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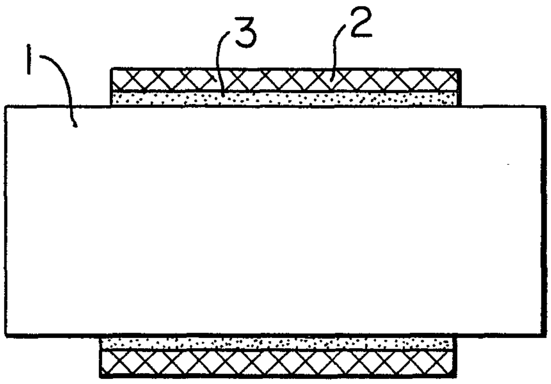
(54) **Non-linear resistor and production thereof.**

(57) A non-linear resistor having each continuous film havin no gas permeability and lower electrical resistivity than the resistivity of a sintered body between the sintered body having non-linear resistance characteristics and an electrode, has excellent stability for application of rated voltage for a long period of time.



NON-LINEAR RESISTOR AND PRODUCTION THEREOF

This invention relates to a non-linear resistor used for voltage stabilizers, surge absorbers, arresters, etc., and a process for producing the same.

A conventional non-linear resistor has a structure as shown in Fig. 1, wherein electrodes 2 are formed individually on upper and lower major surfaces of a sintered body 1 having as a major component zinc oxide and non-linear resistance characteristics. Such a non-linear resistor is produced by a well-known ceramic sintering technique. For example, in the production of a zinc oxide type non-linear resistor, bismuch oxide, cobalt oxide, chromium oxide, manganese oxide, nickel oxide and the like are added to zinc oxide powder and sufficiently mixed, followed by addition of a suitable binder such as water, poly(vinyl alcohol), or the like to form granules, which are pressed into a body of a desired shape and size. The body is then sintered in an electric furnace at a temperatxre of 900 - 1400°C. The side surface of the body may be coated with a Bi_2O_3-Sb_2O_3-SiO_2 paste in order to prevent corona discharge and the like along the side surface before the sintering. Then, two major surfaces at which electrodes are to be formed are abraded to a desired thickness, followed by the formation of electrodes by a conventional process such as flame spraying, baking of a paste, or the like. When the thus produced non-linear resistor is used as high-voltage transmission lightning arrester, a glass film is sometimes formed around the side surface in order to improve prevention of discharge along the side surface. Further, the thus produced non-linear resistor is excellent in non-lineality of voltage-current characteristics, but rather poor in stability and there is a problem in that its properties are subjected to deterioration by the load test which is carried out by applying a rated voltage for a long period of time, causing a gradual increase of leakage current and finally inducing thermal runaway.

For example, the life of non-linear resistor elements used for lightning arresters for transmitting 1200 kV under the conditions of use temperature 40°C, and an applied voltage ratio (AVR) of 80% (100% AVR is the 1 mA voltage at the initial condition) should be longer than 100 years, but non-linear resistor elements having such a long life have not been obtained by using conventional non-linear resistors.

As to the deterioration of properties, it is known the following facts: (1) when a non-linear resistor element is heat treated in a nitrogen atmosphere, there occurs the same pattern of property deterioration as that caused by the load test with rated voltage application, and (2) the element which was deteriorated in properties can recoup its original properties when the element is heated in air or oxygen-containing atmosphere. Taking these facts into consideration, causes of the property deterioration seems to be that the oxygen in grain bondary layers in the sintered body or the oxygen adsorbed on grain surfaces is released into the ambient atmosphere at the time of rated voltage application, resulting in lowered potential barrier at the grain boundaries to increase a leakage current.

The following methods have been proposed for minimizing such property deterioration of the zinc oxide based non-linear resistors by improving stability to voltage application:

(1) Bismuth oxide or bismuth oxide-containing gases is diffused from the entire surface of a sintered body (e.g. U.S. Patent No. 3,723,175).

(2) Boron oxide or glass containing boron oxide is added for sintering (e.g. U.S. Patent No. 3,663,458).

But, even the zinc oxide based non-linear resistors produced by the above-mentioned processes were still unsatisfactory in stability when applied rated voltage for a long period of time.

It is objects of this invention to provide a non-linear resistor which is particularly stable for application of rated voltage for a long period of time and a process for producing such a non-linear resistor.

This invention provides a non-linear resistor comprising a sintered body having non-linear resistance characteristics and one or more electrodes formed on the upper and/or lower major surfaces of said sintered body, characterized in that one or more continuous films having no gas permeability and lower electrical resistivity than the resistivity of said sintered body are individually formed between the sintered body and one or more electrodes.

This invention also provides a process for producing a non-linear resistor which comprises

forming a layer of material on upper and/or lower surface area, at which an electrode is to be formed, of a sintered body having non-linear resistance characteristics,

baking the layer of material at a temperatxre of 350 to 520°C for providing a continuous film having no gas permeability and lower electrical resistivity than the resistivity of the sintered body, and

forming each electrode on each continuous film thus provided.

In the attached drawings, Fig. 1 is a cross-sectional view of a conventional non-linear resistor, Fig. 2 is a cross-sectional view of a non-linear resistor of this invention, Fig. 3 is a graph showing a relationship between resistivity and In_2O_3 content in a mixture of indium oxide and tin oxide which mixture forms the continuous film between the sintered body and an electrode, and Fig. 4 is a graph showing a relationship between a non-linearity coefficient and a heat treatment temperature of a sintered body containing zinc oxide as a major component.

According to this invention, since the continuous film is formed between the sintered body and the electrodes, said film being constructed so dense that it has no gas permeability and having lower electrical resistivity than the resistivity of the sintered body and no γ-bismuth oxide phase, various advantages are obtained, particularly by preventing the release of constituting atoms of the sintered body, e.g. oxygen ions or a gas adsorbed in the sintered body, e.g., oxygen gas, from the sintered body at the time of voltage application, which results in giving stability to the properties for a long period of time, e.g. more than 100 years under ordinary conditions.

This invention is explained in detail referring to Fig. 2. As shown in Fig. 2, the continuous film 3 is interposed between the sintered body 1 having non-linear characteristics and the electrode 2.

