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[54] VOLTAGE VARIABLE RESISTORS

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[56]

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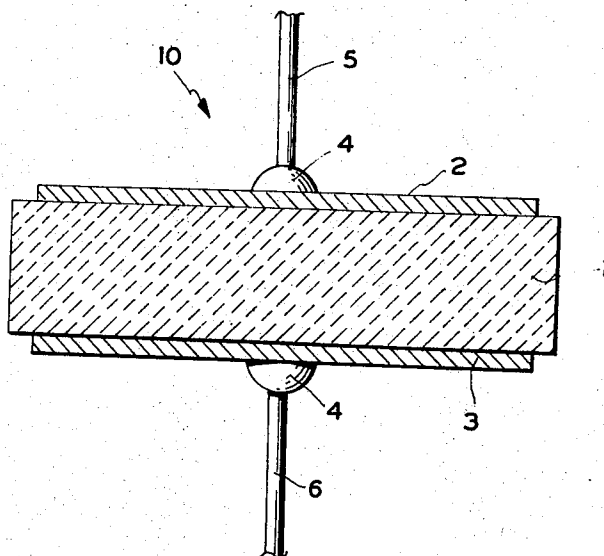
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ABSTRACT

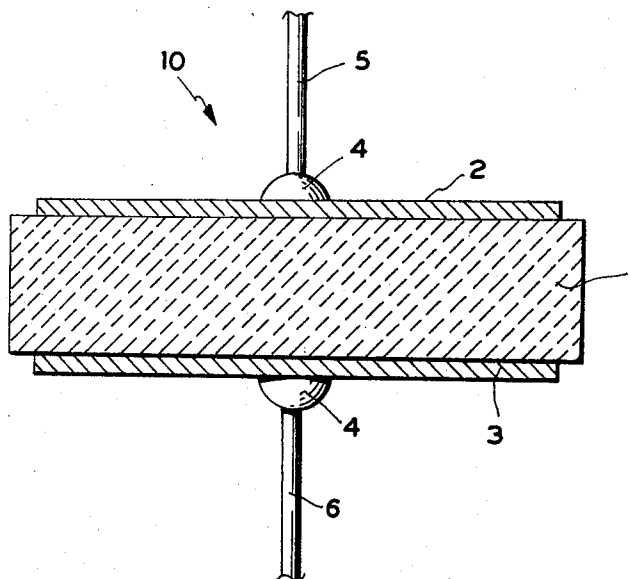
Voltage variable resistors comprising a sintered wafer consisting essentially of zinc oxide (ZnO), 0.05 to 8.0 mole percent of bismuth oxide (Bi_2O_3) and 0.05 to 10.0 mole percent of at least one member selected from the group consisting of niobium oxide (Nb_2O_5), zirconium oxide (ZrO_2), vanadium oxide (V_2O_5) and tungsten oxide (WO_3) and two electrodes applied to opposite surfaces of said sintered wafer, at least one of said two electrodes being a silver paint electrode.

7 Claims, 1 Drawing Figure



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VOLTAGE VARIABLE RESISTORS

This invention relates to voltage variable resistors having non-ohmic resistance and more particularly relates to varistors comprising zinc oxide and having silver electrodes applied thereto.

Various voltage variable resistors such as silicon carbide varistors, selenium or cuprous oxide rectifiers and germanium or silicon PN junction diodes, are known. The electrical characteristics of such voltage variable 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 equivalent 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:

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

where V_1 and V_2 are the voltages at given currents I_1 and I_2 , respectively. Conveniently, I_1 and I_2 are 10 mA and 100 mA, respectively. The desired value of C depends upon the use to which the resistor is to be put. It is ordinarily desired that the value of n be as large as possible since this exponent determines the degree to which the resistors depart from ohmic characteristics.

Silicon carbide varistors are most widely used as voltage variable resistors and are manufactured by mixing fine particles of silicon carbide with water, a ceramic binder and/or conductive material such as graphite or metal powder, pressing the mixture in a mold to the desired shape, and then drying and firing the pressed body in air or a non-oxidizing atmosphere. Silicon carbide varistors with conductive materials are characterized by a low electric resistance, i.e., a low value of C and a low value of n whereas silicon carbide varistors without conductive materials have a high electric resistance, i.e., a high value of C and a high value of n . It has been difficult to manufacture silicon carbide varistors characterized by a high n and a low C . For example, silicon carbide varistors with graphite have been known to exhibit n values from 2.5 to 3.3 and C -values from 6 to 13 at a given current of 100 mA, and silicon carbide varistors without graphite show n -values from 4 to 7 and C -values from 30 to 800 at a given current of 1 mA for a given size of varistor, e.g., 30mm in diameter and 1mm in thickness.

