

PATENT SPECIFICATION

(11) 1 358 482

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(21) Application No. 15087/72 (22) Filed 30 March 1972

(44) Complete Specification published 3 July 1974

(51) International Classification: C04B 35/00 // H01C 7/10

(52) Index at acceptance

GIJ 11 14 17 21 28 31 7

CIA N39B

HIK 213 236 272 274 276 283 284 294 297 300 304 312

314 323 333 334 424 441 455 483 502 52Y 53Y

578 604 60Y 627 628

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(54) VOLTAGE-DEPENDENT RESISTORS

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

This invention is concerned with voltage dependent resistors of the bulk type.

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

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

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 n is a number greater than 1. The value of n can be calculated from the following equation:

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

where V₁ and V₂ are the voltages at given currents I₁ and I₂, respectively. The given currents I₁ and I₂ are conveniently 0.1 mA and 1 mA, respectively. The desired value of C depends upon the kind of use to which the resistor is to be put. It is ordinarily desirable that the value of n be as large as possible since the size of n determines the extent to which the resistors depart from Ohm's law.

Voltage dependent resistors which comprise a sintered body of zinc oxide (with or without additives) and silver paint electrodes applied thereto, are known. The non-linearity of these

varistors is attributed to the interface between the sintered body and the silver paint electrode and is controlled mainly by changing the composition of the sintered body and/or silver paint electrode. Thus, it is not easy to control the C-value over a wide range after the sintered body has been prepared. Similarly, in varistors 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 varistors is attributed not to the bulk but to the p-n junction. On the other hand, silicon carbide varistors have non-linearity due to the contact between 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 a dimension in the direction in which the current flows through the varistors. The silicon carbide varistors, however, have a relatively low n value, usually from 3 to 6.

We have now devised a sintered body useful for a voltage dependent resistor of the bulk type, and from which body resistors can be made which are characterized by a high C-value, a high n value and high stability to temperature, humidity and electric load. Further, resistors can be made from the sintered bodies of the invention, which have a high resistance to surge current.

According to the invention, there is provided a sintered body consisting essentially of a major proportion of ZnO and a minor proportion of an additive which is from 0.05 to 20.0 mole percent SiO₂ and from 0.05 to 18.0 mole percent, in total, of one or more of the oxides Bi₂O₃, CoO, MnO, BaO, SrO, PbO, Sb₂O₃, Cr₂O₃, and NiO, each of the latter oxides not being present in an amount of more than 10.0 mole percent.

Unless otherwise stated, all the mole percentages given herein are based on the whole of the sintered body.

Preferably, Sb₂O₃, Cr₂O₃, or NiO or a mixture of two or more thereof are present only when Bi₂O₃ is present.

The invention also includes a voltage

dependent resistor which comprises a sintered body according to the invention and a pair of electrodes in contact with said body.

- 5 In one preferred sintered body of the invention, the additive is SiO_2 and one or more of Bi_2O_3 , CoO , MnO , BaO , SrO and PbO .

- 10 Generally, higher n values can be obtained when the additive consists essentially of 0.1 to 10 mole percent SiO_2 and one or more of the oxides Bi_2O_3 , CoO , MnO , BaO , SrO and PbO , the amount of each of the latter oxides present being from 0.1 to 3.0 mole percent.

- 15 Other preferred sintered bodies of the invention are as follows:

- 20 (a) those wherein the additive consists essentially of 0.1 to 10.0 mole percent SiO_2 , 0.1 to 3.0 mole percent Bi_2O_3 , and one or more of 0.1 to 3.0 mole percent Sb_2O_3 , 0.1 to 3.0 mole percent Cr_2O_3 and 0.1 to 3.0 mole percent NiO ;

- 25 (b) those wherein the additive consists essentially of 0.1 to 10.0 mole percent SiO_2 , 0.1 to 3.0 mole percent Bi_2O_3 , 0.1 to 3.0

mole percent CoO and one or more of 0.1 to 3.0 mole percent Sb_2O_3 , 0.1 to 3.0 mole percent Cr_2O_3 and 0.1 to 3.0 mole percent NiO ;

- 30 (c) those wherein the additive consists essentially of 0.1 to 10.0 mole percent SiO_2 , 0.1 to 3.0 mole percent Bi_2O_3 , 0.1 to 3.0 mole percent MnO and one or more of 0.1 to 3.0 mole percent Sb_2O_3 , 0.1 to 3.0 mole percent Cr_2O_3 , and 0.1 to 3.0 mole percent NiO ;

- 40 (d) those wherein the additive consists essentially of 0.1 to 10.0 mole percent SiO_2 , 0.1 to 3.0 mole percent Bi_2O_3 , 0.1 to 3.0 mole percent CoO , 0.1 to 3.0 mole percent MnO and one or more of 0.1 to 3.0 mole percent Sb_2O_3 , 0.1 to 3.0 mole percent Cr_2O_3 , and 0.1 to 3.0 mole percent NiO .

45 Table 1 hereinafter shows some optimum additive compositions for producing a voltage dependent resistor having a high n value, a high C value, a high stability to temperature, humidity and electric load and a high resistance to surge current.