The sintered body used in this invention may be any one having non-linear resistance characteristics and showing deterioration in non-linear characteristics by the release of atoms constituting the sintered body or adsorbed gas in the sintered body. Examples of such a sintered body are sintered bodies of oxides such as zinc oxide, titanium oxide, and the like and those of chalcogen such as selenium and the like. Particularly, non-linear resistors containing zinc oxide as a major component are excellent in non-linear resistance characteristics but show the property deterioration at the time of voltage application due to the release of oxygen from crystal grains or crystal boundary layers, so that the effects of this invention are greatly exhibited when this invention is applied to such zinc oxide based non-linear resistors.

The continuous film 3 formed between the sintered body 1 and the electrode 3 is preferably required to have the following properties:

First, it is important that the continuous film has low resistivity (or good electroconductivity) in order to remove a problem of heat generation by passing a currett between the sintered body and the electrode. When a sitered body containing zinc oxide as a major component is used as the sintered body, it is preferable that the continuous film has resistivity of 1 ohm·cm or less since the resistivity of zinc oxide grains is 1 to 10 ohm·cm. Fig. 3 shows changes of resistivity depending on the indium oxide content in a continuous film made of a mixture of indium oxide and tin oxide. As is clear from Fig. 3, even in the case of a single film of indium oxide or tin oxide, the resistivity is lower than 1 ohm·cm and the resistivity is further lowered when there are used films of mixtures of indium oxide and tin oxide. In this invention, the continuous film should have lower electrical resistivity than the resistivity of the sintered body.

Second, it is important that the continuous film is good in denseness and adhesion to the sintered body. The words "good in denseness" mean that a gas such as oxygen is not permeable through the continuous film. As mentioned above, it is very important to prevent the release of atoms constituting the sintered body or a gas such as oxygen adsorbed in the sintered body from the sintered body at the time of voltage application, and the continuous film plays such a role effectively. Further the continuous film adheres to the sintered body strongly without a reaction therewith. Such a good adhesion of the continuous film to the sintered body is important for preventing the release as mentioned above and reducing contact resistance between the sintered body and the film.

Thirdly, in the case of using as a sintered body that containing zinc oxide as a major component, it is important that such a continuous and electroconductive film can be backed on the sintered body at a temperature of 520°C or lower. When a sintered body obtained by sintering powders containing zinc oxide as a major component is heat treated, the non-linearity coefficient (α) of the resistor is lowered in a temperature range higher than 520°C and lower than 1000°C as shown in Fig. 4 but it increases to the same level or larger than that of before the heat treatment when the heat treatment temperature is 520°C or lower. A reason for lowering the non-linearity coefficient (α) by the heat treatment in a temperature range higher than 520°C and lower than 1000°C seems to be due to suspected phase change in the bismuth oxide into γ-phase. In the case when the sintered body is heat treated at a temperature of 1000°C or higher, the non-linearity coefficient increases again. But at the temperature of 1000°C or higher, a sintered material of indium oxide type, tin oxide type or a mixture of indium oxide-tin oxide type generally begins to react with a zinc oxide type sintered material violently. Therefore, when there are used as the sintered body that having zinc oxide as a major component and as the continuous film that made of indium oxide type compound, tin oxide type compound or a mixture of indium oxide and tin oxide type compounds, it is important that the continuous and electroconductive film can be baked on the sintered body at a temperature of 520°C or lower.

The continuous film is different from γ-bismuth oxide phase layer formed on the surface portions of the sintered body. In addition, it is preferable that the continuous film is low in hygroscopicity so as to produce non-linear resistors which can be used in high humidity.

Considering the above-mentioned required properties, it is preferable to use as the continuous film interposed between the sintered body and the electrode that made of indium oxide or the like compound, tin oxide or the like compound or a mixture of indium oxide and tin oxide or the like compounds.

The continuous film may contain other components which have thermal expansion coefficients near that of the sintered body so long as not lowering the properties of the film of indium oxide, tin oxide or indium oxide-tin oxide mixture. Examples of such other components are antimony oxide, tantalum oxide, manganese oxide, and the like.

Thickness of the continuous film changes depending on the kinds of sintered body and materials used for the film. When a sintered body containing zinc oxide as a major component is used, a preferable thickness of the continuous film is 1 to 30 μm in the case of indium oxide, tin oxide or the like compound being used singly and 1 to 50 μm in the case of a mixture of indium oxide and tin oxide type compounds. It is also preferable to use the continuous film having the same area and shape as the electrode to be formed thereon, considering the prevention of deterioration of the film during the production.

Zinc oxide sintered body has a thermal expansion coefficient of about $80 \times 10^{-7} {}^\circ C^{-1}$, while an indium oxide-tin oxide type film has a thermal expansion coefficient of about $160 \times 10^{-7} {}^\circ C^{-1}$. Therefore, if the film thickness of the indium oxide-tin oxide type film becomes too large, the film may easily be cracked due to differences of thermal expansion coefficients of the two. Since cracks are easily formed in the film when the film thickness is larger than 50 μm as shown in Table 10 below, it is preferable to make the film thickness 50 μm or less. Further, as shown in Table 10, since lifetime properties under the acceleated life test with rated voltage application become worse when the film thickness is less than 1 μm, it is preferable to make the film thickness 1 μm or more. As mentioned above, the film thickness of 1 to 50 μm is preferable in the case of the film of a mixture of indium oxide and tin oxide type compounds when the sintered body contains zinc oxide as a major component. The same reasons may be applied to the case of the film of indium oxide or tin oxide or the like compound being used singly.

As the sintered body, there may be used any sintered body containing zinc oxide as a major component, more concretely 70% by mole or more. The sintered body may further contain bismuth oxide and manganese oxide in amounts of 0.01 to 10% by mole, respectively and the resulting sintered body is more preferable. Particularly preferable sintered bodies are those containing bismuth oxide, manganese oxide, cobalt oxide, antimony oxide, chromium oxide, boron oxide, silicon oxide and nickel oxide in amounts of 0.01 to 10% by mole, respectively, but not more than 30% by mole as a total in addition to zinc oxide. These sintered body can usually be obtained by sintering raw material particles containing zinc oxide at a temperature of 900 to 1400°C. It is preferable that the sintered body contain no or substantially no γ-bismuth oxide phase therein even after the heat treatment for baking the continuous film formed on the sintered body.

