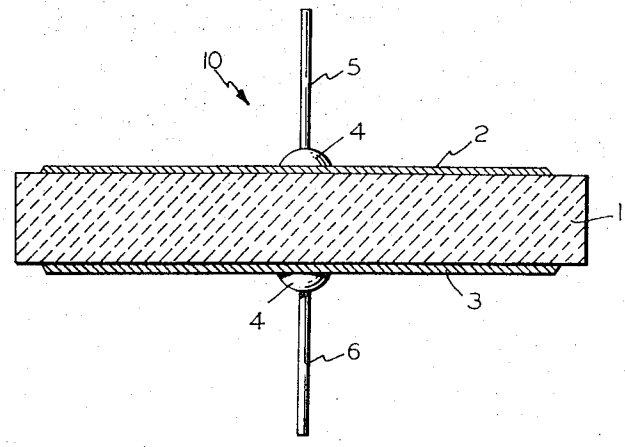
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NONLINEAR RESISTOR AND NONLINEAR RESISTOR COMPOSITION

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NONLINEAR RESISTOR AND NONLINEAR RESISTOR COMPOSITION

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ABSTRACT OF THE DISCLOSURE

A resistor composition having a nonlinear voltage characteristic consisting essentially of zinc oxide and, as an additive bismuth fluoride, and a nonlinear resistor made from said composition. The resistor composition and the resistor have the electrical properties thereof further improved by the addition of at least one member selected from the group consisting of cobalt fluoride, manganese fluoride, stannous fluoride, nickel fluoride, chromium fluoride, bismuth oxide, cobalt oxide, and manganese oxide.

This invention relates to resistor composition and resistors having a nonlinear voltage characteristic, i.e. nonohmic resistance, due to the bulk thereof and more particularly to varistors comprising zinc oxide and bismuth fluoride.

Various nonlinear 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 nonlinear resistor are expressed by the relation:

$$I=\left(\frac{V}{C}\right)^{n} \tag{1}$$

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:

$$n=\frac{\log_{10}(I_2/I_1)}{\log_{10}(V_2/V_1)} \tag{2}$$

where V_1 and V_2 are the voltages at 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 extent to which the resistors depart from ohmic characteristics.

It is difficult in varistors comprising germanium or silicon p-n junction diodes to control the C-value over a wide range because the nonlinearity of these varistors is not attributable to the bulk but to the p-n junction. On the other hand, silicon carbide varistors have nonlinear characteristics due to the contacts among the individual grains of silicon carbide bonded together by a ceramic binding material, i.e. to the bulk, and the C-value is controlled by changing the dimension in the direction in which the current flows through the varistors. Silicon carbide varistors, however, have a relatively low n-value and are prepared by firing in a non-oxidizing atmosphere, especially for the purpose of obtaining a lower C-value.

An object of the present invention is to provide a resistor having a nonlinear voltage characteristic due to the bulk thereof and characterized by a high n-value.

Another object of the invention is to provide a resistor composition from which such resistors can be made.

The details 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 resistor having a nonlinear voltage characteristic in accordance with the invention.

Before proceeding with a detailed description of the resistors and the resistor compositions contemplated by the invention, the resistor construction will be described with reference to the aforesaid figure of drawing wherein reference character **10** designates, as a whole, a nonlinear resistor comprising, as its active element, a sintered body having a pair of electrodes **2** and **3** applied to opposite surfaces thereof. Said sintered body **1** is prepared in a manner hereinafter set forth and can be in any form such as circular, square or rectangular plate form. Wire leads **5** and **6** are attached conductively to the electrodes **2** and **3**, respectively, by a connection means **4** such as solder or the like.

A nonlinear resistor according to the invention comprises a sintered body of a batch composition consisting essentially of, as a major part, 99.95 to 9.0 mole percent of zinc oxide and, as an additive, 0.05 to 10.0 mole percent of bismuth fluoride. Such a nonlinear resistor 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 the opposite surfaces of a body thereof. A shorter distance results in a lower C-value.

