, which resulted in inconvenience in the manufacture.

The contamination of the side of the element occurs not only during the manufacturing process but also in use by the environment surrounding the element, for example, when the element is left in an atmosphere of carbon dioxide gas, sulfur dioxide gas, chlorine gas or the like, the gas deposits on the side of the element, and reacts with water molecules in the air to produce carbonic acid ions (CO_3^{--}), hydrogen sulfite ions (HSO_3^-) or chlorine ions (Cl^-), which in turn significantly deteriorate the stability of the side of the element. In a loaded durability test in such an atmosphere, the varistor voltage and the α -value tend to significantly decrease in 100 to 200 hours. Furthermore, it has been proved that when the element manufactured by the above method was boiled in pure water no substantial change in the characteristic was observed, but when it was boiled in salt water considerable changes in the varistor voltage and the α -value before and after the boiling were observed.

As described above, the element manufactured by the above method has problems concerning the characteristics as well as drawbacks in appearance and commercial value.

It is an object of the present invention to provide a non-linear voltage dependent resistor element which alleviates or overcomes the above drawbacks.

According to one aspect of the invention there is provided a non-linear voltage dependent resistor element comprising a polycrystalline, high resistance layer including at least one or both of zinc silicate (Zn_2SiO_4) and zinc antimonate ($\text{Zn}_7\text{Sb}_2\text{O}_{12}$) formed on a side of a sintered body mainly consisting of zinc oxide and itself having non-linear voltage dependent properties, and a non-crystalline, insulating layer formed on the polycrystalline layer.

Another aspect of the invention provides a method for manufacturing a non-linear voltage dependent resistor element including a sintered body which shows non-linear voltage dependent properties itself comprising the steps of applying material including at least

one or both of silicon and antimony on a side of a molded body mainly consisting of zinc oxide, firing them to form a sintered body and a polycrystalline, high resistance layer on the side of the sintered body, applying material including glass thereon, and heat treating it to form non-crystalline, insulating layer on the polycrystalline layer.

The above aspects and other features of the invention will be described and with reference to the accompanying drawings in which:—

Fig. 1 is a sectional view of one embodiment of a non-linear voltage dependent resistor element of the present invention;

Fig. 2 shows a comparative chart of test results for the element produced in accordance with the method of the present invention and elements produced by other methods, in atmospheres of chlorine gas, carbon dioxide gas and sulfur dioxide gas;

Fig. 3 shows the change in the characteristics of the element caused by heat treatment.

Figs. 4A and B show the comparison of the adherence of a glass to the sintered body when the glass is baked by the process of the present invention and when the glass is directly baked onto the sintered body mainly consisting of zinc oxide.

The invention will be explained in detail with reference to an example.

Example:

Added to a powder of zinc oxide (ZnO) were powders of bismuth oxide (Bi_2O_3), cobalt oxide (CoO), manganese oxide (MnO) and antimony oxide (Sb_2O_3) in the range of 0.01—10 mol %, respectively, and they were fully blended and compressed and molded into a body of 40 mm diameter and 30 mm thickness.

A mixture of silicon dioxide (SiO_2), antimony oxide (Sb_2O_3) and bismuth oxide (Bi_2O_3) was mixed with a binder consisting of one part by weight of ethyl cellulose and three parts by weight of butyl carbitol, at the mixing ratio of 1 to 3 by weight, and they were blended to produce a homogeneous blend. The paste thus produced was applied on the side of the molded body, dried and then fired at a temperature of $800^\circ\text{--}1,500^\circ\text{C}$. The sintered body thus produced had its upper and lower planes polished. Glass frit having a melting point in the range of 360° to 650°C was blended with a binder consisting of 5 parts by weight of ethyl cellulose and 95 parts by weight of butyl carbitol at the mixing ratio of 5 to 2 by weight, and they were mixed to produce a homogeneous blend. The resulting paste was applied on the side of the sintered body and baked. Thereafter, aluminum electrodes were formed on the upper and lower planes of the sintered body.