The non-linear resistor of this invention can be produced, for example, by the following processes.

On two major surface areas, on which electrodes are to be found, of a sintered body having non-linear resistance characteristics, there are formed individual layers containing indium compound and/or tin compound as major components, and then the layers are baked at a temperature of 350 to 520°C to form a continuous and electroconductive film having lower electrical resistivity than the resistivity of the sintered body and no gas permeability, followed by formation of electrodes on individual surfaces of these films.

As materials for forming the above-mentioned continuous and electroconductive film, there can be used as the indium compound and/or tin compound not only indium oxide and tin oxide but also any indium compounds which can yield indium oxide by pyrolysis at a temperature preferably 520°C or lower such as indium nitrate, etc., and any tin compounds which can yield tin oxide by pyrolysis at a temperature preferably 520°C or lower such as tin nitrate, etc.

Using these raw materials, a film forming layer may be formed on the sintered body by a conventional process such as a chemical vapor deposition method (CVD), sputtering, a solution coating method such as dipping, brushing, or the like.

In the case of the solution coating method, when a solution containing above-mentioned raw materials, for example, a solution containing an indium compound and a tin compound, is coated on a major surface electrode forming area of the sintered body, a part of the solution penetrates into the inner portion of the sintered body, while the remaining part of the solution forms a film on the surface. The raw materials penetrated into the inner portion of the sintered body fill pores and crystal grain boundaries present near the major surface portions of the sintered body on baking the raw material layer, which results in making greater the preventing effect of the release of atoms constituting the sintered body or the gas adsorbed in the sintered body.

The raw material layer formed on the electrode forming surface of the sintered body is baked at a temperature of 520°C or lower considering the decrease in non-linearity coefficient and the formation of γ-bismuth oxide phase. In order to prevent the lowering in resistance to humidity of the baked film, it is preferable to bake the raw material layer at a temperature of 350°C or higher.

When the continuous and electroconductive film is formed by sputtering, the baking operatin of the raw material layer mentioned above is not necessary.

Electrodes are formed on individual continuous and electroconductive film thus formed by a conventional process such as flame spraying, baking of a paint, etc., to give a non-linear resistor.

The nonlinear resistor of this invention has excellent stability to the load lifetime test for a long period of time and can be used for voltage stabilizers, surge absorbers, arresters and the like with usual modifications. For example, an arrester can be formed by putting a plurality of non-linear resistors piled in a housing means such as a metal tank or an insulator.

Such an arrester has a long service lifetime and high reliability because of the long lifetime (under continuous AC operating stress) of the non-linear resister used therein. Generally, there exists a problem in that, due to the floating capacity between the non-linear resistor element and the ground, a strong electric field is applied to the elements in the upper portion to shorten the lifetime of such elements. In order to avoid such a problem, it is usually practiced to provide one or more capacitors or a metallic shield to thereby correct the electric field exerted. In the arrester of this invention, however, since the non-linear resistor element adopted therein has a long lifetime even if used in a high electric field, it is possible to omit the field corrector element from the mechanism in the housing means. This reduces the number of the arrester parts, which results in facilitating the manufacture of the arrester and improving its reliability as a whole. Also, since the housing means can be reduced in size, it is possible to attain a reduction of size and weight of the arrester and to improve its earth quake resistance.

This invention is illustrated by way of the following Examples.

Example 1

Zinc oxide (ZnO) in an amount of 2360 g, 70 g of bismuth oxide (Bi_2O_3), 25 g of cobalt oxide (Co_2O_3), 85 g of antimony oxide (Sb_2O_3), 18 g of manganese oxide (MnO_2), 25 g of chromium oxide (Cr_2O_3), 189 g of silicon oxide (SiO_2), 2 g of boron oxide (B_2O_3) and 18 g of nickel oxide (NiO) were mixed in a wet ball mill for 20 hours. The resulting mixed powders were dried, granulated, and pressed into a body of 20 mm in diameter and 7 mm in thickness. After coating a Bi_2O_3-Sb_2O_3-SiO_2-containing paste on the side surface of the body, the body was sintered in air at 1250°C for 2 hours. During the sintering, the above-mentioned paste was reacted with the zinc oxide to give a highly resistant layer containing Zn_2SiO_4 and $Zn_7Sb_2O_{12}$ mainly. Two major surfaces of the sintered body were abraded so as to give a thickness of 3 mm.

On the other hand, a solution obtained by dissolving indium nitrate [In $(NO_3)_3 \cdot 9H_2O$] in acetylacetone ($CH_3COCH_2COCH_3$) (a 50% by weight solution) was mixed with a solution obtained by dissolving metallic tin (Sn) in nitric acid (HNO_3) (a 25% by weight solution) so as to make the weight ratio of Sn/In = 9/1. The resulting solution was applied to the abraded surfaces of the sintered body by a dip method while masking the non-abraded areas so as to give a film having a thickness in the range of 5 - 10 μm after baked. The thus coated sintered body was heat trated (baked) in air at 450°C for 2 hours while raising the temperature to 450°C at a rate of 200°C/hr. After baking, Al electrodes were formed on the indium oxide-tin oxide films by a conventional flame spraying.

A plurality of non-linear resistors thus produced and conventional non-linear resistors containing no indium oxide-tin oxide film were subjected to an accelerated life test with rated voltage application to obtain expected lifetimes when used as resistors for 1200 kV arresters and their lifetimes and non-linearity coefficients (α) were compared. The results are as shown in Table 1.

Table 1

Nonlinear resistor	Lifetime of nonlinear resistor		Non-linearity coefficient*3 (α)
	Accelerated life test with rated voltage application*1 (hrs)	Expected lifetime as resistors for 1200 kV arresters *2 (years)	
This invention	>700	>430	70 - 80
Conventional one	10	6	40 - 50

Note to Table 1:

*1: Ambinet temperaure 90°C. Applied voltage ratio was 95%.