A higher n-value can be obtained when said additive consists essentially of 0.3 to 2.5 mole percent of bismuth fluoride in accordance with the invention.

According to the present invention, the n-value can be further elevated when said additive further includes 0.05 to 10.0 mole percent of at least one member selected from the group consisting of cobalt fluoride, manganese fluoride, stannous fluoride, nickel fluoride and chromium fluoride. Superior results are obtained with an additive consisting essentially of 0.3 to 2.5 mole percent of bismuth fluoride and 0.1 to 3.0 mole percent of at least one member selected from the group consisting of cobalt fluoride, manganese fluoride, stannous fluoride, nickel fluoride, and chromium fluoride.

According to the present invention, the resistor has an extremely high n-value when said additive consists essentially of 0.3 to 2.5 mole percent of bismuth fluoride and 0.05 to 5.0 mole percent at least one member selected from the group consisting of cobalt oxide and manganese oxide.

Further, an extremely high n-value can be obtained when said additive consists essentialy of 0.3 to 2.5 mole percent of bismuth fluoride, 0.05 to 5.0 mole percent of cobalt oxide and 0.05 to 5.0 mole percent of at least one member selected from the group consisting of manganese fluoride and chromium fluoride.

The n-value is greatly elevated when said additive consists essentially of 0.3 to 2.5 mole percent of bismuth fluoide, 0.05 to 5.0 mole percent of manganese oxide and 0.05 to 5.0 mole percent of ot least one member selected from the group consisting of cobalt fluoride and chromium fluoride.

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 1000 kg./cm.^{2}. The pressed bodies are sintered in air at a temperature of 1000° to 1400° C. for 1 to 3 hours, and then furnace-cooled to room temperature (about 15° to about 30° C.).

The mixtures can be preliminarily calcined at about 700° 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 opposite surfaces of the sintered body be lapped by abrasive powder such as silicon carbide having a particle size of 300 mesh to 1500 mesh.

The sintered bodies are provided, on the opposite surfaces thereof, with electrodes by any available and suitable method.

Lead wires can be attached to the 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 in order to connect the lead wires to the electrodes.

Nonlinear 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 very much after heating cycles and a load life test. It is advantageous for achievement of a high stability with respect to humidity that the resultant nonlinear resistors be embedded in a humidity proof resin such as epoxy resin or phenol resin in a per se well known manner.

Presently preferred illustrative embodiments of the invention are as follows:

EXAMPLE 1

Starting materials listed in Table 1 are mixed in a wet mill for 5 hours.

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

The pressed body is sintered in air for 1 hour at a temperature of 1000° to 1400° C., and then furnace-cooled to room temperature (about 15° to about 30° C.). The sintered disc has the opposite surfaces lapped by silicon carbide abrasive having a particle size of 600 mesh until it is to the thickness listed in Table 1. The opposite surfaces of the sintered disc are provided with a spray metallized film of aluminum by a per se well known technique. Lead wires are attached to the aluminum electrodes by means of conductive silver paint. The electrical 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.

TABLE 1

Composition (mole percent)		Sintering temp. (° C.)	Thickness (mm.)	Electrical characteristics	
ZnO	BiF_3			C (at 1 ma.)	*n*
99.95	0.05	1,200	1.0	42	3.6
99.7	0.3	1,200	1.0	30	4.4
99.5	0.5	1,200	1.0	20	5.0
99.0	1	1,200	1.0	41	4.8
97.5	2.5	1,200	1.0	59	4.6
95.0	5	1,200	1.0	70	3.7
90.0	10	1,200	1.0	85	3.5
99.5	0.5	1,000	1.0	72	8.0
99.5	0.5	1,100	1.0	43	6.1
99.5	0.5	1,200	1.0	20	5.0
99.5	0.5	1,300	1.0	12	4.4
99.5	0.5	1,400	1.0	8	3.9
99.5	0.5	1,200	2.0	40	5.1
99.5	0.5	1,200	1.5	31	5.0
99.5	0.5	1,200	1.0	20	5.0
99.5	0.5	1,200	0.5	11	4.9

EXAMPLE 2

Starting materials according to Table 2 are mixed and pressed in the same manner as described in Example 1.

