United States Patent [19]

Matsuoka et al.

[11] **3,872,582**

[45] **Mar. 25, 1975**

[54] **PROCESS FOR MAKING A VOLTAGE DEPENDENT RESISTOR**

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[22] Filed: **Dec. 27, 1973**

[21] Appl. No.: **428,737**

[30] **Foreign Application Priority Data**

Dec. 29, 1972	Japan	47-483610
Dec. 29, 1972	Japan	47-483619
Apr. 13, 1973	Japan	48-4842488
June 15, 1973	Japan	48-4868066

[52] **U.S. Cl.** **29/621,** 29/610, 252/518, 252/521, 338/20

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

[58] **Field of Search** .... 29/610, 621; 338/20, 21, 338/22 R; 252/518, 521

[56] **References Cited**

UNITED STATES PATENTS

3,496,512	2/1970	Matsuoka et al.	29/621 X
3,503,029	3/1970	Matsuoka	338/20
3,632,528	1/1972	Matsuoka et al.	252/518
3,663,458	5/1972	Masuyama et al.	252/518
3,760,318	9/1973	Masuyama et al.	29/610 X
3,764,566	10/1973	Matsuoka et al.	252/518
3,778,743	12/1973	Matsuoka et al.	338/20

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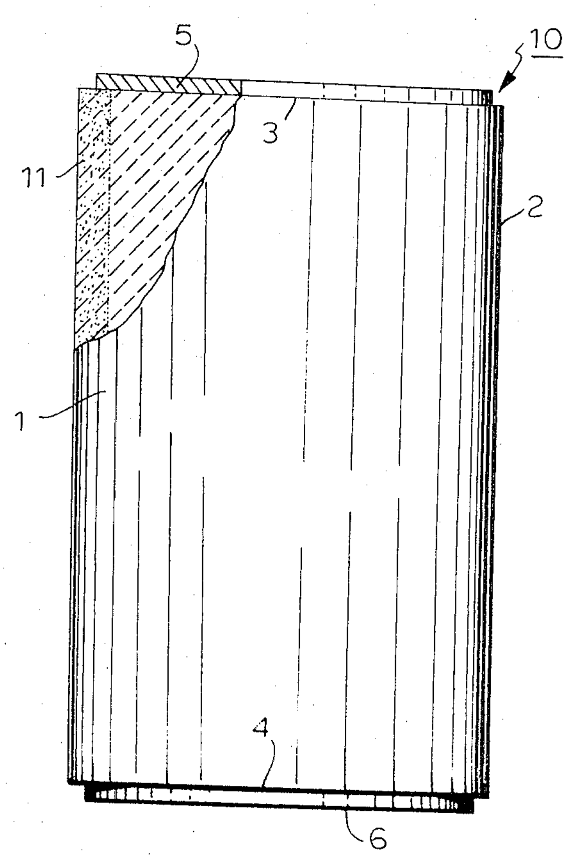
[57] **ABSTRACT**

A process for making a voltage dependent resistor which has a zinc oxide sintered body which itself has voltage dependent properties. The process is made up of the steps of: (1) providing a formed body of a powder mixture having as a major part zinc oxide and additive; (2) coating on the side surfaces of the formed body a paste having as the solid ingredient composition at least one member selected from the group of a) more than 50 mole % of silicon dioxide (SiO_2), and less than 50 mole % of bismuth oxide (Bi_2O_3), b) the same composition as that of said additive, c) more than 30 mole percent of antimony oxide (Sb_2O_3) and less than 70 mole percent of bismuth oxide (Bi_2O_3), and d) more than 50 mole percent of indium oxide (In_2O_3) and less than 50 mole percent of bismuth oxide (Bi_2O_3); (3) sintering the coated body; and (4) applying electrodes to opposite surfaces of the sintered body.

5 Claims, 1 Drawing Figure



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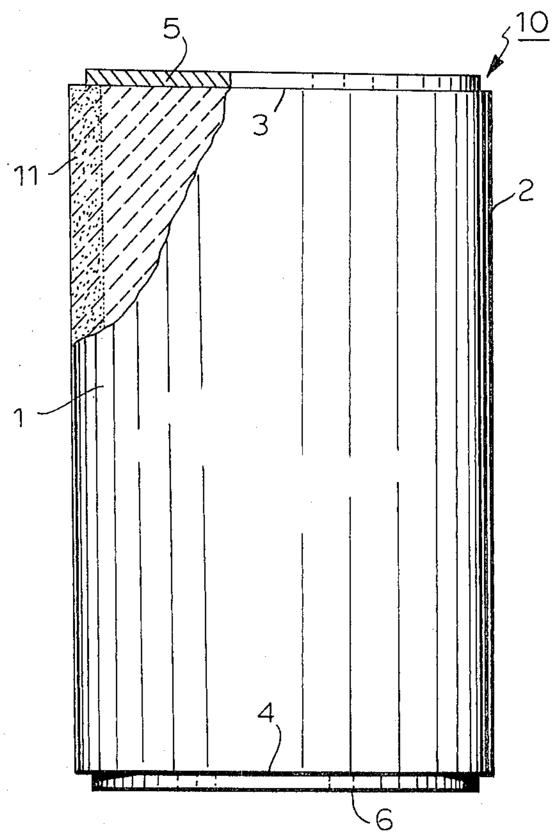

PROCESS FOR MAKING A VOLTAGE DEPENDENT RESISTOR

This invention relates to the preparation of a voltage dependent resistor the properties of which are due to the bulk thereof, and more particularly to a varistor comprising a zinc oxide sintered body having a high resistance layer of a composition such as silicon dioxide, antimony oxide or indium oxide on the side surface of the sintered body.