*2: Ambient temperature 40°C. Applied voltage ratio was 80%.

*3: Non-linearity coefficient α was obtained from the following equation:

$$\alpha = \frac{2}{\log_{10}\left(\frac{V_{1mA}}{V_{10\mu A}}\right)}$$

wherein V_{1mA} is an applied voltage at a given current of 1 mA, and $V_{10\mu A}$ is an applied voltage at a given current of 10 μA.

The above-mentioned conditions are the same in the following Examples.

As is clear from Table 1, the lifetime is prolonged by far remarkably and the non-linearity coefficient is increased considerably by the formation of the continuous and electroconductive film of indium oxide-tin oxide between the sintered body and the electrodes.

Example 2

In a ball mill, 2360 g of ZnO, 70 g of Bi_2O_3, 25 g of Co_2O_3, 87 g of Sb_2O_3, 17 g of MnO_2, 23 g of Cr_2O_3, 2 g of B_2O_3 and 9 g of SiO_2 were wet mixed for 15 hours. The resulting mixed powders were dried, granulated and pressed into a body of 20 mm in diameter and 5 mm in thickness. After coating a Bi_2O_3 - Sb_2O_3 - SiO_2 - containing paste on the side surface of the body, the body was sintered in air at 1250°C for 2 hours. During the sintering, the above-mentioned paste was reacted with the ZnO to give a highly resistant layer containing Zn_2SiO_4 and $Zn_7Sb_2O_{12}$ mainly. Two major surfaces of the sintered body were abraded so as to give a thickness of 4 mm.

On the other hand, a solution was prepared by mixing metallic tin (Sn), $CH_3COCH_2COCH_3$ and HNO_3 in a weight ratio of 1 : 10 : 4. The solution was applied to the abraded surfaces of the sintered body by the dip method so as to give a film having a thickness in the range of 2 - 10 μm after baked. The thus coated sintered body was heat treated (baked) in air at 450°C for 2 hours while raising the temperature to 450°C at a rate of 200°C/hr. After baking, aluminum electrodes were formed on the tin oxide films by a conventional flame spraying.

The same tests as conducted in Example 1 were conducted with the results as shown in Table 2.

As is clear from Table 2, by the formation of the tin oxide film, the lifetime is prolonged remarkably and the non-linearity coefficient is increased considerably.

Table 2

Non-linear resistor	Lifetime of nonlinear resistor		Non-linearity co-efficient (α)
	Accelerated life test with rated voltage application (hrs)	Expected life-time as resistors for 1200 kV arresters (years)	
This invention	>400	>240	75 - 85
Conventional one	10	6	30 - 50

Example 3

A sintered body was prepared in the same manner as described in Example 2. Two major surfaces of the sintered body were abraded so as to give a thickness of 3 mm.

Then, a 50% by weight solution prepared by dissolving indium nitrate [$In(NO_3)_3 \cdot 9H_2O$] in $CH_3COCH_2COCH_3$ was applied to the abraded surfaces of the sintered body by the dip method so as to give a film having a thickness of in the range of 2 - 10 μm after baked. The thus coated sintered body was heat treated, followed by the electrode formation in the same manner as described in Example 2.

The same tests as conducted in Example 1 were conducted with the results as shown in Table 3.

As is clear from Table 3, by the formation of the indium oxide film, the lifetime is prolonged remarkably and the non-linearity coefficient is increased considerably.

Table 3

Nonlinear resistor	Lifetime of nonlinear resistor		Non-linearity coefficient (α)
	Accelerated life test with rated voltage application (hrs)	Expected life-time as resistors for 1200 kV arresters (years)	
This invention	>400	>300	70 - 80
Conventional one	10	6	30 - 50

Example 4

In the same manner as described in Example 2, 2360 g of ZnO, 70 g of Bi_2O_3, 25 g of Co_2O_3, 17 g of MnO_2, 85 g of Sb_2O_3, 23 g of Cr_2O_3, 2 g of B_2O_3, and 10 g of SiO_2 were wet mixed, dried, granulated and pressed into a body of 20 mm in diameter and 5 mm in thickness. After coating a Bi_2O_3-Sb_2O_3-SiO_2-containing paste on the side surface of the body, the body was sintered in air at 1250°C for 2 hours. After abrading two major surfaces of the sintered body to a thickness of 4 mm, a solution containing tin obtained in the same manner as described in Example 2 together with antimony (3% by weight) was applied to the abraded surfaces of the sintered body by the dip method so as to give a film having a thickness in the range of 15 - 20 µm after baked. The thus coated sintered body was heat treated (baked) in air at a temperature of 250°C, 300°C, 350°C, 450°C, 520°C or 600°C for 30 minutes, while raising the temperature to the prescribed one at a rate of 100°C/hr.

The resulting tin oxide films were subjected to a humidity resistance test and resistivities of the films were also measured.

On the other hand, aluminum electrodes were formed on the tin oxide films by a conventional flame spraying. The resulting resistors were subjected to the same tests as in Example 1 with the results as shown in Table 4.

The humidity resistance test was conducted by dipping a tin oxide film coated sintered body in boiling water for 30 minutes and judging the surface appearance as to discoloration or peeling of the tin oxide film.

As shown in Table 4, when the tin oxide films were baked at 250°C and 300°C, peeling and discoloration took place after dipped in boiling water and the resistivity was also larger than 1 ohm·cm. On the other hand, when baked at 600°C, the non-linearity coefficient of the resulting resistor was lowered greatly. Thus, the baking temperature of 350 to 520°C is preferable for giving the tin oxide film having good properties.