TABLE 1

Optimum Composition of Additives (mole %)

SiO_2	Bi_2O_3	CoO	MnO	Sb_2O_3	Cr_2O_3	NiO
0.1~10	0.1~3.0	—	—	0.1~3.0	—	—
0.1~10	0.1~3.0	—	—	—	0.1~3.0	—
0.1~10	0.1~3.0	—	—	—	—	0.1~3.0
0.1~10	0.1~3.0	—	—	0.1~3.0	0.1~3.0	—
0.1~10	0.1~3.0	—	—	0.1~3.0	—	0.1~3.0
0.1~10	0.1~3.0	—	—	—	0.1~3.0	0.1~3.0
0.1~10	0.1~3.0	—	—	0.1~3.0	0.1~3.0	0.1~3.0
0.1~10	0.1~3.0	0.1~3.0	—	0.1~3.0	—	—
0.1~10	0.1~3.0	0.1~3.0	—	—	0.3~3.0	—
0.1~10	0.1~3.0	0.1~3.0	—	—	—	0.1~3.0
0.1~10	0.1~3.0	0.1~3.0	—	0.1~3.0	0.1~3.0	—
0.1~10	0.1~3.0	0.1~3.0	—	0.1~3.0	—	0.1~3.0
0.1~10	0.1~3.0	0.1~3.0	—	—	0.1~3.0	0.1~3.0
0.1~10	0.1~3.0	0.1~3.0	—	0.1~3.0	0.1~3.0	0.1~3.0

TABLE 1 (continued)

SiO ₂	Bi ₂ O ₃	CoO	MnO	Sb ₂ O ₃	Cr ₂ O ₃	NiO
0.1~10	0.1~3.0	—	0.1~3.0	0.1~3.0	—	—
0.1~10	0.1~3.0	—	0.1~3.0	—	0.1~3.0	—
0.1~10	0.1~3.0	—	0.1~3.0	—	—	0.1~3/0
0.1~10	0.1~3.0	—	0.1~3.0	0.1~3.0	0.1~3.0	—
0.1~10	0.1~3.0	—	0.1~3.0	0.1~3.0	—	0.1~3.0
0.1~10	0.1~3.0	—	0.1~3.0	—	0.1~3.0	0.1~3.0
0.1~10	0.1~3.0	—	0.1~3.0	0.1~3.0	0.1~3.0	0.1~3.0
0.1~10	0.1~3.0	0.1~3.0	0.1~3.0	0.1~3.0	—	—
0.1~10	0.1~3.0	0.1~3.0	0.1~3.0	—	0.1~3.0	—
0.1~10	0.1~3.0	0.1~3.0	0.1~3.0	—	—	0.1~3.0
0.1~10	0.1~3.0	0.1~3.0	0.1~3.0	0.1~3.0	0.1~3.0	—
0.1~10	0.1~3.0	0.1~3.0	0.1~3.0	0.1~3.0	—	0.1~3.0
0.1~10	0.1~3.0	0.1~3.0	0.1~3.0	—	0.1~3.0	0.1~3.0
0.1~10	0.1~3.0	0.1~3.0	0.1~3.0	0.1~3.0	0.1~3.0	0.1~3.0

One form of resistor of the invention is illustrated, merely by way of example, in the accompanying drawing which is a partly cross-sectional view thereof. Referring to the drawing, the voltage dependent resistor 10 comprises, as its active element, a sintered body 1 having a pair of electrodes 2 and 3 applied to opposite surfaces thereof. The sintered body 1 is prepared in a manner herein-after described and is in any shape such as circular, square or rectangular plate form. Wire leads 5 and 6 are attached to the electrodes 2 and 3, respectively, by a connection means 4, such as solder.

The sintered bodies of the invention can be prepared by well known sintering techniques. Thus, for example, the components are mixed in a wet mill to produce a homogeneous mixture. The mixtures are dried and pressed in a mould to the desired shape at a pressure from 100 kg/cm² to 1000 kg/cm². The pressed bodies are sintered in air at 1000°C to 1450°C for from 1 to 10 hours, and then furnace-cooled to room temperature (about 15° to about 30°C).

The mixture can be preliminarily calcined at 700° to 1000°C and pulverized for easy fabrication in the subsequent pressing step.

The mixture to be pressed can include a suitable binder such as water or polyvinyl alcohol.

It is advantageous that the sintered body be lapped at the opposite surfaces by abrasive powder such as silicon carbide generally with a particle size of from 10 to 53 microns.

The sintered bodies may be provided, at opposite surfaces thereof, with electrodes for example, of aluminium and/or copper by any available and suitable method, for example, by spray metallization.

Lead wires can be attached to the electrodes in a conventional manner, for example by using solder having a low melting point. It is often 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.

Voltage dependent resistors according to this invention have a high stability to temperature and in the load life test, which is carried out at 70°C at a power rating for 1000 hours. The n value and C value do not change much after heating cycles and the load life test. Similarly, voltage dependent resistors according to this invention show a high surge resistance. It is advantageous for

achievement of a high stability to humidity that the voltage dependent resistors be embedded in a humidity proof resin such as an epoxy resin or phenol resin. The n value is independent of the thickness of the sintered body, while the C value varies in proportion to the thickness of the sintered body. The variation in the C value with thickness of the sintered body indicates that the nonlinearity of the voltage dependent resistor is attributable to the bulk of the sintered body and not to

the barrier between the electrodes and the sintered body.

In order that the invention may be more fully understood, the following Examples are given by way of illustration only.

Example 1.

The materials listed in Table 2 are mixed in a wet mill for 5 hours. The mixture is dried and pressed in a mould into a disc of 13 mm in diameter and 2.5 mm in thickness at a pressure of 340 kg/cm².