Conventional rectifiers comprising selenium or cuprous oxide have an n -value of 5 to 10 and a C -value less than 2 at a given current of 100mA for a rectifier size of 20mm in diameter. In this case, the thickness of the rectifier does not affect the C -value.

A germanium or silicon PN junction resistor has an extremely high value of n but its C -value is constant, e.g., on the order of 0.3 or 0.7 at a given current of 100mA because its diffusion voltage in the V - I characteristic is constant and cannot be changed greatly. It is necessary for obtaining a desirable C -value to combine several diodes in series and/or in parallel. Another disadvantage of such diodes is the complicated steps involved in their manufacture, with resultant high cost. As a practical matter, the use of diode resistors is not widespread at the present because of their high cost even though they may have a high value of n .

Voltage variable resistors comprising sintered bodies of zinc oxide (ZnO) with bismuth oxide (Bi_2O_3) and having silver paint electrodes applied thereto have previously been disclosed. The non-linearity of such varistors is attributed to the interface between the sintered body and the silver electrodes. However, the sintered bodies available for such varistors are limited to those sintered at a temperature above 1,200° C because bodies sintered below 1,200° C themselves have non-linear characteristics with a high C and are not suitable for varistors with a low C value. In addition, the sintered bodies sintered above 1,200° C do not have a value of n which is increased very much.

An object of this invention is to provide a voltage variable resistor having a high value of n and a low value of C for sintered bodies sintered over a wide range of temperature.

A further object of this invention is to provide a voltage variable resistor capable of being made by a simple manufacturing method and consequently at a low cost.

A further object of this invention is to provide a voltage variable resistor characterized by a high stability with respect to temperature, humidity and electric load.

Another object of this invention is to provide a voltage variable resistor, the C -value of which can be controlled.

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 through a voltage variable resistor in accordance with the invention.

Before proceeding with a detailed description of the voltage variable resistors contemplated by the invention, their construction will be described with reference to the aforesaid figure wherein reference character 10 designates, as a whole, a voltage variable resistor having, as its active element, a sintered wafer 1 of electrically conductive ceramic material according to the present invention.

Sintered wafer 1 is prepared in a manner hereinafter set forth, and is provided with a pair of electrodes 2 and 3 having specified compositions and applied in a suitable manner hereinafter set forth, on two opposite surfaces of the wafer.

The wafer 1 is a sintered plate having any one of such various shapes as circular, square, rectangular, etc. Wire leads 5 and 6 are attached conductively to the electrodes 2 and 3, respectively, by a connection means 4 (solder or the like).

According to the present invention, sintered wafer 1 consists essentially of zinc oxide (ZnO) having incorporated therein a minor proportion of bismuth oxide (Bi_2O_3) and a least one additive selected from the group consisting of niobium oxide (Nb_2O_5), zirconium oxide (ZrO_2), vanadium oxide (V_2O_5) and tungsten oxide (WO_3).

It has been discovered according to the invention that such a sintered body 1 has superior non-linear electrical characteristics, when it is provided with silver electrodes prepared by applying silver paint to at least one of opposite surfaces thereof and fired at a temperature of from 300° C to 850° C in an oxidizing atmosphere such as air and oxygen. The n -value and C -value of thus produced voltage variable resistors vary with the compositions of the sintered body and electrodes, and their method of preparation.

Since the non-linearity of the novel resistors is attributed to a non-ohmic contact between said sintered body 1 and electrodes 2 and 3, it is necessary for obtaining a desired C -value and n -value to control the compositions of the sintered body 1 and the electrodes 2 and 3. The control of the C -value and n -value can also be obtained by applying an ohmic electrode as the electrode 3 in place of the silver electrode.