Various voltage dependent resistors such as silicon carbide varistors, selenium rectifiers and germanium or silicon p-n junction diodes have been widely used for stabilization of voltage or current of electrical circuits. The electrical characteristics of such a voltage dependent resistor are expressed by the relation:

$I = (V/C)^n$

where V is the voltage across the resistor, I is the current flowing through the resistor, C is a constant corresponding to the voltage at a given current and exponent n is a numerical value greater than **1**. The value of n is calculated by the following equation:

$n = \log_{10}(I_2/I_1)/\log_{10}(V_2/V_1)$

where V_1 and V_2 are voltages at a given currents I_1 and I_2, respectively. The desired value of C depends upon the kind of application to which the resistor is to be put. It is ordinarily desirable that the value of n be as large as possible since this exponent determines the degree to which the resistors depart from ohmic characteristics.

There have been known voltage dependent resistors comprising sintered bodies of zinc oxide with or without additives and having silver paint electrodes applied thereto, as disclosed in the U.S. Pat. No. 3,496,512. The non-linearity of such voltage dependent resistors is attributed to the interface between the sintered body of zinc oxide with or without additives and the silver paint electrode and is controlled mainly by changing the composition of said sintered body and said silver paint electrode. Therefore, it is not easy to control the C-value over a wide range after the sintered body is prepared. Similarly, in the voltage dependent resistors comprising germanium or silicon p-n junction diodes it is difficult to control the C-value over a wide range because the non-linearity of these voltage dependent resistors is not attributed to the bulk thereof but to the p-n junction. On the other hand, silicon carbide varistors have non-linearity due to the contacts among individual grains of silicon carbide bonded together by a ceramic binding material i.e. to the bulk and are controlled with respect to the C-value by changing the dimension in the direction in which the current flows through the varistors. The silicon carbide varistors, however, have a relatively low n-value ranging from 3 to 6 and are prepared by firing in a non-oxidizing atmosphere, especially for the purpose of obtaining a lower C-value. In U.S. Pat. Nos. 3,663,458, 3,669,058, 3,637,529, 3,632,528, 3,634,337 and 3,598,763, there have been disclosed voltage dependent resistors comprising sintered bodies of zinc oxide with additives such as bismuth oxide, uranium oxide, strontium oxide, lead oxide, barium oxide, cobalt oxide and manganese oxide. The non-linearity of such voltage dependent resistors is attributable to the bulk thereof and is independent of the interface between the sintered bodies and the electrodes. Therefore, it is easy to control the C-value over a wide range by changing the thickness of the sintered body itself. Such voltage dependent resistors of the bulk type have more excellent properties with respect to the n-value, transient power dissipation and AC power dissipation than do SiC varistors.

A disadvantage of the zinc oxide voltage-dependent resistors is their poor stability in an electric load life test in a high ambient humidity. When D.C. power is applied to the zinc oxide sintered body in a high ambient humidity, the sintered body shows a decrease in the surface electrical resistance. This decrease causes in particular an increase in the leakage current in the zinc oxide voltage-dependent resistor of the bulk type and results in a poor non-linear property. The deterioration of the non-linear property of the voltage-dependent resistor occurs even at a load of low power such as a load lower than **0.01** watt in a high ambient humidity, for example 90 percent R.H at 70°C. Therefore, it is necessary that the sintered body is completely protected against outside moisture by a protective coating.

Another disadvantage of the zinc oxide voltage dependent resistors aforesaid exists in their poor ability to withstand impulse current. When an impulse wave is applied to the zinc oxide sintered body, the sintered body suffers a flashover along its side surface at an impulse voltage above 500V/mm, and despite no deterioration in the interior of sintered body the side surface of the sintered body is heavily damaged. The poor ability to withstand impulse current is unfavorable particularly for application of the varistor as a lightning arrester.

There is other prior art that relates to a voltage dependent resistor comprising a sintered body comprising zinc oxide and other additives and being characterized by a high C-value, high n-value, high stability with respect to temperature, humidity and electric load, and good ability to withstand impulse current. Such a resistor is disclosed in U.S. Pat. No. 3,760,318. More specifically, a zinc oxide sintered body according to said U.S. Pat. No. 3,760,318 has Li ions or Na ions diffused into said sintered body from the side surface thereof at a temperature of 600°C to 1000°C. This diffusing process inevitably results in lowering the n-value of the resultant resistor in the current region lower than 10 μA. The low n-value in such low current region is undesirable for an application requiring low leakage current.

An object of the present invention is to provide a method for making a voltage dependent resistor characterized by a high stability with respect to a d.c. load in high humidity and a good ability to withstand impulse current.

Another object of the present invention is to provide a method for making a voltage dependent resistor characterized by a high n-value even in a low current region and a high stability with respect to a d.c. load in high humidity and a good ability to withstand impulse current.

These and other objects of the invention will become apparent upon consideration of the following description taken together with the accompanying drawing in which the single FIGURE is a partly cross-sectional view of a voltage-dependent resistor in accordance with the invention.

Before proceeding with a detailed description of the manufacturing process for the voltage-dependent resistor contemplated by the invention, the construction of the resultant resistor will be described with reference to the aforesaid FIGURE wherein reference character **10** designates, as a whole, a voltage-dependent resistor comprising, as its active element, a sintered body having surfaces consisting of a side surface **2** and opposite end surfaces **3** and **4** to which a pair of electrodes **5** and **6** are applied. Said sintered body **1** is prepared in a manner hereinafter set forth and has a high resistance layer **11** at said side surface **2** and can have any cross-sectional form such as circular, square or rectangular.