Table 4

Electro-conductive film	Baking temp. (°C)	Humidity resistance	Resistivity (ohm.cm)	Non-linearity coefficient (α)	Accelerated life test with rated voltage application (hrs)
Tin oxide	250	Partly peeled	2.9	63 - 75	19
	300	Disclored	1.1	62 - 79	190
	350	Good	2.4×10^{-1}	68 - 81	>400
	450	Good	6.5×10^{-2}	75 - 85	>400
	520	Good	5.5×10^{-2}	70 - 86	>400
	600	Good	3.9×10^{-2}	10 - 20	-
None	-	-	-	30 - 50	10

Example 5

In a ball mill, 2360 g of ZnO, 70 g of Bi_2O_3, 25 g of Co_2O_3, 17 g of MnO_2, 85 g of Sb_2O_3, 23 g of Cr_2O_3, 2 g of B_2O_3 and 10 g of SiO_2 were wet mixed for 15 hours, and then dried, granulated, and pressed into a body of 20 mm in diameter and 6 mm in thickness. The body was sintered in air at 1250°C for 2 hours. Two major surfaces of the sintered body were abraded so as to give a thickness of 4 mm. Solutions having a Sn/In ratio of 5/95, 10/90, 20/80, 50/50, or 80/20 were prepared by using the indium solution and the tin solution used in Example 1. Each solution was applied to the abraded surfaces of the sintered body by the dip method so as to give a film having a thickness in the range of 15 - 20 μm after baked. The thus coated sintered body was heat treated (baked) in air at 400°C for 30 minutes, while raising the temperature to 400°C at a rate of 150°C/hr. Single film of indium oxide and that of tin oxide were formed in the same manner as mentioned above. Aluminum electrodes were formed on each film of indium oxide-tin oxide, indium oxide or tin oxide by a conventional flame spraying.

The resulting resistors were subjected to the same tests as in Example 1 with the results as shown in Table 5.

As is clear from Table 5, the films made of indium oxide-tin oxide mixtures are particularly superior to the film made of indium oxide or tin oxide singly in the accelerated life test.

Table 5

Electroconductive film		Non-linearity coefficient (α)	Accelerated life test with rated voltage application (hrs)
Kind	Mixing ratio		
Indium oxide-tin oxide	Sn/In = 5/95	68 - 78	630
	Sn/In = 10/90	70 - 81	>700
	Sn/In = 20/80	64 - 80	>700
	Sn/In = 50/50	73 - 80	>700
	Sn/In = 80/20	69 - 75	620
Indium oxide	Sn/In = 0/100	63 - 76	490
Tin oxide	Sn/In = 100/0	70 - 78	460
None	-	30 - 50	10

Example 6

In a ball mill, 2360 g of ZnO, 20 g of Bi_2O_3, 25 g of Co_2O_3, 17 g of MnO_2, 85 g of Sb_2O_3, 23 g of Cr_2O_3, 2 g of B_2O_3 and 10 g of SiO_2 were wet mixed for 15 hours, and then dried, granulated and pressed into a body of 20 mm in diameter and 6 mm in thickness. The body was sintered in air at 1250°C for 2 hours. Two major surfaces of the sintered body were abraded so as to give a thickness of 4 mm. The same indium solution as used in Example 3 was applied to the abraded surfaces of the sintered body by the dip method so as to give a film having a thickness in the range of 15 - 20 µm after baked. The thus coated sintered body was heat treated (baked) in air at a temeprature of 250°C, 300°C, 350°C, 450°C, 520°C or 600°C for 30 minutes, while raising the temperature to the prescribed one at a rate of 100°C/hr.

The resulting indium oxide films were subjected to the humidity resistance test and resistivities of the films were also measured in the same manner as described in Example 4. The results are shown in Table 6.

On the other hand, aluminum electrodes were formed on the indium oxide films by a conventional flame spraying. The resulting resistors were subjected to the same tests as in Example 1 with the results as shown in Table 6.

As shown in Table 6, when the indium oxide films were baked at 250°C and 300°C, peeling and discoloration took place after dipped in boiling water and the resistivity was also larger than 1 ohm·cm or slightly lower than 1 ohm·cm. On the other hand, when baked at 600°C, the non-linearity coefficient of the resulting resistor was lowered greatly. Thus, the baking temperature of 350 to 520°C is preferable for giving the indium oxide film having good properties.

Table 6

Electro-conductive film	Baking temp. (°C)	Humidity resistance	Resistivity (ohm·cm)	Non-linearity coefficient (α)	Accelerated life test with rated voltage application (hrs)
Indium oxide	250	Partly peeled	3.6	67 - 74	18
	300	Discolored	9.0×10^{-1}	60 - 80	170
	350	Good	3.0×10^{-1}	63 - 76	>400
	450	Good	8.2×10^{-2}	70 - 80	>400
	520	Good	6.8×10^{-2}	68 - 81	>400
	600	Good	4.9×10^{-2}	10 - 20	-
None	-	-	-	30 - 50	10

Example 7

In a ball mill, 2360 g of ZnO, 95 g of Bi_2O_3, 25 g of Co_2O_3, 17 g of MnO_2, 85 g of Sb_2O_3, 23 g of Cr_2O_3, 2 g of B_2O_3 and 10 g of SiO_2 were wet mixed for 15 hours, and then dried, granulated and pressed into a body of 20 mm in diameter and 6 mm in thickness. The body was sintered in air at 1250°C for 2 hours. Two major surfaces of the sintered body were abraded so as to give a thickness of 4 mm. A solution prepared by mixing the indium solution and the tin solution as used in Example 1 so as to give a Sn/In ratio of 20/80 was applied to the abraded surfaces of the sintered body by the dip method so as to give an indium oxide-tin oxide film having a thickness in the range of 20 - 25 μm after baked. The thus coated sintered body was heat treated (baked) in air at a temperature of 250°C, 300°C, 350°C, 450°C, 520°C or 600°C for 30 minutes, while raising the temperature to the prescribed one at a rate of 100°C/hr.

The resulting indium oxide-tin oxide films were subjected to the humidity resistance test and resistivities of the films were also measured in the same manner as described in Example 4. The results are shown in Table 7.

On the other hand, aluminum electrodes were formed on the indium oxide-tin oxide films by a conventional flame spraying. The resulting resistors were subjected to the same tests as in Example 1 with the results as shown in Table 7.

As shown in Table 7, when the indium oxide-tin oxide films were baked at 250°C and 300°C, peeling and discoloration took place after dipped in boiling water and the resistivity was also larger than 1 ohm·cm. On the other hand, when baked at 600°C, the non-linearity coefficient of the resulting resistor was lowered greatly. Thus, the baking temperature of 350 to 520°C is preferable for giving the indium oxide-tin oxide film having good properties.