It is necessary for achieving a low value of C of the voltage-variable resistors that the sintered body have an electrical resistivity less than 10 ohm-cm, said electrical resistivity being measured by a four point method in a per se conventional way. According to the present invention, a voltage variable resistor with low C and high n can be obtained when said resistor has a sintered wafer which consists essentially of 82.0 to 99.9 mole percent of zinc oxide (ZnO), 0.05 to 8.0 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 niobium oxide (Nb_2O_5), zirconium oxide (ZrO_2), vanadium oxide (V_2O_5) and tungsten oxide (WO_3), and further has two electrodes applied to opposite surfaces of said sintered wafer, at least one of said two electrodes consisting of a silver paint electrode.

It has been discovered according to the invention that the C -value is further lowered when one of said electrodes applied to said sintered wafer is a silver paint electrode and the other is an ohmic electrode.

The n -value is further elevated when said sintered wafer consists of 94.0 to 99.8 mole percent of zinc oxide, 0.1 to 3.0 mole percent of bismuth oxide (Bi_2O_3) and 0.1 to 3.0 mole percent of at least one member selected from the group consisting of niobium oxide (Nb_2O_5), zirconium oxide (ZrO_2), vanadium oxide (V_2O_5) and tungsten oxide (WO_3).

The stability during an electric load life test and at ambient temperature is improved when said silver electrode or electrodes has a composition consisting essentially of 70 to 99.5 wt. percent of silver, 0.3 to 27 wt. percent of lead oxide (PbO), 0.1 to 15 wt. percent of silicon dioxide (SiO_2) and 0.05 to 15 wt. percent of boron trioxide (B_2O_3).

The stability during an electric load life test and at ambient temperature is also improved also when said silver electrode or electrodes have a composition consisting essentially of 70 to 99.5 wt. percent of silver, 0.3 to 27 wt. percent of bismuth oxide (Bi_2O_3), 0.03 to 15 wt. percent of silicon dioxide (SiO_2) and 0.05 to 15 wt. percent of boron trioxide (B_2O_3).

According to the present invention, the stability, during an electric load life test at ambient temperature is remarkably improved when said silver electrode or electrodes have a composition consisting essentially of 70 to 99.5 wt. percent of silver, 0.3 to 27 wt. percent of lead oxide (PbO), 0.1 to 15 wt. percent of silicon dioxide (SiO_2), 0.05 to 15 wt. percent of boron trioxide (B_2O_3) and at least one member selected from the group consisting of 0.05 to 6.0 wt. percent of cobalt oxide (CoO) and 0.05 to 6.0 wt. percent of manganese oxide (MnO).

The stability during an electric load life test at ambient temperature is also greatly improved when said silver electrode or electrodes have a composition consisting essentially of 70 to 99.5 wt. percent of silver, 0.3 to 27 wt. percent of bismuth oxide (Bi_2O_3), 0.03 to 15 wt. percent of silicon dioxide (SiO_2), 0.05 to 15 wt. percent of boron trioxide (B_2O_3) and at least one member selected from the group consisting of 0.05 to 6.0 wt. percent of cobalt oxide (CoO) and 0.05 to 6.0 wt. percent of manganese oxide (MnO).

The sintered body 1 can be prepared by a per se well known ceramic technique. The starting materials in the compositions described in the foregoing description are mixed in a wet mill so as to produce homogeneous mixtures. The mixtures are dried and pressed in a mold into desired shapes at a pressure of from 100 Kg/cm^2 to 1,000 Kg/cm^2 . The pressed bodies are sintered in air at 1,100° to 1,450° C for 1 to 3 hours, and then furnace-cooled to room temperature (about 15° to about 30° C). The pressed bodies are preferably sintered in a non-oxidizing atmosphere such as nitrogen or argon when it is desired to reduce the electrical resistivity. The electrical resistivity also can be reduced by air-quenching from the sintering temperature to room temperature even when the pressed bodies are fired in air.

The mixtures can be preliminary calcined at 600° to 1,000° C and pulverized for easy fabrication in the subsequent pressing step. The mixture to be pressed can be admixed with a suitable binder such as water, polyvinyl alcohol, etc.

It is advantageous that the sintered body have the opposite surfaces lapped by abrasive powder such as silicon carbide having a particle size of from 300 mesh to 1,500 mesh.