The process for making a voltage dependent resistor of a bulk type characterized by a high humidity resistance and a good ability to withstand current surges according to the invention comprises: (1) providing a formed body of a powder mixture comprising, as a major part, zinc oxide, and an additive including BiO_2; (2) coating on the side surfaces of said body a paste comprising, solid ingredient composition, at least one member selected from the group consisting of a more than 50 mole percent of silicon dioxide (SiO_2) and less than 50 mole percent of bismuth oxide (Bi_2O_3), b) the same composition as that of said addition, c) more than 30 mole percent of antimony oxide (Sb_2O_3) and less than 70 mole percent of bismuth oxide (Bi_2O_3), and d) more than 50 mole percent of indium oxide (In_2O_3) and less than 50 mole percent of bismuth oxide (Bi_2O_3); (3) sintering said coated body; and (4) applying two electrodes to the opposite end surfaces of said sintered body.

Said zinc oxide sintered body which itself has voltage dependent properties can be prepared by using a composition described in U.S. Pat. Nos. 3,663,458, 3,669,058, 3,636,529, 3,632,528, 3,634,337 and 3,598,763. Among various compositions, a better result can be obtained with a composition consisting essentially of, as a major part, 80.0 to 99.9 mole percent of zinc oxide and, as an additive, 0.05 to 10.0 mole percent of bismuth oxide (Bi_2O_3) and 0.05 to 10.0 mole percent, in total, of at least one member selected from the group consisting of cobalt oxide (CoO), manganese oxide (MnO), antimony oxide (Sb_2O_3), barium oxide (BaO), strontium oxide (SrO) and lead oxide (PbO).

According to the present invention, the resultant resistor has an excellent ability to withstand current surges in an impulse current test, when said coating paste comprises, as the solid composition, 70 to 95 mole percent of silicon dioxide (SiO_2) and 30 to 5 mole percent of bismuth oxide (Bi_2O_3). Similarly, the ability to withstand surge current can be improved greatly by using coating paste comprising, as the solid ingredient composition, 70 to 95 mole percent of antimony oxide (Sb_2O_3) and 30 to 5 mole percent of bismuth oxide (Bi_2O_3).

According to the present invention, the ability to withstand surge current can be further improved by using coating paste comprising, as the solid ingredient composition, 50 to 95 mole percent of silicon dioxide (SiO_2), 2 to 45 mole percent of antimony oxide (Sb_2O_3) and 2 to 20 mole percent of bismuth oxide (Bi_2O_3).

It has been discovered according to the invention that the D.C. stability in high humidity and the ability to withstand surge current of the resultant resistor is improved when said powder mixture consists essentially of, as a major part, 99.9 to 80.0 mole percent of zinc oxide (ZnO) and, as an additive, 0.05 to 10.0 mole percent of bismuth oxide (Bi_2O_3) and 0.05 to 10.0 mole percent, in total, of at least one member selected from the group consisting of cobalt oxide (CoO), manganese oxide (MnO) antimony oxide (Sb_2O_3), barium oxide (BaO), strontium oxide (SrO) and lead oxide (PbO).

The sintered body **1** can be prepared by a per se well known ceramic technique. The starting materials comprising zinc oxide powder and additives such as bismuth oxide, cobalt oxide, manganese oxide, antimony oxide, barium oxide, strontium oxide, lead oxide, uranium oxide and tin oxide are mixed in a wet mill so as to produce a homogeneous mixture. The mixtures are dried and pressed in a mold into desired shapes at a pressure from 100 kg/cm^2 to 1000 kg/cm^2. When a rod-shaped resistor is desired, the mixed slurry can be fabricated into the desired shape by extruding and then dried. The mixtures may be preliminarily calcined at a temprature of 700° to 1000°C and pulverized for easy fabrication in the subsequent pressing step. The mixtures may be admixed with a suitable binder such as water, polyvinyl alcohol, etc.

After the mixtures are formed into the desired shapes, the formed bodies are coated, on the side surfaces, with a paste including powder having the same composition as said additive, or a combination of bismuth oxide with silicon dioxide, antimony oxide or indium oxide, so as to form a high resistance layer at the side surfaces after sintering. Said paste comprises, as the solid ingredient composition, at least one member selected from the group consisting of a more than 50 mole percent of silicon dioxide (SiO_2) and less than 50 mole percent of bismuth oxide (Bi_2O_3), b) the same composition as that of said additive, c) more than 30 mole percent of antimony oxide (Sb_2O_3) and less than 70 mole percent of bismuth oxide (Bi_2O_3), and d) more than 50 mole percent of indium oxide (In_2O_3) and less than 50 mole percent of bismuth oxide (Bi_2O_3), and, as a binding material, an organic resin such as epoxy, vinyl or phenol resin in an organic solvent such as butyl acetate, toluene or the like. Said silicon dioxide, bismuth oxide, antimony oxide and indium oxide can be replaced, respectively, with any silicon compound, bismuth compound, antimony compound and indium compound such as an oxalate, carbonate, nitrate, sulfate, iodide, fluoride or hydroxide which is converted into the corresponding oxide at the sintering temperature.

After being coated with said paste, the formed bodies are sintered in air at a temperature of 1000° to 1450°C for **1** to 5 hours, and then furnace-cooled to room temperature. The sintering temperature is determined based on the desired electrical resistivity, nonlinearity stability and the thickness of the high resistance layer formed at the side surface of the sintered body. Also, the electrical resistivity can be reduced by air-quenching from the sintering temperature to room temperature. The sintered body has non-ohmic resistance due to the bulk itself. Therefore, its C-value can be changed without impairing the n-value by changing the distance between said opposite end surfaces. A shorter distance results in a lower C-value. The coating paste forms a high resistance layer, as can be proved by measurement of the resistance distribution in the cross-section of the sintered body, which will show a high resistance at the side surface of the sintered body. The high resistance layer is controlled so as to have a thickness more than 10μ. Particularly, it can be shown from an x-ray analysis of the cross-sectional portion of sintered body, that the paste comprising a combination of silicon dioxide and bismuth oxide, or antimony oxide and bismuth oxide forms a layer having a thickness of more than 3μ and that said layer comprises, in a region to a 3μ depth from the side surface, more than 70 mole percent of at least zinc silicate (Zn_2SiO_4) and/or zinc antimonate ($Zn_7Sb_2O_{12}$).