TABLE 2

Composition of Sintered Body (mol. %)			Sintering Temp. (°C)	Thickness (mm)	Electrical Characteristics	
ZnO	SiO ₂	Further Additives			C (at 1mA)	n
94.5	5	Bi ₂ O ₃ 0.5	1200	2.0	170	6.2
				1.5	126	6.3
				1.0	85	6.1
94.5	5	CoO 0.5	1250	2.0	205	7.4
				1.5	153	7.4
				1.0	112	7.3
94.5	5	MnO 0.5	1250	2.0	224	8.0
				1.5	167	8.1
				1.0	111	8.1
94.5	5	BaO 0.5	1300	2.0	340	7.5
				1.5	253	7.4
				1.0	170	7.4
94.5	5	SrO 0.5	1250	2.0	300	5.4
				1.5	225	5.3
				1.0	151	5.4
94.5	5	PbO 0.5	1200	2.0	720	5.9
				1.5	540	5.9
				1.0	355	5.8

The pressed body is sintered in air for 1 hour at the temperature shown in Table 2, and then furnace-cooled to room temperature (about 15°C to about 30°C). The sintered disc is lapped to the thickness listed in Table 2 at the opposite surfaces thereof by silicon

carbide abrasive having a particle size of about 28 microns. The opposite surfaces of the sintered disc are provided with a spray metallized film of aluminium in the conventional manner. Lead wires are attached to the aluminium electrodes by means of conductive

silver paint. The electrical characteristics of the resultant resistor are shown in Table 2. It will be understood that the C value changes in proportion to the thickness of the sintered body.

Example 2.

The materials shown in Table 3 are mixed and pressed in the same manner as described in Example 1.

- 10 In each case, the pressed body is sintered in air at 1250°C for 1 hour and then furnace-cooled to room temperature (about 15° to about 30°C). The sintered disc is lapped at the opposite surfaces thereof using a silicon carbide abrasive having a particle size of about 28 microns. The resulting sintered disc is 10 mm in diameter and 1.5 mm thick. The opposite surfaces of the sintered disc are provided with a spray metallized film of aluminium. Lead wires are attached to the aluminium electrodes by means of conductive silver paint. The resultant resistors are tested in accordance with methods widely used in the electronic components field. The load life test is carried out at 70°C ambient temperature at 1.5 watt power rating for 1000 hours.

The heating cycle test is carried out by repeating 5 times a cycle in which the resistors are kept at 85°C ambient temperature for 30 minutes, cooled rapidly to -20°C and then kept at this temperature for 30 minutes. Further, the impulse test is carried out by applying 100 times $8 \times 20 \mu\text{s}$ impulses of 1500 A. peak (that is, impulses having a peak current of 1500 amperes). The electrical characteristics of the resultant resistor are shown in Table 3. It will be readily understood that the resistors have a high n value, a high C value at a given current of 1 mA and a high stability.

Example 3.

The materials shown in Table 4 are pressed, fired, lapped, attached to electrodes and then tested in the same manner as in Example 2. The electrical characteristics of the resultant resistors are shown in Table 4. It will be understood that the resistors with a composition given in Table 4 have a high n value, high C value and excellent stability, particularly for the impulse test.

TABLE 3

Composition of Sintered Body (mol. %)				Electric Characteristics	Change Rate (%)						
					Load Life Test		Heating Cycle Test		Impulse Test		
					ΔC	Δn	ΔC	Δn	ΔC	Δn	
ZnO	SiO ₂	Further Additives	C (at 1 mA)	n							
99.90	0.50	Bi ₂ O ₃ 0.05	85	4.4	-9.3	-9.3	-8.8	-9.2	-4.9	-4.9	
88.95	0.05	Bi ₂ O ₃ 10	100	4.2	-9.7	-9.4	-9.1	-9.4	-4.7	-4.8	
79.95	20	Bi ₂ O ₃ 0.05	200	4.1	-9.6	-8.8	-9.4	-9.6	-4.6	-4.8	
70.0	20	Bi ₂ O ₃ 10	350	4.3	-9.9	-9.0	-9.1	-8.9	-4.9	-4.7	
99.8	0.1	Bi ₂ O ₃ 0.1	115	5.8	-7.3	-5.8	-7.7	-7.7	-3.7	-4.0	
96.9	0.1	Bi ₂ O ₃ 3	150	5.6	-7.2	-7.3	-7.4	-7.6	-3.7	-4.0	
89.9	10	Bi ₂ O ₃ 0.1	255	5.4	-5.9	-7.4	-7.3	-7.2	-3.6	-4.0	
87.0	10	Bi ₂ O ₃ 3	270	5.4	-5.7	-7.0	-7.8	-8.0	-3.9	-3.7	
94.5	5	Bi ₂ O ₃ 0.5	100	6.0	-5.2	-5.0	-4.6	-4.8	-3.5	-3.3	
99.90	0.05	CoO	130	4.7	-9.0	-8.9	-9.0	-8.9	-4.7	-4.5	
89.95	0.05	CoO	160	4.9	-9.1	-8.9	-9.1	-9.0	-4.9	-4.7	
79.95	20	CoO	390	5.0	-8.9	-9.0	-8.7	-9.5	-4.7	-4.5	
70.0	20	CoO	500	4.7	-9.1	-9.2	-9.0	-8.7	-4.8	-4.9	
99.8	0.1	CoO	140	6.5	-7.2	-6.3	-7.1	-7.2	-4.0	-3.8	
96.9	0.1	CoO	185	6.7	-7.7	-7.1	-7.2	-6.4	-3.9	-3.4	
89.9	10	CoO	220	5.9	-7.0	-6.9	-6.8	-6.5	-3.7	-3.7	
87.0	10	CoO	270	6.3	-7.0	-7.5	-7.1	-6.8	-3.5	-3.5	
94.5	5	CoO	153	7.4	-5.0	-4.9	-5.1	-5.2	-3.3	-3.1	