The sintered bodies are coated on one or both surfaces thereof with a silver electrode paint in a per se conventional manner such as by a spray method, screen printing method or brushing method. Solid ingredients having the compositions described in the foregoing description can be prepared in a per se conventional manner by mixing commercially available powders with organic resin such as epoxy, vinyl and phenol resin in an organic solvent such as butyl acetate, toluene or the like so as to produce silver electrode paints.

The silver powder can be in the form of metallic silver, or in the form of silver carbonate or silver oxide, or in any other form which on firing at the temperatures employed will be converted to metallic silver. Therefore, the term "silver" as used throughout this specification and the claims appended hereto in connection with the silver composition before it is

fired, is meant to include silver in any form which on firing will be converted to metallic silver. The viscosity of the resultant silver electrode paints can be controlled by the amounts of resin and solvent. The particle size of the solid ingredients is also required to be controlled so as to be in the range of 0.1 μ to 5 μ .

The sintered bodies with a silver electrode on only one surface thereof have an ohmic electrode applied to the other surface thereof in a conventional manner such as by a spraying of Al, Zn and Sn, a vacuum evaporation method of applying Al, In and Zn or an electrolytic or electroless method of applying Ni, Cu and Sn.

Lead wires can be applied to the silver electrodes in a per se conventional manner by using conventional solder having a low melting point. It is convenient to employ a conductive adhesive comprising silver powder and resin in an organic solvent for connecting the lead wires to the silver electrodes.

Voltage variable resistors according to this invention have a high stability with respect to temperature and in a load life test, which is carried out at 70° C at a rating power for 500 hours. The n -value and C -value do not change greatly after heating cycles and a load life test. It is preferable for achieving a high stability with respect to humidity that the resultant voltage variable resistors be embedded in a humidity proof resin such as epoxy resin or phenol resin in a per se well known manner.

According to the invention, it has been discovered that the method of curing the applied silver electrode paint has a great effect on the n -value of the resultant voltage variable resistors. The n -value will not be optimal when the applied silver electrode paint is heated in a non-oxidizing atmosphere such as nitrogen and hydrogen for curing. It is necessary for obtaining a high n -value that the applied silver electrode paint be cured by heating in an oxidizing atmosphere such as air or oxygen.

Silver electrodes prepared by any other method than by silver painting result in a poor n -value. For example, the sintered body does not act as a voltage variable resistor when it is provided with silver electrodes on the opposite surfaces by electroless plating or electrolytic plating in conventional manner. Silver electrodes applied by vacuum evaporation or chemical deposition result in an n -value less than 3.

The following examples are given as illustrative of the presently-preferred method of proceeding according to the present invention. However, it is not intended that the scope of said invention be limited to the specific examples.

EXAMPLE 1

Starting material according to Table 1 is mixed in a wet mill for 5 hours.

The mixture is dried and pressed in a mold into a disc 13 mm in diameter and 2.5 mm thick at a pressure of 340 Kg/cm^2 .

The pressed body is sintered in air at 1,350° C for 1 hour, and then quenched to room temperature (about 15° to about 30° C). The opposite surfaces of the sintered disc are lapped with silicon carbide having a particle size of 600 mesh. The thus produced sintered disc has a size of 10 mm diameter and 1.5 mm thickness. The sintered disc is coated on the opposite surfaces thereof with a silver electrode paint by a conventional brushing method. The silver electrode paint employed has a solid ingredient composition according to Table 2 and is prepared by mixing with vinyl resin in amyl acetate. The coated disc is fired at the temperatures listed in Table 2 for 30 minutes in air.

Lead wires are attached to the silver electrodes by means of silver paint. The electrical characteristics of the resultant resistor and of other similarly prepared resistors are shown in Table 1.

It will be readily understood that the resultant resistors have a low C -value and high n -value.