After sintering, the sintered body has electrodes applied to the opposite end surfaces of the sintered body. Said electrodes can be made by any available method such as heating of noble metal paint, electroless or electrolytic plating of Ag, Cu, Ni, Sn etc. vacuum evaporating of Al, Zn, Sn etc. and flame spraying of Cu, Sn, Al, Zn etc. in accordance with the prior well known techniques.

Lead wires can be attached to the electrodes in a per se conventional manner by using conventional solder. It is convenient to employ a conductive adhesive comprising silver powder and resin in an organic solvent in order to connect the lead wires to the silver electrodes. The n-value of a voltage-dependent resistor according to this invention does not deteriorate even in a low current region due to the introduction of the covering layer at the side surface of the sintered body, and it has a high stability with respect to temperature and humidity and in the load life test, which is carried out at 70°C, 90 percent RH at a rating power for 500 hours. The n-value and C-value do not change appreciably after the load life test. From a surge test, which is carried out by applying a 4×10 μsec impulse current twice, it is shown that this voltage-dependent resistor has the ability to withstand surges of more than 2000A/cm^2.

EXAMPLE 1.

Starting materials listed in Table 1 were mixed in a wet mill for 5 hours. Each mixture was dried and pressed in a mold into a disc of 40 mm in diameter and 25 mm in thickness at a pressure of 340 kg/cm^2. The pressed bodies had the side surface covered by coating paste including solid ingredients listed in Table 1, and were dried. Then, the bodies were sintered in air for 5 hours at 1200°C and furnace-cooled. The sintered bodies were lapped to the thickness listed in table 1 by lapping the opposite end surfaces thereof with silicon carbide abrasive having a particle size of 600 mesh. The opposite end surfaces of the sintered discs were provided with a spray metallized film of aluminum by a per se well known technique. The electric characteristics of the resultant resistors are, shown in Table 1. It will be readily understood that the C-value changes in proportion to the thickness of the sintered body.

Size of disc: 32 mm in dia.

Thickness of high resistive layer: 30μ

Table 1

Composition of Sintered Body (mol. %)	Solid Ingredient of Paste (mol. %)	Thickness of Sintered Body (mm)	C(V) (at 1mA)	n (0.1–1mA)
ZnO (99.0), Bi_2O_3 (0.5), CoO (0.5)	SiO_2 (50), Bi_2O_3 (50)	5	150	15
		10	302	14
		20	605	15
	SiO_2 (90), Bi_2O_3 (10)	5	153	15
		10	310	16
		20	605	16
	SiO_2 (100), Bi_2O_3 (0)	5	155	14
		10	310	15
		20	615	15
	Sb_2O_3 (90), Bi_2O_3 (10)	5	150	15
		10	300	15
		20	603	15
	In_2O_3 (90), Bi_2O_3 (10)	5	145	14
		10	300	14
		20	600	15
	SiO_2 (72), Sb_2O_3 (20), Bi_2O_3 (8)	5	160	16
		10	315	16
		20	615	16
ZnO (97.5), Bi_2O_3 (0.5), CoO (0.5), MnO (0.5), Sb_2O_3 (1.0)	SiO_2 (90), Bi_2O_3 (10)	5	510	44
		10	1025	45
		20	2040	45
	Sb_2O_3 (90), Bi_2O_3 (10)	5	500	45
		10	1010	45
		20	2010	46
	In_2O_3 (90), Bi_2O_3 (10)	5	505	45
		10	1010	44
		20	2015	46
	SiO_2 (72), Sb_2O_3 (20), Bi_2O_3 (8)	5	515	46
		10	1025	46
		20	2040	46
ZnO (99.0), Bi_2O_3 (0.5), MnO (0.5)	Sb_2O_3 (90), Bi_2O_3 (10)	5	250	22
		10	505	22
		20	1000	23
ZnO (99.0), Bi_2O_3 (0.5), Sb_2O_3 (0.5)	SiO_2 (90), Bi_2O_3 (10)	5	240	8.2
		10	490	8.4
		20	985	8.4
ZnO (99.0), Bi_2O_3 (0.5), BaO (0.5)	In_2O_3 (90), Bi_2O_3 (10)	5	200	10
		10	410	10
		20	815	10
ZnO (99.0), Bi_2O_3 (0.5), SrO (0.5)	SiO_2 (72), Sb_2O_3 (20), Bi_2O_3 (8)	5	205	11
		10	400	11
		20	810	12

EXAMPLE 2

Starting materials of Table **2** were fabricated into voltage dependent resistors by the same process as that of Example 1. An impulse test was carried out by applying a 4×10μs impulse and the ability to withstand current surges was thus determined. A humidity test was carried out by boiling the disc in the pure water for 24 hours. The electric characteristics of the resultant resistors are shown in Table 2.

Size of disc: 32 mm in dia. and 20 mm in thickness
Sintering: 1200°C for 5 hours
Thickness of high resistance layer: 30μ

EXAMPLE 3

Starting materials of Table 3 were fabricated into voltage dependent resistors by the same process as that of Example 1. Then the tests were carried out by the same methods as those of Example 2. The electric characteristics of the resultant resistors are shown in Table 3.