Fig. 1 is a sectional view of the non-linear

voltage dependent resistor element produced in the manner described above, wherein reference numeral 1 designates the sintered body mainly consisting of zinc oxide having non-linear voltage dependent properties, 2 designates the polycrystalline, high resistance layer (first layer) which may be formed by the diffusion of silicon, antimony or bismuth or by reaction with zinc oxide. The polycrystalline, high resistance layer 2 is a high resistance layer including at least one or both of zinc silicate (Zn_2SiO_4) and zinc antimonate ($Zn_7Sb_2O_{12}$). The reference numeral 3 designates the non-crystalline, high resistance layer (second layer) formed by glass, and 4 and 5 designate the electrodes. It has been proved by X-ray diffraction that the polycrystalline, high resistance layer consisted of zinc silicate and zinc antimonate. Table 1 shows the effects of the change of the glass frit composition on various electric characteristics. In the Table, for a mixture consisting of silicon dioxide (SiO_2), antimony oxide (Sb_2O_3) and bismuth oxide (Bi_2O_3) in the mol ratio of 70 to 20 to 10 as the first layer forming material, $V_{1\mu A/mm}$ and $V_{1mA/mm}$ represent voltages per unit thickness when currents of $1\mu A$ and $1mA$ flowed, respectively. Such voltages per unit thickness were used because the sintered body mainly consisting of zinc oxide showed a non-linear bulk characteristic. The symbol α represents the non-linear exponent which can be determined by the previously shown relationship between the current and the voltage using the voltage value across the electrodes when current of $0.1mA$ and $1mA$ flow. The voltage variation rate $\Delta V_{1\mu A}$ shows the change of the voltage $V_{1\mu A}$ before and after the test. The test condition represented by the symbol I is atmospheric tem-

perature of $70^\circ C$, relative humidity of 95%, applied D.C. voltage of 1000 volts, and voltage application period of 1000 hours. The test conditions represented by the symbols II, III and IV include, in addition to the same conditions as I, an atmosphere of chlorine (Cl_2) gas, carbon dioxide (CO_2) gas and sulfur dioxide (SO_2) gas, respectively, at partial pressures of 50 mmHg, 250 mmHg and 50 mmHg, respectively. The test conditions represented by the symbols V and VI include in addition to the same condition as in I, boiling in pure water for 100 hours and in salt water for 100 hours, respectively. I_F represents a maximum current which does not cause creeping discharge when an impulse current (wave form: $4 \times 10\mu$ seconds) is applied.

The ingredients for the various compositions shown in the Table 1, the amounts of the ingredients, the baking temperatures (fusing temperature) and the coefficients of thermal expansion are shown in Table 2. In the Table 2, the figures shown in the columns of the composition numbers represent the amounts of the ingredients shown in the leftmost column in Fig. 1 in mol %.

As seen from the Tables 1 and 2, for the prior art example having only the first layer, considerable deterioration in voltage value occurs in the atmosphere of the conditions II, III, IV and VI, but for the compositions 1 to 4 in which the second layer of glass having a melting point in the range of at least $350^\circ C$ to $600^\circ C$ is formed, they are little influenced by the atmosphere and their other characteristics are not inferior to those of the prior art. Particularly, the composition 4 shows the most excellent result.

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TABLE 1

Characteristic Composition	V_{1mA} (V) mm	$V_{1\mu A}$ (V) mm	a	$\Delta V_{1\mu A}$ (%)						I_F (kA)
				I	II	III	IV	V	VI	
1	105	85	46	0	-0.4	-0.1	-0.2	0	-3.2	90
2	107	85	47	0	-0.2	0	0	0	-0.8	90
3	105	81	44	0	-0.9	-0.3	-0.6	-0.1	-2.5	90
4	106	86	47	0	-0.1	0	0	0	-0.2	96
5	98	71	32	-0.8	-4.1	-1.1	-3.7	0	-0.1	95
6	82	49	21	-3.2	-9.6	-4.6	-8.5	-0.1	-0.1	96
First Layer only	106	87	46	0	-15.4	-8.4	-12.6	0	-57	90
X	105	78	41	-0.5	-18.3	-10.1	-15.3	-5.5	-62	40

TABLE 2

(mol %)