TABLE 1

ZnO (mol. percent)	Bi ₂ O ₃ (mol. percent)	Further addi- tive (mol. percent)	Silver paint A		Silver paint B	
			C (at 100 ma.)	n	C (at 100 ma.)	n
99.90	0.05	Nb ₂ O ₅ (0.05)	4.0	6.0	6.1	8.0
89.95	0.05	Nb ₂ O ₅ (10)	3.9	5.8	5.9	8.1
91.95	8	Nb ₂ O ₅ (0.05)	4.2	5.7	6.0	7.9
82.0	8	Nb ₂ O ₅ (10)	4.1	6.0	5.8	8.0
99.8	0.1	Nb ₂ O ₅ (0.1)	3.4	7.1	5.0	12
96.9	0.1	Nb ₂ O ₅ (3)	3.2	7.3	4.8	13
96.9	3	Nb ₂ O ₅ (0.1)	3.3	7.5	5.1	10
94.0	3	Nb ₂ O ₅ (3)	3.1	7.4	4.9	12
99.0	0.5	Nb ₂ O ₅ (0.05)	2.8	10	4.0	18
99.90	0.05	ZrO ₂ (0.05)	4.2	4.8	5.9	6.0
89.95	0.05	ZrO ₂ (10)	4.1	4.7	5.7	6.6
91.95	8	ZrO ₂ (0.05)	4.6	4.9	6.0	6.4
82.0	8	ZrO ₂ (10)	4.5	4.9	4.6	6.5
99.8	0.1	ZrO ₂ (0.1)	3.5	7.1	4.8	11
96.9	0.1	ZrO ₂ (3)	3.5	6.9	4.6	11
96.9	3	ZrO ₂ (0.1)	3.6	7.7	4.7	10
94.0	3	ZrO ₂ (3)	3.4	7.0	4.6	10
99.0	0.5	ZrO ₂ (0.5)	3.0	9.0	4.8	17
99.90	0.05	V ₂ O ₅ (0.05)	3.9	6.0	5.9	9.0
89.95	0.05	V ₂ O ₅ (10)	4.0	5.9	5.8	9.0
91.95	8	V ₂ O ₅ (0.05)	4.1	5.8	6.2	9.2
82.0	8	V ₂ O ₅ (10)	4.0	5.9	6.0	8.9
99.8	0.1	V ₂ O ₅ (0.1)	3.2	7.3	5.3	10
96.9	0.1	V ₂ O ₅ (3)	3.3	7.1	5.1	11
96.9	3	V ₂ O ₅ (0.1)	3.2	7.2	5.3	12
94.0	3	V ₂ O ₅ (3)	3.3	7.2	5.1	12
99.0	0.5	V ₂ O ₅ (0.5)	2.8	9.5	4.1	16
99.90	0.05	WO ₃ (0.05)	6.0	6.8	8.0	8.5
89.95	0.05	WO ₃ (10)	5.9	6.7	8.1	8.6
91.95	8	WO ₃ (0.05)	5.7	6.5	7.9	8.1
82.0	8	WO ₃ (10)	5.9	6.4	7.9	8.4
99.8	0.1	WO ₃ (0.1)	3.9	7.9	5.8	11
96.9	0.1	WO ₃ (3)	4.0	8.0	5.9	11
96.9	3	WO ₃ (0.1)	4.1	8.1	6.0	11
94.0	3	WO ₃ (3)	4.0	8.0	6.1	12
99.0	0.5	WO ₃ (0.5)	3.5	11	5.0	18
99.3	0.5	{Nb ₂ O ₅ (0.1) ZrO ₂ (0.1)}	2.6	12	3.9	20
99.3	0.5	{Nb ₂ O ₅ (0.1) V ₂ O ₅ (0.1)}	2.7	12	3.8	20
99.3	0.5	{Nb ₂ O ₅ (0.1) WO ₃ (0.1)}	2.8	13	4.1	21
99.3	0.5	{ZrO ₂ (0.1) V ₂ O ₅ (0.1)}	2.8	12	4.0	20
99.3	0.5	{ZrO ₂ (0.1) WO ₃ (0.1)}	2.8	12	4.5	20
99.3	0.5	{V ₂ O ₅ (0.1) WO ₃ (0.1)}	2.8	13	3.8	20
99.2	0.5	{Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1)}	2.2	14	3.0	23
99.2	0.5	{Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) WO ₃ (0.1)}	2.3	13	3.2	22
99.2	0.5	{Nb ₂ O ₅ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)}	2.3	14	3.7	23
99.2	0.5	{ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)}	2.5	14	3.9	22
99.1	0.5	{Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)}	2.0	15	2.8	26

TABLE 2

Silver paint	Firing temp. (° C.)	Ag (wt. percent)	PbO (wt. percent)	Bi ₂ O ₃ (wt. percent)	SiO ₂ (wt. percent)	B ₂ O ₃ (wt. percent)
A	500	90	7		2	1
B	800	90		7	2	1

EXAMPLE 2

Starting material according to Table 3 is mixed in a wet mill for 5 hours. The mixture is dried, pressed, sintered and lapped in the same manner as Example 1. The lapped disc is coated on one surface thereof with the same silver electrode paints as those used in Example 1 by a conventional brushing method. The coated disc is fired at the temperature listed in Table 2 for 30 minutes in air. The fired disc is provided on another surface thereof with the ohmic electrode by means of a spraying of aluminum or an evaporating of aluminum.