Size of disc: 32 mm in dia. and 20 mm in thickness
Sintering: 1200°C for 5 hours
Thickness of high resistance layer: 30μ

TABLE 2

Composition of Sintered Body (mol. %)	Solid Ingredient of Paste (mol %)				Electric Characteristics of Resultant Resistor: C(V) (at 1mA)	n 0.1–1mA	Impulse Withstand, (KA)	Boiling Test ΔC (%)
ZnO (99.0), Bi_2O_3(0.5), CoO (0.5)	SiO_2	(50)	Bi_2O_3	(50)	605	15	20	−5.0
	SiO_2	(60)	Bi_2O_3	(40)	605	15	20	−4.7
	SiO_2	(70)	Bi_2O_3	(30)	600	15	25	−4.7
	SiO_2	(80)	Bi_2O_3	(20)	600	16	30	−3.8
	SiO_2	(90)	Bi_2O_3	(10)	605	16	35	−2.9
	SiO_2	(95)	Bi_2O_3	(5)	610	16	30	−3.2
	SiO_2	(100)	Bi_2O_3	(0)	615	15	30	−3.5
	Sb_2O_3	(30)	Bi_2O_3	(70)	600	14	20	−5.3
	Sb_2O_3	(50)	Bi_2O_3	(50)	600	14	25	−4.5
	Sb_2O_3	(70)	Bi_2O_3	(30)	600	15	25	−3.5
	Sb_2O_3	(90)	Bi_2O_3	(10)	603	15	35	−2.7
	Sb_2O_3	(95)	Bi_2O_3	(5)	605	15	30	−3.0
	Sb_2O_3	(100)	Bi_2O_3	(0)	610	14	25	−3.3
	In_2O_3	(50)	Bi_2O_3	(50)	595	14	20	−5.7
	In_2O_3	(70)	Bi_2O_3	(30)	600	14	25	−4.3
	In_2O_3	(90)	Bi_2O_3	(10)	600	15	35	−3.1
	In_2O_3	(95)	Bi_2O_3	(5)	600	15	30	−3.4
	$In_{2\ 3}$	(100)	Bi_2O_3	(0)	610	14	30	−3.5
SnO (97.5), Bi_2O_3(0.5), CoO (0.5), MnO (0.5), Sb_2O_3(1.0)	SiO_2	(50)	Bi_2O_3	(50)	1960	42	25	−5.5
	SiO_2	(60)	Bi_2O_3	(40)	1980	42	30	−4.8
	SiO_2	(70)	Bi_2O_3	(30)	2000	44	35	−3.9
	SiO_2	(80)	Bi_2O_3	(20)	2100	44	40	− 3.2
	SiO_2	(90)	Fi_2O_3	(10)	2040	45	40	−1.5
	SiO_2	(95)	Bi_2O_3	(5)	2040	45	35	−2.1
	SiO_2	(100)	Bi_2O_3	(0)	2030	44	30	−2.3
	Sb_2O_3	(30)	Bi_2O_3	(70)	1980	44	25	−5.1
	Sb_2O_3	(50)	Bi_2O_3	(50)	2000	44	30	−4.9
	Sb_2O_3	(70)	Bi_2O_3	(30)	2000	45	35	−3.8
	Sb_2O_3	(90)	Bi_2O_3	(10)	2010	46	40	−2.5
	Sb_2O_3	(95)	Bi_2O_3	(5)	2015	45	40	−3.1
	Sb_2O_3	(100)	Bi_2O_3	(0)	2020	45	30	−3.5
	In_2O_3	(50)	Bi_2O_3	(50)	1990	44	25	−5.3
	In_2O_3	(70)	Bi_2O_3	(30)	2005	44	30	−4.9
	In_2O_3	(90)	Bi_2O_3	(10)	2015	46	40	−3.1
	In_2O_3	(95)	Bi_2O_3	(5)	2015	45	40	−3.4
	In_2O_3	(100)	Bi_2O_3	(0)	2000	45	25	−3.4

Composition	SiO_2	Sb_2O_3	Bi_2O_3	C(V)	n	Impulse	Boiling
ZnO (99.0), Bi_2O_3(0.5), CoO (0.5)	50	45	5	600	15	30	−4.4
	50	30	20	600	15	30	−4.8
	95	3	2	615	16	35	−3.2
	95	2	3	615	16	40	−3.4
	58	40	2	610	15	35	−3.0
	78	2	20	610	15	40	−2.5
	72	20	8	620	17	45	−1.7
ZnO (97.5), Bi_2O_3(0.5), CoO (0.5), MnO (0.5), Sb_2O_3(1.0)	50	45	5	2050	44	40	−3.4
	50	30	20	2065	45	45	−2.8
	95	3	2	2045	45	50	−2.7
	95	2	3	2075	46	50	−2.7
	58	40	2	2060	44	50	−2.0
	78	2	20	2080	46	55	−1.2
	72	20	8	2100	48	60	−0.5