The pressed body is sintered in air at 1200° C. for 1 hour and then furnace-cooled to room temperature (about 15° to about 30° C.). The sintered disc has the opposite surfaces lapped by silicon carbide abrasive having a particle size of 600 mesh. The resulting sintered disc has a size of 10 mm. diameter and 1.5 mm. thickness. The opposite surfaces of the sintered disc are provided with a spray metallized film of aluminum by a per se well known technique. Lead wires are attached to the aluminum electrodes by means of conductive silver paint. The electrical characteristics of the resultant resistors are shown in Table 2. It will be readily understood that the *n*-value can be raised by the addition of at least one member selected from the group consisting of cobalt fluoride, manganese fluoride, stannous fluoride, nickel fluoride and chromium fluoride. For example, the addition of 0.3 mole percent of bismuth fluoride, 0.1 mole percent of cobalt fluoride and 0.1 mole percent of manganese fluoride results in a 60 volt C-value at 1 ma. and an *n*-value of 14.

TABLE 2

Composition (mole percent)				Electrical characteristics	
ZnO	BiF_3	Additive		C (at 1 ma.)	*n*
99.90	0.05	CoF_2	0.05	85	8.0
89.95	0.05	CoF_2	10	80	7.9
89.95	10	CoF_2	0.05	75	7.8
80.0	10	CoF_2	10	77	7.9
99.6	0.3	CoF_2	0.1	55	13
97.7	0.3	CoF_2	3.0	50	14
97.4	2.5	CoF_2	0.1	49	15
94.5	2.5	CoF_2	3.0	53	15
99.0	0.5	CoF_2	0.5	40	20
99.90	0.05	MnF_2	0.05	110	8.5
89.95	0.05	MnF_2	10	100	8.0
89.95	10	MnF_2	0.05	98	8.7
80.0	10	MnF_2	10	95	9.0
99.6	0.3	MnF_2	0.1	70	14
96.7	0.3	MnF_2	3.0	72	15
97.4	2.5	MnF_2	0.1	71	19
94.5	2.5	MnF_2	3.0	69	18
99.0	0.5	MnF_2	0.5	55	25
99.90	0.05	SnF_2	0.05	90	7.2
89.95	10.05	SnF_2	10	88	6.9
89.95	10	SnF_2	0.05	90	7.9
80.0	10	SnF_2	10	84	8.0
99.6	0.3	SnF_2	0.1	60	12
96.7	0.3	SnF_2	3.0	63	11
97.4	2.5	SnF_2	0.1	62	14
94.5	2.5	SnF_2	3.0	60	14
99.0	0.5	SnF_2	0.5	50	18
99.90	0.05	NiF_2	0.05	80	6.9
89.95	0.05	NiF_2	10	78	7.0
89.95	10	NiF_2	0.05	77	7.8
80.0	10	NiF_2	10	82	8.3
96.4	0.3	NiF_2	0.1	57	12
97.7	0.3	NiF_2	3.0	63	11
97.4	2.5	NiF_2	0.1	59	12
94.5	2.5	NiF_2	3.0	60	13
99.0	0.5	NiF_2	0.5	45	17
99.90	0.05	CrF_3	0.05	130	7.0
89.95	0.05	CrF_3	10	125	7.5
89.95	10	CrF_3	0.05	128	6.4
80.0	10	CrF_3	10	120	8.4
96.4	0.3	CrF_3	0.1	85	11
96.7	0.3	CrF_3	3.0	73	12
97.4	2.5	CrF_3	0.1	75	14
94.5	2.5	CrF_3	3.0	73	14
99.0	0.5	CrF_3	0.5	60	18