TABLE 3 (continued)

Composition of Sintered Body (mol. %)				Electric Characteristics		Change Rate (%)					
						Load Life Test		Heating Cycle Test		Impulse Test	
				ZnO	SiO ₂	Further Additives	C (at 1 mA)	n	ΔC	Δn	ΔC
99.90	0.05	MnO	0.05	190	5.2	-9.1	-8.9	-9.0	-8.8	-4.8	-4.9
89.95	0.05	MnO	10	220	5.0	-9.6	-8.7	-8.7	-8.8	-4.7	-4.8
79.95	20	MnO	0.05	540	4.7	-9.7	-9.2	-8.8	-9.0	-4.7	-4.9
70.0	20	MnO	10	650	4.9	-8.9	-9.0	-9.4	-9.5	-4.9	-4.7
99.8	0.1	MnO	0.1	220	6.5	-7.2	-3.7	-6.3	-7.1	-3.8	-4.0
96.9	0.1	MnO	3	250	6.6	-7.3	-4.0	-7.0	-7.0	-3.7	-4.0
89.9	10	MnO	0.1	380	6.5	-6.5	-3.6	-6.9	-6.7	-3.9	-3.7
87.0	10	MnO	3	395	6.7	-7.0	-4.0	-7.1	-6.7	-3.9	-3.7
94.5	5	MnO	0.5	167	8.1	-5.2	-5.4	-5.3	-5.4	-3.4	-3.3
99.90	0.05	BaO	0.05	200	4.4	-8.7	-9.0	-9.2	-9.3	-4.8	-4.5
89.95	0.05	BaO	10	240	4.5	-9.5	-8.8	-9.2	-9.2	-4.7	-4.9
79.95	20	BaO	0.05	670	4.5	-8.8	-8.8	-9.4	-8.7	-4.5	-4.7
70.0	20	BaO	10	800	4.3	-8.9	-9.2	-8.9	-9.2	-4.2	-4.2
99.8	0.1	BaO	0.1	310	5.9	-7.4	-7.4	-7.0	-7.1	-3.7	-4.0
96.9	0.1	BaO	3	335	5.8	-7.0	-7.0	-7.1	-7.1	-3.5	-3.9
89.9	10	BaO	0.1	415	5.7	-7.0	-6.7	-6.4	-6.4	-3.3	-4.0
87.0	10	BaO	3	470	5.9	-6.8	-6.6	-6.8	-7.0	-3.7	-3.7
94.5	5	BaO	0.5	270	7.3	-4.4	-4.6	-5.0	-4.8	-3.1	-3.5

TABLE 3 (continued)

Composition of Sintered Body (mol. %)			Electric Characteristics		Change Rate (%)					
ZnO	SiO ₂	Further Additives	C (at 1 mA)	n	Load Life Test		Heating Cycle Test		Impulse Test	
					ΔC	Δn	ΔC	Δn	ΔC	Δn
99.90	0.50	SrO 0.05	175	4.2	-8.7	-9.4	-8.4	-9.0	-4.7	-4.5
89.95	0.05	SrO 10	180	4.3	-8.6	-9.5	-9.0	-9.1	-4.9	-4.7
79.95	20	SrO 0.05	580	4.1	-8.9	-8.9	-8.7	-8.7	-4.9	-4.9
70.0	20	SrO 10	700	4.2	-8.2	-7.7	-8.2	-8.4	-4.5	-4.7
99.8	0.1	SrO 0.1	290	4.7	-6.9	-7.0	-6.9	-6.3	-4.0	-3.8
96.9	0.1	SrO 3	300	4.8	-7.1	-6.2	-7.1	-6.5	-3.7	-3.7
89.9	10	SrO 0.1	415	4.8	-6.3	-6.3	-6.2	-6.0	-3.5	-3.7
87.0	10	SrO 3	450	4.6	-6.7	-6.5	-6.2	-6.7	-3.8	-3.6
94.5	5	SrO 0.5	225	5.3	-4.5	-4.9	-4.2	-4.2	-3.3	-3.3
99.90	0.05	PbO 0.05	290	4.2	-9.0	-9.1	-8.6	-8.7	-4.6	-4.1
89.95	0.05	PbO 10	420	4.1	-8.2	-9.3	-8.7	-8.8	-4.7	-4.0
79.95	20	PbO 0.05	1050	4.1	-9.0	-9.1	-8.5	-9.4	-4.9	-4.3
70.0	20	PbO 10	1200	4.3	-9.3	-8.9	-9.1	-9.1	-4.6	-4.5
99.8	20.1	PbO 0.1	400	5.0	-6.4	-7.0	-6.6	-6.3	-4.1	-4.0
96.9	0.1	PbO 3	580	4.8	-6.4	-6.7	-6.5	-6.3	-3.9	-3.7
89.9	10	PbO 0.1	690	4.9	-5.9	-6.0	-7.1	-6.6	-3.8	-3.6
87.0	10	PbO 3	750	5.0	-6.4	-6.7	-6.4	-5.8	-3.9	-3.5
94.5	5	PbO 0.5	490	5.7	-4.4	-4.2	-4.2	-4.4	-3.7	-3.2