TABLE 3

Composition of Sintered Body (mol %)				Solid Ingredient of Paste (mol %)		Electric Characteristics of Resultant Resistor			
ZnO	Bi_2O_3	Further Additives				C(V) (at 1mA)	n 0.1–1mA	Impulse with-stand. (KA)	Boiling Test ΔC(%)
99.90	0.05	CoO	0.05	SiO_2 Bi_2O_3	(90) (10)	350	10	15	−6.2
89.95	0.05	CoO	10			420	12	18	−6.2
89.95	10	CoO	0.05			420	13	20	−3.9
80.00	10	CoO	10			750	14	20	−4.0
99.0	0.5	CoO	0.5			605	16	35	−6.3
99.90	0.05	MnO	0.05	Sb_2O_3 Bi_2O_3	(90) (10)	500	13	15	−6.3
89.95	0.05	MnO	10			600	14	15	−5.9
89.95	10	MnO	0.05			900	18	25	−3.3
80.00	10	MnO	10			1250	17	25	−3.5
99.0	0.5	MnO	0.5			1000	23	35	−2.8
99.90	0.05	Sb_2O_3	0.05	In_2O_3 Bi_2O_3	(90) (10)	300	7.9	15	−7.0
89.95	0.05	Sb_2O_3	10			800	7.2	15	−5.5
89.95	10	Sb_2O_3	0.05			720	8.2	17	−3.9
80.00	10	Sb_2O_3	10			1300	8.6	18	−4.2
99.0	0.5	Sb_2O_3	0.5			990	8.4	25	−2.0
99.90	0.05	BaO	0.05	SiO_2 Bi_2O_3	(90) (10)	320	7.2	18	−5.3
89.95	0.05	BaO	10			470	8.0	15	−4.9
89.95	10	BaO	0.05			510	9.4	20	−2.9
80.00	10	BaO	10			1200	0.5	20	−3.4
99.0	0.5	BaO	0.5			815	10	25	−2.5
99.90	0.05	SrO	0.05	Sb_2O_3 Bi_2O_3	(90) (10)	300	9.2	12	−7.2
89.95	0.05	SrO	10			1150	8.1	14	− 5.7
89.95	10	SrO	0.05			1200	11	17	−4.3
80.00	10	SrO	10			1400	11	18	−4.5
99.0	0.5	SrO	0.5			810	12	20	−3.3
98.5	0.5	CoO MnO	0.5 0.5	SiO_2 Sb_2O_3 Bi_2O_3	(72) (20) (8)	850	27	45	−3.5
98.5	0.5	CoO Sb_2O_3	0.5 0.5			1700	40	50	−4.2
98.5	0.5	CoO BaO	0.5 0.5			1000	22	35	−4.5
98.5	0.5	CoO SrO	0.5 0.5			950	25	40	−5.3
98.5	0.5	MnO Sb_2O_3	0.5 0.5			1800	40	50	−4.7
98.5	0.5	MnO BaO	0.5 0.5			1300	32	40	−3.8
98.5	0.5	MnO SrO	0.5 0.5			1250	30	40	−3.8
98.5	0.5	Sb_2O_3 BaO	0.5 0.5			1300	20	30	−4.7
98.5	0.5	Sb_2O_3 SrO	0.5 0.5			1220	20	30	−5.2
98.5	0.5	BaO SrO	0.5 0.5			750	17	25	−7.0
98.0	0.5	CoO MnO Sb_2O_3	0.5 0.5 0.5	SiO_2 Sb_2O_3 Bi_2O_3	(72) (20) (8)	1800	40	50	−1.5
98.0	0.5	CoO MnO BaO	0.5 0.5 0.5			800	29	35	−2.5
98.0	0.5	CoO MnO SrO	0.5 0.5 0.5			770	26	35	−3.0
98.0	0.5	CoO Sb_2O_3 BaO	0.5 0.5 0.5			1500	33	40	−2.7
98.0	0.5	CoO Sb_2O_3 SrO	0.5 0.5 0.5			1450	31	35	−2.2
98.0	0.5	CoO BaO SrO	0.5 0.5 0.5			880	18	25	−3.3
98.0	0.5	MnO Sb_2O_3 BaO	0.5 0.5 0.5			1650	35	40	−3.1
98.0	0.5	MnO Sb_2O_3 SrO	0.5 0.5 0.5			1600	33	40	−2.4
98.0	05	MnO BaO SrO	0.5 0.5 0.5			1000	21	35	−2.5
98.0	0.5	Sb_2O_3 BaO SrO	0.5 0.5 0.5			1050	18	30	−3.0

EXAMPLE 4

The fabrication process and testing method were the same as those of Example 2 and the thickness of the high resistance layer was varied with the results as shown in Table **4.** It is easily understood that the ability to withstand impulses increases with an increase in the thickness of the high resistance layer and the rate of change of the C-value caused by the boiling test decreases with an increase of thickness of the high resistance layer.

Size of disc: 32 mm in dia. and 20 mm in thickness

Sintering: 1200°C for 5 hours

EXAMPLE 5

Starting materials of Table **5** were fabricated into voltage dependent resistors by the same process as in Example 1. The pressed bodies were sintered at a temperature between 1000°C to 1450°C for 5 hours after covering the side surface with coating pastes as listed in Table 5. The test conditions were the same as those of Example 2. The electric characteristics of resulting resistors are shown in Table 5.

Size of disc: 32 mm in dia. and 20mm

Thickness of high resistive layer; 30μ.

TABLE 4

Composition of Sintered Body (mol %)	Solid Ingredient of Paste (mol %)	Thickness of High-Resistive layer (μ)	Electric Characteristics of Resultant Resistor: C(V) (at 1 mA)	n 0.1–1 mA	Impulse Withstand (KA)	Boiling Test ΔC (%)
ZnO (99.0), Bi_2O_3(0.5), CoO (0.5	SiO_2 (90), Bi_2O_3 (10)	10	600	16	30	−4.3
		30	605	16	35	−2.9
		100	605	16	40	−3.2
		300	615	16	50	−1.2
	Sb_2O_3 (90), Bi_2O_3 (10)	10	600	14	30	−4.2
		30	603	15	35	−2.7
		100	605	15	40	−2.2
		300	610	15	45	−1.7
	In_2O_3 (90), Bi_2O_3 (10)	10	590	15	25	−4.8
		30	600	15	35	−3.1
		100	605	15	40	−3.3
		300	610	16	45	−2.7
	SiO_2 (72), Sb_2O_3 (20), Bi_2O_3 (8)	10	605	17	35	−3.3
		30	620	17	45	−1.7
		100	620	17	50	−1.2
		300	630	18	60	−1.0
ZnO (97.5), Bi_2O_3(0.5), CoO (0.5), MnO (0.5), Sb_2O_3(1.0)	SiO_2 (90), Bi_2O_3 (10)	10	200	43	30	−2.1
		30	2040	45	40	−1.5
		100	2070	45	45	−1.1
		300	2100	46	45	−0.5
	Sb_2O_3 (90), Bi_2O_3 (10)	10	1950	43	30	−3.3
		30	2010	46	40	−2.5
		100	2030	46	40	−2.0
		300	2050	46	50	−1.6
	In_2O_3 (90), Bi_2O_3 (10)	10	2000	44	30	−4.7
		30	2015	46	40	−3.1
		100	2050	46	55	−2.2
		300	2100	47	60	−1.8
	SiO_2 (72), Sb_2O_3 (20), Bi_2O_3 (8)	10	2050	46	50	−1.2
		30	2100	48	60	−0.5
		100	2120	50	70	−0.5
		300	2150	50	80	−0.4