Lead wires are attached to the silver electrodes by means of silver paint. The electrical characteristics of the resultant resistor and of other similarly prepared resistors are shown in Table 3 wherein electrical characteristics are measured with the polarity applying silver electrode to high voltage terminal.

It will be easily realized that the combination of the silver electrode and ohmic electrode produces a low C and a high n.

TABLE 3

ZnO (mol. percent)	Bi ₂ O ₃ (mol. percent)	Further additive (mol. percent)	Silver paint A		Silver paint B	
			C (at 100 ma.)	n	C (at 100 ma.)	n
99.90	0.05	Nb ₂ O ₅ (0.05)	0.62	9.0	0.85	10
89.95	0.05	Nb ₂ O ₅ (10)	0.61	9.1	0.83	11
91.95	8	Nb ₂ O ₅ (0.05)	0.63	9.0	0.82	10
82.0	8	Nb ₂ O ₅ (10)	0.64	8.9	0.83	10
99.8	0.1	Nb ₂ O ₅ (0.1)	0.59	11	0.79	15
96.9	0.1	Nb ₂ O ₅ (3)	0.60	10	0.78	14
96.9	3	Nb ₂ O ₅ (0.1)	0.60	11	0.79	14
94.0	3	Nb ₂ O ₅ (3)	0.59	11	0.77	15
99.0	0.5	Nb ₂ O ₅ (0.5)	0.57	13	0.72	21
99.90	0.05	ZrO ₂ (0.05)	0.67	8.5	0.90	9.0
89.95	0.05	ZrO ₂ (10)	0.68	8.7	0.89	9.0
91.95	8	ZrO ₂ (0.05)	0.67	9.0	0.88	8.8
82.0	8	ZrO ₂ (10)	0.70	8.6	0.90	8.9
99.8	0.1	ZrO ₂ (0.1)	0.65	9.3	0.82	11
96.9	0.1	ZrO ₂ (3)	0.63	9.4	0.83	11
96.9	3	ZrO ₂ (0.1)	0.64	9.8	0.84	12
94.0	3	ZrO ₂ (3)	0.63	9.9	0.85	14
99.0	0.5	ZrO ₂ (0.5)	0.60	12	0.78	19
99.90	0.05	V ₂ O ₅ (0.05)	0.73	8.1	0.95	10
89.95	0.05	V ₂ O ₅ (10)	0.73	8.5	0.92	10
91.95	8	V ₂ O ₅ (0.05)	0.71	8.0	0.91	11
82.0	8	V ₂ O ₅ (10)	0.72	8.7	0.93	10
99.8	0.1	V ₂ O ₅ (0.1)	0.69	10	0.88	14
96.9	0.1	V ₂ O ₅ (3)	0.68	11	0.87	14
96.9	3	V ₂ O ₅ (0.1)	0.68	10	0.87	15
94.0	3	V ₂ O ₅ (3)	0.69	10	0.88	14
99.0	0.5	V ₂ O ₅ (0.5)	0.65	12	0.81	20
99.90	0.05	WO ₃ (0.05)	0.90	8.5	1.03	11
89.95	0.05	WO ₃ (10)	0.89	8.7	1.00	11
91.95	8	WO ₃ (0.05)	0.88	8.5	0.97	10
82.0	8	WO ₃ (10)	0.90	8.5	0.99	10
99.8	0.1	WO ₃ (0.1)	0.85	10	0.95	14
96.9	0.1	WO ₃ (3)	0.83	10	0.96	15
96.9	3	WO ₃ (0.1)	0.82	11	0.97	16
94.0	3	WO ₃ (3)	0.81	10	0.95	15
99.0	0.5	WO ₃ (0.5)	0.75	12	0.92	21
99.3	0.5	{Nb ₂ O ₅ (0.1) ZrO ₂ (0.1)}	0.63	16	0.72	23
99.3	0.5	{Nb ₂ O ₅ (0.1) V ₂ O ₅ (0.1)}	0.60	16	0.75	22
99.3	0.5	{Nb ₂ O ₅ (0.1) WO ₃ (0.1)}	0.61	17	0.85	23
99.3	0.5	{ZrO ₂ (0.1) V ₂ O ₅ (0.1)}	0.63	16	0.74	22
99.3	0.5	{ZrO ₂ (0.1) WO ₃ (0.1)}	0.65	17	0.87	23
99.3	0.5	{V ₂ O ₅ (0.1) WO ₃ (0.1)}	0.65	18	0.88	23
99.2	0.5	{Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1)}	0.57	19	0.73	26
99.2	0.5	{Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) WO ₃ (0.1)}	0.60	19	0.83	24
99.2	0.5	{Nb ₂ O ₅ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)}	0.61	20	0.85	25
99.2	0.5	{ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)}	0.61	21	0.87	26
99.1	0.5	{Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)}	0.62	24	0.78	30