EXAMPLE 3

Starting materials according to Table 3 are pressed, fired, lapped and electrodes attached in the same manner as described in Example 2. The electrical characteristics of the resultant resistors are shown in Table 3. It can be easily understood that when the zinc oxide sintered body including bismuth fluoride further includes cobalt oxide or manganese oxide, and other fluorides such as listed in Table 3, the resultant sintered body has excellent nonlinear properties. Similar results can be obtained from the addition of bismuth fluoride, cobalt oxide and manganese oxide. For example, the addition of 0.5 mole percent of bismuth fluoride, 0.5 mole percent of cobalt oxide and 0.5 mole percent of manganese oxide results in an 80 volt C-value at 1 ma. and an *n*-value of 25.

TABLE 3

Composition (mole percent)					Electrical characteristics	
ZnO	BiF_3	Additives			C (at 1 ma.)	n
99.65	0.3	CoO	0.05		95	16
99.0	0.5	CoO	0.5		60	23
92.5	2.5	CoO	5.0		88	17
99.65	0.3	MnO	0.05		263	19
99.0	0.5	MnO	0.5		125	26
92.5	2.5	MnO	5.0		240	18
99.6	0.3	CoO	0.05	MnF_2	0.05	112	20
98.5	0.5	CoO	0.5	MnF_2	0.5	75	35
87.5	2.5	CoO	5.0	MnF_2	5.0	105	21
99.6	0.3	CoO	0.05	CrF_3	0.05	243	22
98.5	0.5	CoO	0.5	CrF_3	0.5	120	30
87.5	2.5	CoO	5.0	CrF_3	5.0	220	18
99.6	0.3	MnO	0.05	CoF_2	0.05	183	22
98.5	0.5	MnO	0.5	CoF_2	0.5	62	34
87.5	2.5	MnO	5.0	CoF_2	5.0	200	21
89.6	0.3	MnO	0.05	CrF_3	0.05	304	18
98.5	0.5	MnO	0.5	CrF_3	0.5	140	31
97.5	2.5	MnO	5.0	CrF_3	5.0	295	19

EXAMPLE 4

The resistors of Examples 1, 2 and 3, were tested in accordance with a method widely used in testing electronic components parts. The load life test was carried out at 70° C. ambient temperature at 1 watt rating power for 500 hours. The heating cycle test was carried out by repeating 5 times a cycle in which said resistors were kept at 85° C. ambient temperature for 30 minutes, cooled rapidly to −20° and then kept at such temperature for 30 minutes. Table 4 shows the average change rates of the C-value and the *n*-value of the resistors after the heating cycles and the load life test.

TABLE 4

Composition (mole percent)					Change rate after life test (percent)		Change rate after heating cycle test (percent)	
ZnO	BiF_3	Additives			Δc	Δn	Δc	Δn
99.5	0.5				−7.4	−6.9	+3.8	−7.9
99.0	0.5	CoF_2	0.5		−4.3	−4.0	−3.0	−6.9
99.0	0.5	MnF_2	0.5		−3.9	−3.9	−3.6	−5.8
99.0	0.5	SnF_2	0.5		−3.0	−2.2	+2.5	−4.0
99.0	0.5	NiF_2	0.5		−2.6	−3.5	+2.4	−3.3
99.0	0.5	CrF_3	0.5		−2.8	−3.5	−4.1	−3.9
99.0	0.5	CoO	0.5		−3.3	−4.0	+1.2	−4.4
99.0	0.5	MnO	0.5		−2.9	−2.8	−1.3	−3.3
98.5	0.5	CoO	0.5	MnF_2	0.5	+2.0	−2.2	−3.4	−2.0
98.5	0.5	CoO	0.5	CrF_2	0.5	−1.2	−1.2	+1.0	−1.5
98.5	0.5	MnO	0.5	CrF_2	0.5	−1.0	−1.2	+1.0	−1.5
98.5	0.5	MnO	0.5	CrF_2	0.5	−0.5	−1.0	−1.2	−0.9

What is claimed is:

1. A resistor having a nonlinear voltage characteristic comprising a sintered body having a composition consisting essentially of, as a major part, 99.95 to 90.0 mole percent of zinc oxide and, as an additive, 0.05 to 10.0 mole percent of bismuth fluoride which body has been sintered in air at 1000–1400° C. for from 1–3 hours.