Composition Ingredient	1	2	3	4	5	6
SiO ₂	3			6	66	77
B ₂ O ₃	22	37	48	32.5	25	15
ZnO	9	38.5	20	44	7	4.5
ZrO ₂		2.5				
Al ₂ O ₃			2	1		
PbO						5
PbF ₂	59	20	30	15.5		
TiO ₂	5					
Bi ₂ O ₃	2			1	2	
Baking Temp. (°C) (Fusing Temp.)	350	480	600	560	700	900
Coeff. of Thermal Expansion (X10 ⁻⁷ /°C)	125	72	83	64	75	48

Fig. 2 shows the relationship between test time and the voltage variation rate $\Delta V_{1\mu A}$ for an element on which the second layer has been formed by baking the glass of the composition 4 at 560°C, tested under the conditions II, III and IV. For comparison purpose, the relationships for the prior art example are shown by dotted lines. As is apparent from Fig. 2, the element in accordance with the present invention shows a very small voltage variation rate $\Delta V_{1\mu A}$ and is stable compared with the prior art example. However, when the glasses of the compositions 5 and 6 are used as the second layer, the magnitudes of the voltage $V_{1mA/mm}$ and $V_{1\mu A/mm}$ and the α -value are slightly smaller than those of other examples.

Fig. 3 plots the relationship between the voltage variation rate $\Delta V_{1\mu A}$ and the heat treatment temperature, with α being a parameter, when a sintered body having only the first layer was heat treated at various temperatures. As is apparent from Fig. 3, the magnitude of $\Delta V_{1\mu A}$ increases slightly in the negative direction in the range of 650°C to 1000°C and the α -value tends to decrease. It is thus readily understood that when a glass having a melting point at a high temperature such as the glass of the composition 5 or 6 in the Table 1 is baked the characteristics

are slightly changed by the high temperature. It should be understood, however, that the change by the heat treatment at high temperature is not large enough to deteriorate the characteristics of the element as a varistor.

It would not be unnatural from the above description to suppose that a method of baking the glass directly on the side of the sintered body mainly consisting of zinc oxide, to form a high resistance layer is also effective. However, this is not so as shown by the composition X in the Table 1. The composition X represents the one in which the glass of the composition 4 was directly baked onto the side of the body. In this case, the creeping discharge is more likely to occur than in the other cases and a large voltage variation rate $\Delta V_{1\mu A}$ is exhibited in the loaded durability test in the environment of chlorine gas, carbon dioxide gas or sulfur dioxide gas. This is due to the adherence of the glass to the body. When double high resistance layers are provided, the creeping discharge always occurs at the interface between the second layer and the atmosphere. On the other hand, where the glass only is provided, the creeping discharge tends to occur at the interface between the body and the glass layer. It is apparent from Fig. 4 that the affinity between

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the glass and the body during fusing is remarkably improved by providing the first layer. Fig. 4A and B show the geometries of fused glass formed by placing 0.1 gram of glass paste of the composition 4 in the Table 2 on a sintered body mainly consisting of zinc oxide and on a similar sintered body having a coating of the first layer, respectively, in such a manner that the contact area is a circular plane of 0.02 cm² area, and firing it at 560°C for five minutes. In Fig. 4, the reference numeral 1 designates the sintered body mainly consisting of zinc oxide, and 2 the polycrystalline, high resistance layer formed by the diffusion of the silicon, antimony or bismuth component or by the reaction with zinc oxide. 6 designates the paste including the glass component, and 3 the non-crystalline, high resistance layer after having been baked. As seen from the drawing, when the first layer is formed on the surface of the body, the spreading is considerably facilitated compared with that without the first layer. Such spreading of the glass is also observed for glasses of other compositions.

As described hereinabove, when the two high resistance layers are provided in accordance with the present invention, the characteristics of the element are very stable not only against humidity and impulse current but also against the external atmosphere and contamination. Such stability could not be attained heretofore when the polycrystalline, high resistance layer or the non-crystalline, high resistance layer alone was used. Consequently, the effect of the present invention is not a mere combination of both layers. The element of the present invention, which is stable against the various atmospheres and against contamination can be advantageously used in an out-door application such as an arrester for a distribution line and in a microwave oven application.