EXAMPLE 3

A sintered disc having a composition listed in Table 4 is prepared in the same manner as in Example 1. The sintered disc is 10 mm in diameter and 1.5 mm thick after lapping. Various silver electrode paints are applied to the opposite surfaces of the sintered disc and fired at the temperatures listed in Table 4 for 30 minutes in air. The silver electrode paints have solid ingredient compositions as shown in Table 4 and are prepared by mixing 100 weight parts of said solid ingredient compositions with 1 to 20 weight parts of epoxy resin in 20 to 40 weight parts of butyl alcohol. The resultant resistors have desirable C-values and n-values as indicated in Table 4. It will be readily understood that the electrode compositions have a great effect on the electrical characteristics of the resultant voltage variable resistors and particularly electrode compositions containing cobalt oxide and manganese oxide result in a higher value of n.

TABLE 4

Sintered body			Silver paint								Electric characteristics	
ZnO (mol. percent)	Bi ₂ O ₃ (mol. percent)	Further additive (mol. percent)	Firing temp. (° C.)	Ag (wt. percent)	PbO (wt. percent)	Bi ₂ O ₃ (wt. percent)	SiO ₂ (wt. percent)	B ₂ O ₃ (wt. percent)	CoO (wt. percent)	MnO (wt. percent)	C (at 100 ma.)	n
99.1.....	0.5	Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)	500	90	6		2	2			2.2	16
99.1.....	0.5	Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)	800	90		6	2	2			3.0	28
99.1.....	0.5	Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)	750	80		12	4	4			3.5	25
99.1.....	0.5	Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)	650	70		18	6	6			3.9	21
99.1.....	0.5	Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)	550	90	4		4	2			2.5	14
99.1.....	0.5	Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)	800	90		6	2	1	1		2.7	28
99.1.....	0.5	Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)	800	90		6	2	1		1	3.0	28
99.1.....	0.5	Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)	800	90		6	2	1	0.5	0.5	2.6	30

EXAMPLE 4

A sintered disc having a composition listed in Table 5 is used to make resistors in the same manner as Example 1.

The resistors are tested according to the methods used in testing electronic component parts. The load life test is carried out at 70° C ambient temperature at 1 watt rating power for 500 hours. The heating cycle test is carried out by repeating 5

times a cycle in which said resistors are kept at 85° C ambient temperature for 30 minutes, cooled rapidly to -20° C and then kept at such temperature for 30 minutes. After heating cycles and the load life test, the percentage change of the C-value and n-value are shown in Table 5. It will be easily realized that the change rates are less than 10 percent and especially the compositions of the silver electrodes containing cobalt oxide and manganese oxide result in excellent stability properties.