TABLE 3 (continued)

Composition of Sintered Body (mol. %)			Electric Characteristics		Change Rate (%)					
					Load Life Test		Heating Cycle Test		Impulse Test	
ZnO	SiO ₂	Further Additives	C (at 1 mA)	n	ΔC	Δn	ΔC	Δn	ΔC	Δn
94.0	5	$\left\{ \begin{array}{l} \text{Bi}_2\text{O}_3 \\ \text{CoO} \end{array} \right\}$	150	16	-3.9	-4.0	-3.8	-4.1	-3.4	-3.2
94.0	5	$\left\{ \begin{array}{l} \text{Bi}_2\text{O}_3 \\ \text{MnO} \end{array} \right\}$	190	18	-3.4	-3.9	-4.2	-3.6	-3.5	-3.3
94.0	5	$\left\{ \begin{array}{l} \text{Bi}_2\text{O}_3 \\ \text{BaO} \end{array} \right\}$	350	17	-3.4	-4.3	-3.5	-3.9	-3.7	-3.7
94.0	5	$\left\{ \begin{array}{l} \text{Bi}_2\text{O}_3 \\ \text{SrO} \end{array} \right\}$	290	16	-4.0	-4.7	-3.7	-4.0	-3.7	-3.3
94.0	5	$\left\{ \begin{array}{l} \text{Bi}_2\text{O}_3 \\ \text{PbO} \end{array} \right\}$	400	15	-4.1	-4.7	-3.6	-3.9	-3.5	-3.6
94.0	5	$\left\{ \begin{array}{l} \text{CoO} \\ \text{MnO} \end{array} \right\}$	200	16	-3.7	-4.2	-4.4	-3.5	-3.3	-3.4
94.0	5	$\left\{ \begin{array}{l} \text{CoO} \\ \text{BaO} \end{array} \right\}$	370	19	-4.4	-3.9	-3.8	-3.7	-3.9	-3.9
94.0	5	$\left\{ \begin{array}{l} \text{CoO} \\ \text{SrO} \end{array} \right\}$	450	18	-3.3	-4.4	-4.0	-3.8	-3.4	-3.4
94.0	5	$\left\{ \begin{array}{l} \text{CoO} \\ \text{PbO} \end{array} \right\}$	400	18	-4.0	-4.0	-3.6	-3.5	-3.5	-3.5

TABLE 3 (continued)

Composition of Sintered Body (mol. %)			Electric Characteristics		Change Rate (%)					
ZnO	SiO ₂	Further Additives	C (at 1 mA)	n	Load Life Test		Heating Cycle Test		Impulse Test	
					ΔC	Δn	ΔC	Δn	ΔC	Δn
94.0	5	$\left\{ \begin{array}{l} \text{MnO} \\ \text{BaO} \end{array} \right\}$	300	17	-4.4	-5.0	-3.8	-4.5	-3.8	-3.6
94.0	5	$\left\{ \begin{array}{l} \text{MnO} \\ \text{SrO} \end{array} \right\}$	270	19	-3.8	-4.5	-4.0	-4.5	-3.9	-3.8
94.0	5	$\left\{ \begin{array}{l} \text{MnO} \\ \text{PbO} \end{array} \right\}$	420	15	-4.0	-4.4	-4.1	-3.9	-3.1	-3.6
94.0	5	$\left\{ \begin{array}{l} \text{BaO} \\ \text{SrO} \end{array} \right\}$	320	16	-4.2	-3.4	-2.7	-3.1	-3.2	-3.9
94.0	5	$\left\{ \begin{array}{l} \text{BaO} \\ \text{PbO} \end{array} \right\}$	480	16	-4.1	-3.8	-3.8	-3.5	-3.4	-3.7
95.0	5	$\left\{ \begin{array}{l} \text{SrO} \\ \text{PbO} \end{array} \right\}$	430	15	-4.4	-3.9	-3.9	-4.2	-3.9	-3.9