Table 7

Baking temp. (°C)	Humidity resistance	Resistivity (ohm·cm)	Non-linearity coefficient (α)	Accelerated life test with rated voltage application (hrs)
250	Partly peeled	4.2	63 - 74	25
300	Discolored	1.1	60 - 80	200
350	Good	5×10^{-1}	62 - 78	>700
450	Good	4.2×10^{-2}	73 - 82	>700
520	Good	3.3×10^{-2}	71 - 79	>700
600	Good	1.2×10^{-2}	15 - 23	-

Example 8

In the same manner as described in Example 1, 2340 g of ZnO, 140 g of Bi_2O_3, 25 g of Co_2O_3, 17 g of MnO_2, 88 g of Sb_2O_3, 23 g of NiO, 5 g of Cr_2O_3, 2 g of B_2O_3 and 5 g of SiO_2 were wet mixed, dried, granulated and pressed into a body of 20 mm in diameter and 5 mm in thickness. After coating a Bi_2O_3-Sb_2O_3-SiO_2-containing paste on the side surface of the body, the body was sintered in air at 1270°C for 2 hours. Two major surfaces of the sintered body were abraded so as to give a thickness of 4 mm. The tin solution used in Example 1 was applied to the abraded surfaces of the sintered body by brushing so as to give a tin oxide film having a thickness of 0.5 μm, 1 μm, 10 μm, 20 μm, 30 μm or 40 μm after baked. Each thus coated sintered body was heat treated (baked) in air at 500°C for 30 minutes, while raising the temperature to 500°C at a rate of 100°C/hr. After baked, aluminum electrodes were formed on the tin oxide films having no cracks thereon by a conventional flame spraying. The resulting resistors were subjected to the same accelerated life test as Example 1 with the results as shown in Table 8.

As shown in Table 8, when the electroconductive tin oxide film has a thickness of as thick as 40 μm, cracks take place on the film. This seems to be caused by differences in thermal expansion coefficients between the sintered body and the tin oxide film. Further, when the thickness of the electroconductive tin oxide film is as thin as 0.5 µm, the results of the accelerated life test are not so different from those obtained when no tin oxide film is interposed between the sintered body and the electrode. This seems that the tin oxide film is so thin that pin holes are formed in the film, which results in losing the effect for preventing the release of the oxygen adsorbed on zinc oxide crystal grain surfaces or the oxygen in grain boundary layers from the sintered body at the time of rated voltage application. Thus, a preferable thickness of the electroconductive tin oxide film is in the range of 1 to 30 µm.

Table 8

Electro-conductive film	Film thickness (μm)	Cracks on the film	Accelerated life test with rated voltage application (hrs)
Tin oxide	0.5	No	13
	1	No	>400
	10	No	>400
	20	No	>400
	30	No	>400
	40	Yes	-
None	-	-	10

Example 9

A mixture of powders having the same composition as described in Exmaple 8 was granulated and pressed into a body of 20 mm in diameter and 6 mm in thickness. After coating a SiO_2-Bi_2O_3-Sb_2O_3-containing paste on the side surface of the body, the body was sintered in air at 1270°C for 2 hours. Two major surfaces of the sintered body were abraded so as to give a thickness of 4 mm. The indium solution used in Example 2 was applied to the abraded surfaces of the sintered body by brushing so as to give an indium oxide film having a thickness of 0.5 μm, 1 μm, 10 μm, 20 μm, 30 μm or 45 μm after baked. The thus coated sintered body was heat treated (baked) in air at 500°C for 30 minutes, while raising the temperature to 500°C at a rate of 100 °C/hr. After baked, aluminum electrodes were formed on the indium oxide films having no cracks thereon by a conventional flame spraying. The resulting resistors were subjected to the same accelerated life test as in Example 1 with the results as shown in Table 9.

As shown in Table 9, when the electroconductive indium oxide film has a thickness of as thick as 45 μm, cracks take place on the film. On the other hand, when the thickness of the electroconductive indium oxide film is as thin as 0.5 μm, the results of the accelerted life test are not so different from those obtained when no indium oxide film is interposed.

Table 9

Electro-conductive film	Film thickness (μm)	Cracks on the film	Accelerated life test with rated voltage application (hrs)
Indium oxide	0.5	No	12
	1	No	>400
	10	No	>400
	20	No	>400
	30	No	>400
	45	Yes	-
None	-	-	10

Example 10

On two major surfaces of a sintered body obtained in the same manner as described in Example 2, tin oxide films were formed by a conventional sputtering method, followed by the formation of aluminum electrodes thereon by a conventional flame spraying.

In this case, the lifetime of resulting resistors under the accelerated life test was improved when the thickness of the tin oxide films was 1 μm or more.

Example 11

On two major surfaces of a sintered body obtained in the same manner as described in Example 3, indium oxide films were formed by a conventional sputtering method, followed by the formation of aluminum electrodes thereon by a conventional flame spraying.

In this case, the lifetime of resulting resistors under the accelerated life test was also improved when the thickness of the indium oxide films was 1 μm or more.

Example 12

In a ball mill, 2340 g of ZnO, 140 g of Bi_2O_3, 25 g of Co_2O_3, 18 g of MnO_2, 90 g of Sb_2O_3, 25 g of NiO, 7 g of Cr_2O_3, 2 g of B_2O_3 and 6 g of SiO_2 were wet mixed, and then dried, granulated, and pressed into a body of 20 mm in diameter and 5 mm in thickness. After coating a SiO_2-Bi_2O_3-Sb_2O_3-containing paste on the side surface of the body, the body was sintered at 1270°C for 2 hours. Two major surfaces of the sintered body were abraded so as to give a thickness of 3 mm. A solution was prepared by mixing the indium solution and the tin solution used in Example 1 so as to give a Sn/In ratio of 40/60. The solution was applied to the abraded surfaces of the sintered body by brushing so as to give an indium oxide-tin oxide film having a thickness of 0.5 μm, 1 μm, 10 μm, 20 μm, 30 μm, 50 μm or 65 μm after baked. Each sintered body thus coated was heat treated (baked) in air at 500°C for 30 minutes, while raising the temperature to 500°C at a rate of 100°C/hr. After baked, aluminum electrodes were formed on the tin oxide films having no cracks thereon by a conventional flame spraying. The resulting non-linear resistors were subjected to the same accelerated life test as in Example 1 with the results as shown in Table 10.