TABLE 5

Sintered body			Silver paint								Load life test		Heating cycle test	
ZnO (mol. percent)	Bi ₂ O ₃ (mol. percent)	Further additives (mol. percent)	Firing temp. (° C.)	Ag (wt. percent)	PbO (wt. percent)	Bi ₂ O ₃ (wt. percent)	SiO ₂ (wt. percent)	B ₂ O ₃ (wt. percent)	CoO (wt. percent)	MnO (wt. percent)	ΔC (per- cent)	Δn (per- cent)	ΔC (per- cent)	Δn (per- cent)
99.0.....	0.5	Nb ₂ O ₅ (0.5)	500	90	6		2	2			-6.3	-7.1	-5.9	-4.3
99.0.....	0.5	ZrO ₂ (0.5)	500	90	6		2	2			-6.8	-6.2	-6.0	-4.8
99.0.....	0.5	V ₂ O ₅ (0.5)	500	90	6		2	2			-7.2	-6.0	-4.2	-5.0
99.0.....	0.5	WO ₃ (0.5)	500	90	6		2	2			-8.0	-6.8	-4.8	-4.8
99.1.....	0.5	Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)	500	90	6		2	2			-2.2	-1.8	-2.5	-1.5
99.1.....	0.5	Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)	800	90		6	2	2			-2.3	-2.0	-3.0	-1.9
99.1.....	0.5	Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)	800	90		6	2	1	1		-1.0	-1.1	-1.5	-0.0
99.1.....	0.5	Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)	800	90		6	2	1		1	-0.9	-0.9	-1.2	-0.9
99.1.....	0.5	Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)	800	90		6	1	1	1	1	-0.5	-0.9	-0.8	-0.7
99.1.....	0.5	Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)	750	80		12	4	4			-7.8	-8.0	-7.9	-6.8
99.1.....	0.5	Nb ₂ O ₅ (0.1) ZrO ₂ (0.1) V ₂ O ₅ (0.1) WO ₃ (0.1)	650	70		18	6	6			-9.0	-9.1	-7.4	-8.6

What is claimed is:

1. A voltage variable resistor comprising a sintered wafer consisting essentially of 0.05 to 8.0 mole percent of bismuth oxide (Bi_2O_3), 0.05 to 10.0 mole percent of at least one member selected from the group consisting of niobium oxide (Nb_2O_5), zirconium oxide (ZrO_2), vanadium oxide (V_2O_5) and tungsten oxide (WO_3) and the remainder zinc oxide (ZnO), and two electrodes applied to opposite surfaces of said sintered wafer, at least one of said two electrodes consisting of a silver paint electrode.
2. A voltage variable resistor according to claim 1, wherein one of said electrodes is a silver paint electrode and the other is an ohmic electrode.
3. A voltage variable resistor according to claim 1, wherein said sintered wafer consists essentially of 0.1 to 3.0 mole percent of bismuth oxide (Bi_2O_3) and 0.1 to 3.0 mole percent of at least one member selected from the group consisting of niobium oxide (Nb_2O_5), zirconium oxide (ZrO_2), vanadium oxide (V_2O_5) and tungsten oxide (WO_3), and the remainder zinc oxide (ZnO).
4. A voltage variable resistor according to claim 1 wherein said silver electrode has a composition consisting essentially of 70 to 99.5 wt. percent of silver, 0.3 to 27 wt. percent of lead oxide (PbO), 0.1 to 15 wt. percent of silicon dioxide (SiO_2) and 0.05 to 15 wt. percent of boron trioxide (B_2O_3).

5. A voltage variable resistor according to claim 1 wherein said silver electrode has a composition consisting essentially of 70 to 99.5 wt. percent of silver, 0.3 to 27 wt. percent of bismuth oxide (Bi_2O_3), 0.03 to 15 wt. percent of silicon dioxide (SiO_2), and 0.05 to 15 wt. percent of boron trioxide (B_2O_3).
6. A voltage variable resistor according to claim 1 wherein said silver electrode has a composition consisting essentially of 70 to 99.5 wt. percent of silver, 0.3 to 27 wt. percent of lead oxide (PbO), 0.1 to 15 wt. percent of silicon dioxide (SiO_2), 0.05 to 15 wt. percent of boron trioxide (B_2O_3) and 0.05 to 6.0 wt. percent of at least one member selected from the group consisting of cobalt oxide (CoO) and manganese oxide (MnO).
7. A voltage variable resistor according to claim 1 wherein said silver electrode has a composition consisting essentially of 70 to 99.5 wt. percent of silver, 0.3 to 27 wt. percent of bismuth oxide (Bi_2O_3), 0.03 to 15 wt. percent of silicon dioxide (SiO_2), 0.05 to 15 wt. percent of boron trioxide (B_2O_3) and 0.05 to 6.0 wt. percent of at least one member selected from the group consisting of cobalt oxide (CoO) and manganese oxide (MnO).

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