While bismuth oxide (Bi₂O₃), cobalt oxide (CoO), manganese oxide (MnO) and antimony oxide (Sb₂O₃) were added to zinc oxide in the above example, lead oxide (PbO), calcium oxide (CaO), strontium oxide (SrO), barium oxide (BaO) and uranium oxide (UO₂), or another element which forms a layer having non-linear voltage dependent properties at the particle boundary in the zinc oxide sintered body, can be used. For the purpose of controlling the resistance of the sintered body or for another purpose, nickel oxide (NiO), magnesium oxide (MgO), chromium oxide (Cr₂O₃), tin oxide (SnO₂), silicon oxide (SiO₂) or titanium oxide (TiO₂) may be added without affecting the present invention.

Furthermore, although silicon dioxide and antimony oxide were included in the past to form the first layer in the above example, it should be understood that compounds, such as carbonates or hydroxides, which result in

oxides during firing and react with zinc oxide to produce zinc silicate or zinc antimonate, can attain a similar effect. Bismuth oxide (Bi₂O₃) need not be added but other components which take the place thereof may be added. Furthermore, it should be understood that depending on the particular purpose of the varistor, a material which does not appreciably damage the above effect may be added.

Glass of any composition can be used so long as it reacts with the body or the first layer, without adverse affect, to form a non-crystalline, high resistance layer.

A non-linear voltage dependent resistor element of the present invention is provided with a polycrystalline and a non-crystalline layer of high resistance by forming the polycrystalline, high resistance layer on the side of the sintered body mainly consisting of zinc oxide simultaneously with the sintering of the body and then applying the non-crystalline, high resistance material layer on the polycrystalline layer. The element thus produced has very high resistance to the contamination of its side and is stable against humidity and an impulse current as well as various atmospheres. Furthermore, the element of the present invention is of a high commercial value because it has a surface gloss.

WHAT WE CLAIM IS:—

1. A non-linear voltage dependent resistor element comprising a polycrystalline, high resistance layer including at least one or both of zinc silicate (Zn₂SiO₄) and zinc antimonate (Zn₂Sb₂O₁₂) formed on a side of a sintered body mainly consisting of zinc oxide and itself having non-linear voltage dependent properties, and a non-crystalline, insulating layer formed on the polycrystalline layer.

2. A non-linear voltage dependent resistor element according to Claim 1 wherein said non-crystalline, insulating layer is a glass layer.

3. A method for manufacturing a non-linear voltage dependent resistor element including a sintered body which shows non-linear voltage dependent properties itself comprising the steps of applying material including at least one or both of silicon and antimony on a side of a molded body mainly consisting of zinc oxide, firing them to form a sintered body and a polycrystalline, high resistance layer on the side of the sintered body, applying material including glass thereon, and heat treating it to form a non-crystalline, insulating layer on the polycrystalline layer.

4. A method for manufacturing a non-linear resistor element according to Claim 3 wherein a mixture consisting of silicon dioxide (SiO₂), antimony oxide (Sb₂O₃) and bismuth oxide (Bi₂O₃) in the mol ratio of 70 to 20 to 10 is applied on the side of the molded body mainly consisting of zinc oxide and then

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the glass and the body during fusing is remarkably improved by providing the first layer. Fig. 4A and B show the geometries of fused glass formed by placing 0.1 gram of glass paste of the composition 4 in the Table 2 on a sintered body mainly consisting of zinc oxide and on a similar sintered body having a coating of the first layer, respectively, in such a manner that the contact area is a circular plane of 0.02 cm² area, and firing it at 560°C for five minutes. In Fig. 4, the reference numeral 1 designates the sintered body mainly consisting of zinc oxide, and 2 the polycrystalline, high resistance layer formed by the diffusion of the silicon, antimony or bismuth component or by the reaction with zinc oxide. 6 designates the paste including the glass component, and 3 the non-crystalline, high resistance layer after having been baked. As seen from the drawing, when the first layer is formed on the surface of the body, the spreading is considerably facilitated compared with that without the first layer. Such spreading of the glass is also observed for glasses of other compositions.