TABLE 4

Composition of Sintered Body (mol. %)								Electrical Characteristics						Change Rate (%)			
														Load Life Test		Heating Cycle Test	
ZnO	SiO ₂	Bi ₂ O ₃	CoO	MnO	Sb ₂ O ₃	Cr ₂ O ₃	NiO	C (at 1 mA)	n	ΔC	Δn	ΔC	Δn	ΔC	Δn	ΔC	Δn
99.7	0.1	0.1	—	—	0.1	—	—	160	23	-4.5	-4.5	-4.7	-4.9	-4.8	-4.7	-4.8	-4.7
99.7	0.1	0.1	—	—	—	0.1	—	140	23	-4.7	-4.5	-4.6	-4.7	-4.8	-4.8	-4.8	-4.8
99.7	0.1	0.1	—	—	—	—	0.1	135	23	-4.7	-4.4	-4.7	-4.2	-4.4	-4.2	-4.4	-4.2
99.6	0.1	0.1	—	—	0.1	0.1	—	175	24	-4.7	-4.5	-4.4	-4.3	-4.2	-4.3	-4.2	-4.3
99.6	0.1	0.1	—	—	0.1	—	0.1	170	24	-4.7	-4.6	-4.4	-4.4	-4.3	-4.2	-4.3	-4.2
99.6	0.1	0.1	—	—	—	0.1	0.1	175	23	-4.3	-4.6	-4.5	-4.4	-4.7	-4.3	-4.7	-4.3
99.5	0.1	0.1	—	—	0.1	0.1	0.1	190	25	-4.1	-4.2	-4.0	-4.2	-4.1	-4.0	-4.1	-4.0
84.0	10	3	—	—	3	—	—	300	23	-4.0	-4.0	-4.0	-3.9	-3.9	-3.9	-3.9	-3.9
84.0	10	3	—	—	—	3	—	290	23	-3.9	-3.9	-4.2	-3.8	-3.9	-3.8	-3.9	-3.8
84.0	10	3	—	—	—	—	3	275	23	-4.1	-4.0	-4.1	-3.8	-3.7	-3.8	-3.7	-3.8
81.0	10	3	—	—	3	3	—	325	25	-3.8	-4.0	-4.0	-3.8	-3.7	-3.5	-3.7	-3.5
81.0	10	3	—	—	3	—	3	310	25	-3.9	-4.1	-3.9	-3.7	-3.9	-3.7	-3.9	-3.7
81.0	10	3	—	—	—	3	3	300	24	-4.2	-3.9	-3.8	-3.6	-3.8	-3.6	-3.8	-3.6
78.0	10	3	—	—	3	3	3	380	27	-3.9	-3.9	-3.7	-3.9	-3.5	-3.9	-3.5	-3.1

TABLE 4 (continued)

Composition of Sintered Body (mol. %)										Change Rate (%)							
										Electrical Characteristics		Load Life Test		Heating Cycle Test		Impulse Test	
												ΔC	Δn	ΔC	Δn	ΔC	Δn
ZnO	SiO ₂	Bi ₂ O ₃	CoO	MnO	Sb ₂ O ₃	Cr ₂ O ₃	NiO	C (at 1 mA)	n	ΔC	Δn	ΔC	Δn	ΔC	Δn		
94.0	5	0.5	—	—	0.5	—	—	200	27	-3.7	-3.2	-4.0	-3.9	-3.0	-2.9		
94.0	5	0.5	—	—	—	0.5	—	190	26	-3.6	-3.3	-3.2	-3.5	-3.1	-2.8		
94.0	5	0.5	—	—	—	—	0.5	180	24	-3.5	-3.4	-3.4	-3.8	-3.1	-3.2		
93.5	5	0.5	—	—	0.5	0.5	—	240	32	-3.5	-3.7	-3.7	-3.7	-3.4	-3.3		
93.5	5	0.5	—	—	0.5	—	0.5	230	33	-3.6	-3.3	-3.6	-3.7	-3.0	-3.1		
93.5	5	0.5	—	—	—	0.5	0.5	215	30	-3.7	-3.3	-3.5	-3.8	-3.3	-3.2		
93.0	5	0.5	—	—	0.5	0.5	0.5	270	35	-2.3	-2.2	-2.4	-2.3	-2.4	-2.2		
99.6	0.1	0.1	0.1	—	0.1	—	—	210	27	-4.0	-3.9	-3.9	-4.0	-3.5	-4.0		
99.6	0.1	0.1	0.1	—	—	0.1	—	200	27	-3.7	-4.0	-3.8	-3.7	-4.0	-3.7		
99.6	0.1	0.1	0.1	—	—	—	0.1	195	25	-3.7	-4.0	-3.6	-3.5	-4.0	-4.0		
99.5	0.1	0.1	0.1	—	0.1	0.1	—	240	29	-4.0	-3.3	-3.9	-3.7	-3.7	-4.0		
99.5	0.1	0.1	0.1	—	0.1	—	0.1	240	28	-3.5	-3.7	-4.0	-3.7	-3.9	-3.7		
99.5	0.1	0.1	0.1	—	—	0.1	0.1	235	28	-3.8	-4.0	-3.7	-3.9	-3.8	-3.5		
99.4	0.1	0.1	0.1	—	0.1	0.1	0.1	300	30	-3.5	-3.5	-3.7	-3.7	-3.8	-3.8		

TABLE 4 (continued)