As shown in Table 10, when the indium oxide-tin oxide film has a thickness of as thick as 65 μm, cracks take place on the film. On the other hand, when the thickness of indium oxide-tin oxide film is as thin as 0.5 μm, the results of the accelerated life test are not so different from those obtained when no indium oxide-tin oxide film is interposed. Cracks on the thick film seem to be caused by differences in thermal expansion coefficients between the sintered body and the indium oxide-tin oxide film. On the other hand, when the indium oxide-tin oxide film is so thin as 0.5 μm, pin holes are formed in the film, which results in probably losing the effect for preventing the release of the oxygen adsorbed on zinc oxide crystal grain surfaces or the oxygen in grain boundary layers from the sintered body during the accelerated life test. Thus, a preferable thickness of the indium oxide-tin oxide film is in the range of 1 to 50 μm.

Table 10

Electro-conductive film	Film thickness (µm)	Cracks on the film	Accelerated life test with rated voltage application (hrs)
Indium oxide-tin oxide	0.5	No	15
	1	No	>700
	10	No	>700
	20	No	>700
	30	No	>700
	50	No	>700
	65	Yes	-
None	-	-	10

Example 13

On two major surfaces of a sintered body obtained in the same manner as described in Example 1, indium oxide-tin oxide films were formed by a conventional sputtering method, followed by the formation of aluminum electrodes thereon by a conventional flame spraying.

In this case, the lifetime of resulting resistors under the accelerated life test was improved when the thickness of the indium oxide-tin oxide film was 1 μm or more.

As mentioned above, since a film of tin oxide, indium oxide, or indium oxide-tin oxide, which has no gas permeability and good electroconductiveness, is individually formed between the sintered body and electrodes, the non-linear resistor of this invention is excellent in stability when a rated voltage is applied for a long period of time compared with conventional ones having no such films.

WHAT IS CLAIMED IS:

1. A non-linear resistor comprising a sintered body having non-linear resistance characteristics, continuous films having no gas permeability and lower electrical resistivity than the resistivity of the sintered body formed on the upper and/or lower major surfaces of the sintered body, and one or more electrodes formed on the continuous films.

2. A non-linear resistor according to Claim 1, wherein the continuous film is made of an indium oxide type compound or a tin oxide type compound.

3. A non-linear resistor according to Claim 1, wherein the continuous film is made of a mixture of an indium oxide type compound and a tin oxide type compound.

4. A non-linear resistor according to Claim 2, wherein the continuous film is made of indium oxide or tin oxide and has a thickness of 1 to 30 μm.

5. A non-linear resistor according to Claim 3, wherein the continuous film is made of a mixture of indium oxide and tin oxide and has a thickness of 1 to 50 μm.

6. A non-linear resistor according to Claim 1, wherein the continuous film is baked at a temperature of 350 to 520°C after solution coating on the sintered body and before the formation of electrodes.

7. A non-linear resistor according to Claim 1, wherein the continuous film does not react with the

sintered body.

8. A non-linear resistor according to Claim 1, wherein the sintered body contains zinc oxide as a major component.

9. A non-linear resistor according to Claim 8, wherein the sintered body contains substantially no γ-form bismuth oxide.

10. A non-linear resistor according to Claim 1, wherein the continuous film has resistivity of 1 ohm·cm or less.

11. A non-linear resistor according to Claim 1, wherein the continuous film has the same area and shape as the electrode formed thereon.

12. A process for producing a non-linear resistor which comprises:

forming a layer of material on upper and/or lower major surface area, at which an electrode is to formed, of a sintered body having non-linear resistance characteristics,

baking the layer of material at a temperature of 350 to 520°C for providing a continuous film having no gas permeability and lower electrical resistivity than the resistivity of the sintered body, and

forming each electrode on each continuous film thus provided.

13. A process according to Claim 12, wherein the layer of material is formed by a solution coating method.

14. A process according to Claim 13, wherein the

solution is a solution of one or more indium compounds or tin compounds as major components.

15. A process according to Claim 13, wherein the solution is a solution of a mixture of one or more indium compounds and tin compounds as major components.

16. A process according to Claim 12, wherein the layer of material is a layer of one or more indium compounds or tin compounds.

17. A process according to Claim 12, wherein the layer of material is a layer of a mixture of one or more indium compounds and tin compounds.

18. Use of non-linear resistors of Claim 1 for making an arrester comprising a housing means and one or a plurality of non-linear resistors piled in the housing means.