TABLE 5

Composition of Sintered Body (mol. %)	Solid Ingredient of Paste (mol. %)	Sintering Temp. (°C)	Electric Characteristics of Resultant Resistor: C (V) (at 1 mA)	n 0.1–1mA	Impulse Withstand	Boiling Test ΔC(%)
	SiO_2 (50), Bi_2O_3 (50)	1000	1200	11	15	−9.5
		1100	850	14	17	−7.2
		1200	605	15	20	−5.0
		1300	420	13	18	−5.1
		1450	280	11	18	−5.3
	SiO_2 (90), Bi_2O_3 (10)	1000	1220	13	20	−7.7
		1100	870	14	25	−4.1
		1200	605	16	35	−2.9
		1300	450	16	35	−2.9
		1450	300	15	30	−3.5
	SiO_2 (100), Bi_2O_3 (0)	1000	1250	12	20	−7.0
		1100	900	14	25	−5.1
		1200	615	15	30	−3.5
		1300	470	14	23	−3.7
		1450	330	14	20	−4.0
		1000	1200	11	15	−8.1

TABLE 5 – Continued

Composition of Sintered Body (mol. %)	Solid Ingredient of Paste (mol. %)	Sintering Temp. (°C)	C (V) (at 1 mA)	n 0.1–1mA	Impulse Withstand	Boiling Test ΔC(%)
ZnO (99.0) Bi_2O_3 (0.5) CoO (0.5)	Sb_2O_3 (30) Bi_2O_3 (70)	1200	600	14	20	−5.3
		1450	300	13	18	−5.7
	Sb_2O_3 (90) Bi_2O_3 (10)	1000	1190	13	28	−4.1
		1200	603	15	35	−2.7
		1450	285	14	30	−3.3
	Sb_2O_3 (100) Bi_2O_3 (0)	1000	1220	12	20	−5.0
		1200	610	14	25	−3.5
		1450	310	13	20	−4.0
	In_2O_3 (50) Bi_2O_3 (50)	1000	1200	12	15	−7.5
		1200	595	14	20	−5.7
		1450	320	12	18	−6.0
	In_2O_3 (90) Bi_2O_3 (10)	1000	1230	13	25	−4.7
		1200	600	15	35	−3.1
		1450	295	15	25	−3.6
	In_2O_3 (100) Bi_2O_3 (0)	1000	1200	14	25	−5.1
		1200	610	14	30	−3.5
		1450	305	14	30	−4.0
	SiO_2 (72) Sb_2O_3 (20) Bi_2O_3 (8)	1000	1250	14	35	−3.6
		1100	910	15	40	−2.1
		1200	620	17	45	−1.7
		1300	430	16	40	−1.8
		1450	300	15	40	−2.3
ZnO (97.5) Bi_2O_3 (0.5) CoO (0.5) MnO (0.5) Sb_2O_3 (1.0)	SiO_2 (90) Bi_2O_3 (10)	1000	3800	38	30	−2.9
		1200	2040	45	40	−1.5
		1450	1200	42	35	−2.0
	Sb_2O_3 (90) Bi_2O_3 (10)	1000	3900	41	35	−3.5
		1200	2010	46	40	−2.5
		1450	1250	43	35	−2.7
	In_2O_3 (90) Bi_2O_3 (10)	1000	4000	42	35	−4.7
		1200	2015	46	40	−3.1
		1450	1300	40	40	−3.5
	SiO_2 (72) Sb_2O_3 (20) Bi_2O_3 (8)	1000	4050	40	40	−1.3
		1100	3200	44	550	−0.9
		1200	2100	48	60	−0.5
		1300	1550	44	50	−1.1
		1450	1300	40	45	−1.5

EXAMPLE 6

The mixtures of Table 6 were pressed and covered by coating paste comprising the same oxides as the additives in the body. Then the bodies were sintered in air for 5 hours. The test conditions were the same as those of Example 2. The electric characteristics of the resultant resistors are shown in Table 6. The excellent ability to withstand impulses and the small change in the C-value were obtained by coating paste containing the same materials as the additives in the sintered body.