Composition of Sintered Body (mol. %)										Electrical Characteristics		Change Rate (%)					
												Load Life Test		Heating Cycle Test		Impulse Test	
										C (at 1 mA)	n	ΔC	Δn	ΔC	Δn	ΔC	Δn
ZnO	SiO ₂	Bi ₂ O ₃	CoO	MnO	Sb ₂ O ₃	Cr ₂ O ₃	NiO										
81.0	10	3	3	—	3	—	—	270	29	—	—	-3.7	-3.6	-3.3	-3.8	-3.5	-3.4
81.0	10	3	3	—	—	3	—	360	27	—	—	-3.6	-3.4	-3.5	-3.8	-3.1	-3.2
81.0	10	3	3	—	—	—	3	350	26	—	—	-3.7	-3.6	-3.6	-3.8	-3.4	-3.5
78.0	10	3	3	—	3	3	—	400	33	—	—	-3.5	-3.3	-3.7	-3.7	-3.7	-3.7
78.0	10	3	3	—	3	—	3	400	30	—	—	-3.5	-3.5	-3.3	-3.4	-3.7	-3.6
78.0	10	3	3	—	—	3	3	370	31	—	—	-3.4	-3.6	-3.0	-3.1	-3.3	-3.4
75.0	10	3	3	—	3	3	3	460	37	—	—	-3.0	-2.9	-3.0	-2.9	-3.0	-2.9
93.5	5	0.5	0.5	—	0.5	—	—	260	37	—	—	-2.3	-3.1	-3.3	-2.9	-2.9	-3.0
93.5	5	0.5	0.5	—	—	0.5	—	250	36	—	—	-2.2	-3.2	-2.9	-2.7	-2.2	-2.2
93.5	5	0.5	0.5	—	—	—	0.5	250	37	—	—	-2.4	-3.1	-2.8	-2.4	-2.3	-2.3
93.0	5	0.5	0.5	—	0.5	0.5	—	330	40	—	—	-2.4	-3.0	-2.7	-2.4	-2.5	-2.4
93.0	5	0.5	0.5	—	0.5	—	0.5	330	41	—	—	-2.2	-2.9	-2.5	-2.3	-2.5	-2.5
93.0	5	0.5	0.5	—	—	0.5	0.5	310	41	—	—	-2.4	-2.4	-2.6	-2.7	-2.3	-2.3
92.5	5	0.5	0.5	—	0.5	0.5	0.5	390	45	—	—	-1.9	-1.9	-1.7	-1.9	-2.1	-2.0
99.6	0.1	0.1	—	0.1	0.1	—	—	300	36	—	—	-4.0	-3.9	-4.0	-3.7	-3.9	-3.8
99.6	0.1	0.1	—	0.1	—	0.1	—	290	36	—	—	-3.7	-4.0	-3.7	-4.0	-3.8	-3.7
99.6	0.1	0.1	—	0.1	—	—	0.1	285	34	—	—	-3.9	-4.0	-4.0	-4.0	-3.9	-3.9
99.5	0.1	0.1	—	0.1	0.1	0.1	—	360	38	—	—	-3.7	-3.7	-3.9	-3.7	-3.7	-3.6

TABLE 4 (continued)

Composition of Sintered Body (mol. %)										Electrical Characteristics				Change Rate (%)			
														Load Life Test		Heating Cycle Test	
										ZnO	SiO ₂	Bi ₂ O ₃	CoO	MnO	Sb ₂ O ₃	Cr ₂ O ₃	NiO
99.5	0.1	0.1	—	0.1	0.1	—	0.1	—	350	38	—3.7	—3.9	—3.9	—3.9	—3.7	—3.8	
99.5	0.1	0.1	—	0.1	—	—	0.1	—	330	37	—3.6	—3.6	—3.5	—3.8	—3.9	—3.6	
99.4	0.1	0.1	—	0.1	0.1	0.1	0.1	—	380	40	—3.1	—4.0	—3.6	—3.2	—2.9	—2.8	
81.0	10	3	—	3	3	—	—	—	520	42	—2.9	—3.8	—3.4	—3.8	—3.0	—3.0	
81.0	10	3	—	3	—	3	—	—	570	42	—3.8	—3.7	—3.4	—3.7	—3.1	—3.2	
81.0	10	3	—	3	—	—	3	—	500	42	—3.7	—3.0	—3.9	—3.4	—3.2	—3.4	
78.0	10	3	—	3	3	3	—	—	550	44	—2.7	—3.3	—3.7	—3.3	—3.3	—3.1	
78.0	10	3	—	3	3	—	3	—	540	43	—3.9	—3.7	—3.5	—3.6	—3.1	—3.1	
78.0	10	3	—	3	—	3	3	—	540	43	—3.7	—3.8	—3.6	—3.6	—3.3	—3.2	
75.0	10	3	—	3	3	3	3	—	600	47	—3.1	—3.9	—3.8	—3.7	—3.0	—3.1	
93.5	5	0.5	—	0.5	0.5	—	—	—	415	48	—3.0	—3.0	—2.9	—2.4	—2.5	—2.4	
93.5	5	0.5	—	0.5	—	0.5	—	—	410	48	—3.7	—2.9	—3.0	—2.5	—2.5	—2.5	
93.5	5	0.5	—	0.5	—	—	0.5	—	405	46	—3.0	—3.0	—2.7	—2.8	—2.3	—2.4	
93.0	5	0.5	—	0.5	0.5	0.5	—	—	460	51	—3.0	—2.9	—2.7	—2.3	—2.6	—2.5	
93.0	5	0.5	—	0.5	0.5	—	0.5	—	460	50	—2.9	—2.8	—2.8	—2.4	—2.6	—2.5	
93.0	5	0.5	—	0.5	—	—	0.5	—	440	49	—2.9	—2.8	—2.9	—2.7	—2.7	—2.7	
92.5	5	0.5	—	0.5	0.5	0.5	0.5	—	500	55	—2.0	—1.9	—2.1	—1.8	—1.7	—1.8	

TABLE 4 (continued)