FIG. 1

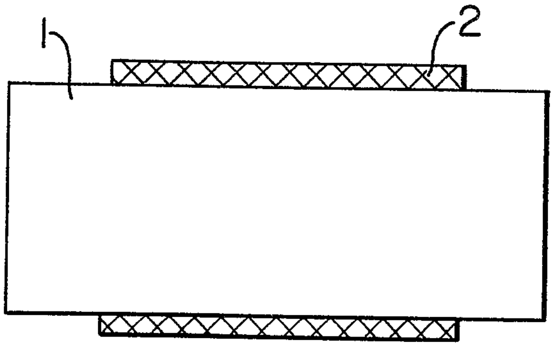


FIG. 2

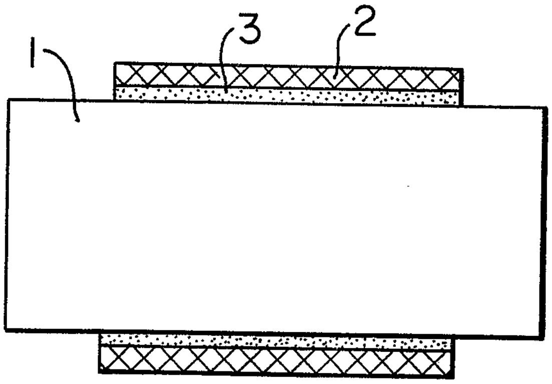


FIG. 3

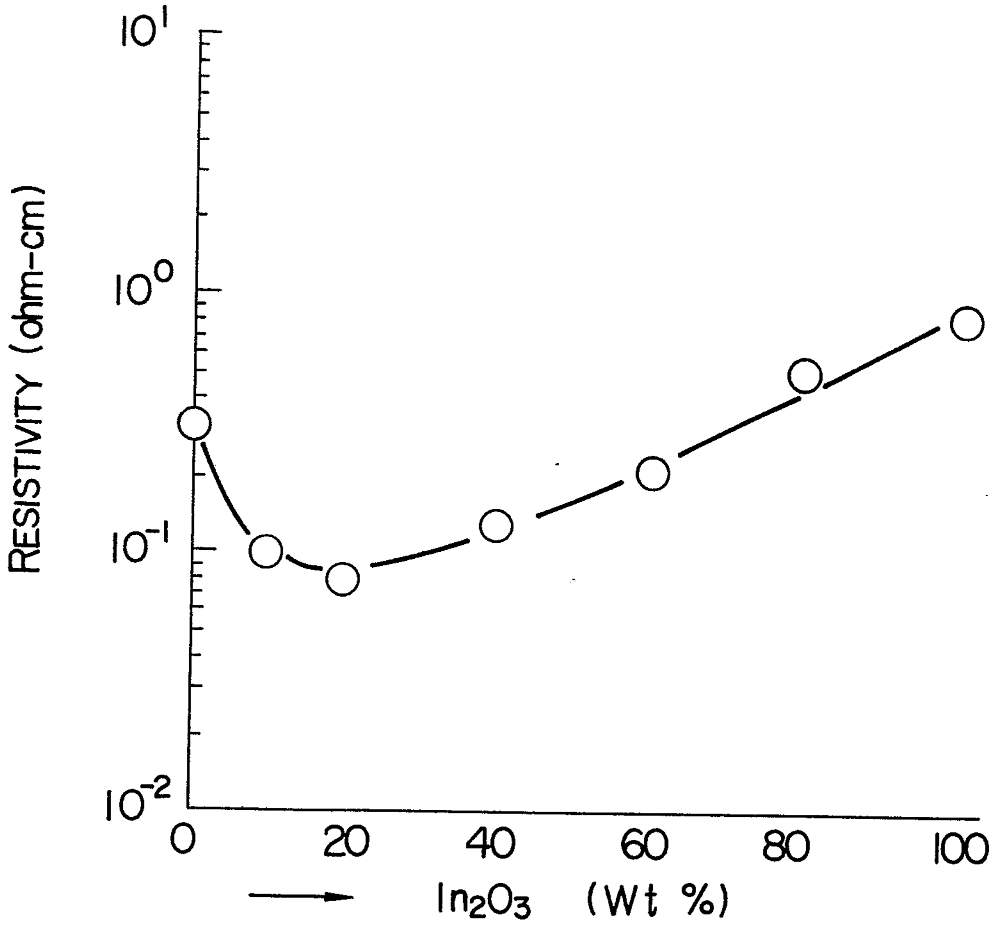
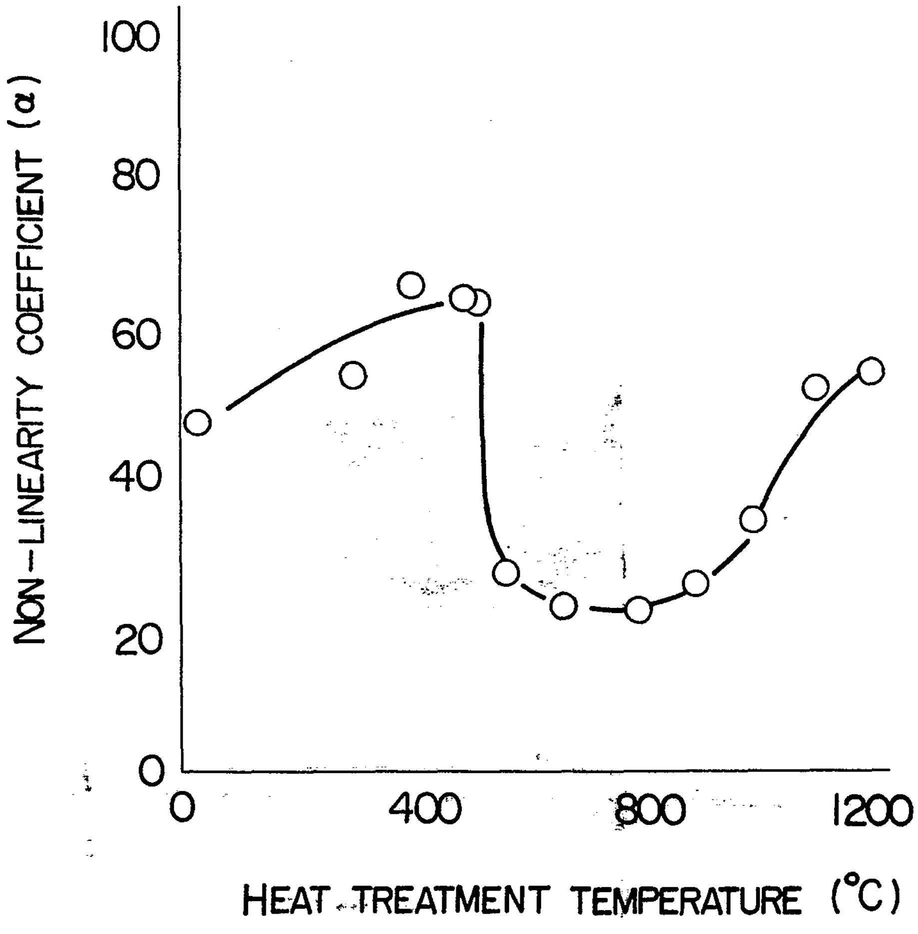


FIG. 4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100
80
60
40
20
0
0
400
800
1200
HEAT TREATMENT TEMPERATURE (°C)