As described hereinabove, when the two high resistance layers are provided in accordance with the present invention, the characteristics of the element are very stable not only against humidity and impulse current but also against the external atmosphere and contamination. Such stability could not be attained heretofore when the polycrystalline, high resistance layer or the non-crystalline, high resistance layer alone was used. Consequently, the effect of the present invention is not a mere combination of both layers. The element of the present invention, which is stable against the various atmospheres and against contamination can be advantageously used in an out-door application such as an arrester for a distribution line and in a microwave oven application.

While bismuth oxide (Bi₂O₃), cobalt oxide (CoO), manganese oxide (MnO) and antimony oxide (Sb₂O₃) were added to zinc oxide in the above example, lead oxide (PbO), calcium oxide (CaO), strontium oxide (SrO), barium oxide (BaO) and uranium oxide (UO₂), or another element which forms a layer having non-linear voltage dependent properties at the particle boundary in the zinc oxide sintered body, can be used. For the purpose of controlling the resistance of the sintered body or for another purpose, nickel oxide (NiO), magnesium oxide (MgO), chromium oxide (Cr₂O₃), tin oxide (SnO₂), silicon oxide (SiO₂) or titanium oxide (TiO₂) may be added without affecting the present invention.

Furthermore, although silicon dioxide and antimony oxide were included in the past to form the first layer in the above example, it should be understood that compounds, such as carbonates or hydroxides, which result in

oxides during firing and react with zinc oxide to produce zinc silicate or zinc antimonate, can attain a similar effect. Bismuth oxide (Bi₂O₃) need not be added but other components which take the place thereof may be added. Furthermore, it should be understood that depending on the particular purpose of the varistor, a material which does not appreciably damage the above effect may be added.

Glass of any composition can be used so long as it reacts with the body or the first layer, without adverse affect, to form a non-crystalline, high resistance layer.

A non-linear voltage dependent resistor element of the present invention is provided with a polycrystalline and a non-crystalline layer of high resistance by forming the polycrystalline, high resistance layer on the side of the sintered body mainly consisting of zinc oxide simultaneously with the sintering of the body and then applying the non-crystalline, high resistance material layer on the polycrystalline layer. The element thus produced has very high resistance to the contamination of its side and is stable against humidity and an impulse current as well as various atmospheres. Furthermore, the element of the present invention is of a high commercial value because it has a surface gloss.

WHAT WE CLAIM IS:—

1. A non-linear voltage dependent resistor element comprising a polycrystalline, high resistance layer including at least one or both of zinc silicate (Zn₂SiO₄) and zinc antimonate (Zn₂Sb₂O₁₂) formed on a side of a sintered body mainly consisting of zinc oxide and itself having non-linear voltage dependent properties, and a non-crystalline, insulating layer formed on the polycrystalline layer.

2. A non-linear voltage dependent resistor element according to Claim 1 wherein said non-crystalline, insulating layer is a glass layer.

3. A method for manufacturing a non-linear voltage dependent resistor element including a sintered body which shows non-linear voltage dependent properties itself comprising the steps of applying material including at least one or both of silicon and antimony on a side of a molded body mainly consisting of zinc oxide, firing them to form a sintered body and a polycrystalline, high resistance layer on the side of the sintered body, applying material including glass thereon, and heat treating it to form a non-crystalline, insulating layer on the polycrystalline layer.

4. A method for manufacturing a non-linear resistor element according to Claim 3 wherein a mixture consisting of silicon dioxide (SiO₂), antimony oxide (Sb₂O₃) and bismuth oxide (Bi₂O₃) in the mol ratio of 70 to 20 to 10 is applied on the side of the molded body mainly consisting of zinc oxide and then



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fired to form the polycrystalline, high resistance layer on the side of the molded body.

5. A non-linear voltage dependent resistor element according to Claim 1 wherein said sintered body comprises zinc oxide (ZnO), to which bismuth oxide (Bi₂O₃), cobalt oxide (CoO), manganese oxide (MnO) and antimony oxide (Sb₂O₃) are added in the amount of 0.01 to 10 mol%, respectively.

6. A non-linear voltage dependent resistor element substantially as hereinbefore described with reference to the accompanying drawings.

7. A method substantially as hereinbefore

described with reference to the accompanying drawings for manufacturing a non-linear voltage dependent resistor element.

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