2. A resistor as claimed in claim **1**, wherein said additive further consists essentially of 0.05 to 10.0 mole percent of at least one member selected from the group consisting of cobalt fluoride, manganese fluoride, stannous fluoride, nickel fluoride and chromium fluoride.

3. A resistor as claimed in claim **1**, wherein said additive consists essentially of 0.3 to 2.5 mole percent of bismuth fluoride.

4. A resistor as claimed in claim **3**, wherein said additive further consists essentially of 0.1 to 3.0 mole percent of at least one member selected from the group consisting of cobalt fluoride, manganese fluoride, stannous fluoride, nickel fluoride and chromium fluoride.

5. A resistor as claimed in claim **1**, wherein said additive consists essentially of 0.3 to 2.5 mole percent of bismuth fluoride and 0.05 to 5.0 mole percent of one member selected from the group consisting of cobalt oxide and manganese oxide.

6. A resistor as claimed in claim **1**, wherein said additive consists essentially of 0.3 to 2.5 mole percent of bismuth fluoride, 0.05 to 5.0 mole percent of cobalt oxide and 0.05 to 5.0 mole percent of at least one member selected from the group consisting of manganese fluoride and chromium fluoride.

7. A resistor as claimed in claim **1**, wherein said additive consists essentially of 0.3 to 2.5 mole percent of bismuth fluoride, 0.05 to 5.0 mole percent of manganese oxide and 0.05 to 5.0 mole percent of at least one member selected from the group consisting of cobalt fluoride and chromium fluoride.

8. A resistor composition having a nonlinear voltage characteristics, said composition consisting essentially of, as a major part, 99.95 to 90.0 mole percent of zinc oxide, and, as an additive, 0.05 to 10.0 mole percent of bismuth fluoride, and said additive further consisting essentially of 0.05 to 10.0 mole percent of at least one member selected from the group consisting of cobalt fluoride, manganese fluoride, stannous fluoride, nickel fluoride and chromium fluoride.

9. A resistor composition having a nonlinear voltage characteristic, said composition consisting essentially of, as a major part, 99.95 to 90.0 mole percent of zinc oxide and, as an additive, 0.3 to 2.5 mole percent of bismuth fluoride, and said additive further consisting essentially of 0.1 to 3.0 mole percent of at least one member selected from the group consisting of cobalt fluoride, manganese fluoride, stannous fluoride, nickel fluoride and chromium fluoride.

10. A resistor composition having a nonlinear voltage characteristic, said comopsition consisting essentially of, as a major part, 99.95 to 90.0 mole percent of zinc oxide, and, as an additive 0.3 to 2.5 mole percent of bismuth fluoride, and said additive further consists essentially of 0.05 to 5.0 mole percent of one member selected from the group consisting of cobalt oxide and manganese oxide.

11. A resistor composition having a nonlinear voltage characteristic, said composition consisting essentially of, as a major part, 99.95 to 90.0 mole percent of zinc oxide, and, as an additive, 0.3 to 2.5 mole percent of bismuth fluoride, and said additive further consists essentially of

0.05 to 5.0 mole percent of cobalt oxide and 0.05 to 5.0 mole percent of at least one member selected from the group consisting of manganese fluoride and chromium fluoride.

12. A resistor composition having a nonlinear voltage characteristic, said composition consisting essentially of, as a major part, 99.95 to 90.0 mole percent of zinc oxide and, as an additive, 0.3 to 2.5 mole percent of bismuth fluoride, and said additive further consists essentially of 0.05 to 5.0 mole percent of manganese oxide and 0.05 to 5.0 mole percent of at least one member selected from the group consisting of cobalt fluoride and chromium fluoride.

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