Size of disc; 32 mm in ida. and 20 mm in thickness

Thickness of high resistive layer; 30μ

Table 6

Composition of Sintered body (mol. %) ZnO	Bi_2O_3	Further Additives		Solid Ingredient of Paste	(mol. %)	Sintering Temp. (°C)	C (V) (at 1mA)	n 0.1–1mA	Impulse Withstand (KA)	Boiling Test ΔC (%)
99.5	0.5	—		Bi_2O_3	100	1200	4000	4.1	10	−7.5
99.5	—	CoO	0.5	CoO	100	1200	2200	3.9	10	−6.2
99.5	—	MnO	0.5	MnO	100	1200	2600	3.4	10	−5.3
99.5	—	Sb_2O_3	0.5	Sb_2O_3	100	1200	3000	3.7	12	−6.2
99.5	—	BaO	0.5	BaO	100	1200	1600	9.0	15	−7.0
99.5	—	SrO	0.5	SrO	100	1200	1500	7.8	12	−8.3
99.5	—	UO_2	0.5	UO_2	100	1200	2000	4.1	10	−7.9
99.5	—	PbO	0.5	PbO	100	1200	4000	4.3	12	−7.1
99.0	0.5	CoO	0.5	Bi_2O_3(50)	CoO (50)	1200	600	15	22	−3.5
99.0	0.5	MnO	0.5	Bi_2O_3(50)	MnO(50)	1200	1000	23	25	−3.7
99.0	0.5	Sb_2O_3	0.5	Bi_2O_3(50)	Sb_2O_3(50)	1200	985	8.3	18	−4.2
99.0	0.5	BaO	0.5	Bi_2O_3(50)	BaO(50)	1200	820	11	20	−3.3
99.0	0.5	SrO	0.5	Bi_2O_3(50)	SrO(50)	1200	800	12	20	−3.7
99.0	—	CoO SnO	0.5 0.5	CoO SrO	50 50	1200	4000	30	40	−5.0
99.0	—	MnO BaO	0.5 0.5	MnO BaO	50 50	1300	3500	30	35	−4.7
99.0	—	BaO SrO	0.5 0.5	BaO SrO	50 50	1100	2000	20	30	−3.3
98.0	1.0	CoO MnO	0.5 0.5	Bi_2O_3 CoO MnO	50 25 25	1200	1800	15	25	−2.7
98.0	1.0	BaO SrO	0.5 0.5	Bi_2O_3 BaO SrO	50 25 25	1200	1650	14	20	−3.5
97.5	0.5	CoO MnO Sb_2O_3	0.5 0.5 1.0	Bi_2O_3 CoO MnO Sb_2O_3	20 20 20 60	1200	2000	46	55	−1.7
		CoO	0.5	Bi_2O_3 CoO	10 10					

Table 6 – Continued

Composition of Sintered body (mol. %)			Solid Ingredient of Paste	Sintering Temp.	Electric Characteristics of Resultant Resistor			
ZnO	Bi_2O_3	Further Additives	(mol. %)	(°C)	C (V) (at 1mA)	n 0.1–1mA	Impulse Withstand (KA)	Boiling Test ΔC (%)
97.0	0.5	MnO 0.5 Sb_2O_3 1.0 SnO_2 0.5	MnO 10 Sb_2O_3 40 SnO_2 30 Bi_2O_3 10	1200	2600	50	60	–0.5
97.0	0.5	CoO 0.5 MnO 0.5 Sb_2O_3 1.0 Cr_2O_3 0.5	CoO 10 MnO 10 Sb_2O_3 60 Cr_2O_3 10 Bi_2O_3 10	1200	2800	50	60	–0.5
96.5	0.5	CoO 0.5 MnO 0.5 Sb_2O_3 1.0 Cr_2O_3 0.5 SiO_2 0.5	CoO 5 MnO 5 Sb_2O_3 25 Cr_2O_3 5 SrO_2 50 Bi_2O_3 5	1200	4400	55	70	–0.3
94.0	0.5	CoO 0.5 MnO 0.5 Sb_2O_3 1.0 Cr_2O_3 0.5 SiO_2 2.0 NiO 1.0	CoO 5 MnO 5 Sb_2O_3 20 Cr_2O_3 3 SiO_2 60 NiO 2	1200	5600	60	70	–0.3
98.0	0.5	CoO 0.5 MnO 0.5 Sb_2O_3 0.5	Bi_2O_3 25 CoO 25 MnO 25 Sb_2O_3 25	1000 1200 1450	3800 1800 850	35 40 41	35 50 40	–1.2 –0.8 –1.3

What we claim is:

1. A process for making a voltage dependent resistor comprised of a zinc oxide sintered body which itself has voltage dependent properties, said process comprising: (1) providing a formed body of powder mixture comprising, as a major part, zinc oxide and the remainder being an additive; (2) coating on the side surface of said body a paste having a solid ingredient composition of at least one member selected from the group consisting of a) more than 50 mole percent of silicon dioxide (SiO_2) and less than 50 mole percent of bismuth oxide (Bi_2O_3), b) the same composition as that of said additive, c) more than 30 mole percent of antimony oxide (Sb_2O_3) and less than 70 mole percent of bismuth oxide (Bi_2O_3), and d) more than 50 mole percent of indium oxide (In_2O_3) and less than 50 mole percent of bismuth oxide (Bi_2O_3); (3) sintering said coated body; and (4) applying two electrodes to the opposite end surfaces of said sintered body.

2. A process according to claim 1, in which the coating paste has a solid ingredient composition of 70 to 95 mole percent of silicon dioxide (SiO_2) and 30 to 5 mole percent of bismuth oxide (Bi_2O_3).

3. A process according to claim 1, in which the coating paste has a solid ingredient composition of 70 to 95 mole percent of antimony oxide (Sb_2O_3) and 30 to 5 mole percent of bismuth oxide (Bi_2O_3).

4. A process according to claim 1, in which the coating paste has a solid ingredient composition of 50 to 95 mole percent of silicon dioxide (SiO_2), 2 to 45 mole percent of antimony oxide (Sb_2O_3) and 2 to 20 mole percent of bismuth oxide (Bi_2O_3).

5. A process according to claim 1 which said powder mixture consists essentially of, as a major part, 99.9 to 80.0 mole percent of zinc oxide (ZnO) and, as an additive, 0.05 to 10.0 mole percent of bismuth oxide (Bi_2O_3) and 0.05 to 10.0 mole percent of at least one member selected from the group consisting of cobalt oxide (CoO), manganese oxide (MnO) antimony oxide (Sb_2O_3), barium oxide (BaO), strontium oxide (SrO) and lead oxide (PbO).

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