Composition of Sintered Body (mol. %)										Change Rate (%)							
										Electrical Characteristics		Load Life Test		Heating Cycle Test		Impulse Test	
												ΔC	Δn	ΔC	Δn	ΔC	Δn
		C		n													
		(at 1 mA)															
ZnO	SiO ₂	Bi ₂ O ₃	CoO	MnO	Sb ₂ O ₃	Cr ₂ O ₃	NiO	C	n	ΔC	Δn	ΔC	Δn				
99.5	0.1	0.1	0.1	0.1	0.1	—	—	440	35	-2.9	-3.0	-2.7	-2.9				
99.5	0.1	0.1	0.1	0.1	—	0.1	—	430	35	-2.6	-2.9	-2.8	-2.7				
99.5	0.1	0.1	0.1	0.1	—	—	0.1	425	33	-2.7	-2.9	-2.9	-2.6				
99.4	0.1	0.1	0.1	0.1	0.1	0.1	—	470	37	-2.8	-2.8	-2.7	-2.7				
99.4	0.1	0.1	0.1	0.1	0.1	—	0.1	470	38	-2.5	-2.8	-2.8	-2.9				
99.4	0.1	0.1	0.1	0.1	—	0.1	0.1	465	37	-2.7	-2.8	-2.7	-2.8				
99.3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	500	43	-2.7	-2.4	-2.5	-2.3				
78.0	10	3	3	3	3	—	—	730	44	-3.0	-2.9	-2.9	-2.7				
78.0	10	3	3	3	—	3	—	720	42	-2.7	-2.7	-2.9	-2.8				
78.0	10	3	3	3	—	—	3	715	42	-2.9	-2.8	-2.9	-2.9				
75.0	10	3	3	3	3	3	—	780	49	-2.7	-2.8	-2.6	-2.6				
75.0	10	3	3	3	3	—	3	750	48	-2.5	-2.7	-2.8	-2.7				
75.0	10	3	3	3	—	3	3	740	47	-2.4	-2.3	-2.2	-2.5				
72.0	10	3	3	3	3	3	3	850	52	-2.0	-2.1	-2.2	-2.4				

TABLE 4 (continued)

Composition of Sintered Body (mol. %)										Change Rate (%)							
										Electrical Characteristics		Load Life Test		Heating Cycle Test		Impulse Test	
										G (at 1 mA)	n						
ZnO	SiO ₂	Bi ₂ O ₃	CoO	MnO	Sb ₂ O ₃	Cr ₂ O ₃	NiO	590	n	ΔC	Δn	ΔC	Δn	ΔC	Δn		
93.0	5	0.5	0.5	0.5	0.5	—	—	590	54	-1.5	-1.9	-1.4	-1.2	-1.7	-1.1		
93.0	5	0.5	0.5	0.5	—	0.5	—	570	54	-1.2	-1.4	-1.1	-1.1	-1.0	-1.7		
93.0	5	0.5	0.5	0.5	—	—	0.5	565	53	-1.3	-1.2	-1.1	-1.3	-1.3	-1.2		
92.5	5	0.5	0.5	0.5	0.5	0.5	—	620	60	-1.3	-1.3	-1.4	-1.5	-1.2	-1.1		
92.5	5	0.5	0.5	0.5	0.5	—	0.5	600	59	-1.3	-1.9	-1.1	-1.1	-1.0	-1.2		
92.5	5	0.5	0.5	0.5	—	0.5	0.5	600	57	-1.2	-1.9	-1.8	-1.2	-1.1	-1.1		
92.0	5	0.5	0.5	0.5	0.5	0.5	0.5	660	65	-0.5	-0.5	-0.4	-0.5	-0.8	-0.9		

WHAT WE CLAIM IS:—

1. A sintered body consisting essentially of a major proportion of ZnO and a minor proportion of an additive which is from 0.05 to 20.0 mole percent SiO₂ and from 0.05 to 18.0 mole percent, in total, of one or more of the oxides Bi₂O₃, CoO, MnO, BaO, SrO, PbO, Sb₂O₃, Cr₂O₃ and NiO, each of the latter oxides not being present in an amount of more than 10.0 mole percent.

2. A sintered body according to claim 1 wherein Sb₂O₃, Cr₂O₃ or NiO or a mixture of two or more thereof are present only when Bi₂O₃ is present.

3. A sintered body according to claim 1,

wherein the additive is SiO₂ and one or more of Bi₂O₃, CoO, MnO, BaO, SrO and PbO.

4. A sintered body according to claim 3, wherein the additive consists essentially of 0.1 to 10.0 mole percent SiO₂ and one or more of the oxides Bi₂O₃, CoO, MnO, BaO, SrO and PbO, the amount of each of the latter oxides present being from 0.1 to 3.0 mole percent.

5. A sintered body according to claim 2, wherein the additive consists essentially of 0.1 to 10.0 mole percent SiO₂, 0.1 to 3.0 mole percent Bi₂O₃ and one or more of 0.1 to 3.0 mole percent Sb₂O₃, 0.1 to 3.0 mole percent Cr₂O₃ and 0.1 to 3.0 mole percent NiO.

TABLE 4 (continued)

Composition of Sintered Body (mol. %)								Electrical Characteristics		Change Rate (%)					
										Load Life Test		Heating Cycle Test		Impulse Test	
C		n		ΔC	Δn	ΔC	Δn	ΔC	Δn	ΔC	Δn				
ZnO	SiO ₂	Bi ₂ O ₃	CoO	MnO	Sb ₂ O ₃	Cr ₂ O ₃	NiO	(at 1 mA)	n						
93.0	5	0.5	0.5	0.5	0.5	—	—	590	54	-1.5	-1.9	-1.4	-1.2	-1.7	-1.1
93.0	5	0.5	0.5	0.5	—	0.5	—	570	54	-1.2	-1.4	-1.1	-1.1	-1.0	-1.7
93.0	5	0.5	0.5	0.5	—	—	0.5	565	53	-1.3	-1.2	-1.1	-1.3	-1.3	-1.2
92.5	5	0.5	0.5	0.5	0.5	0.5	—	620	60	-1.3	-1.3	-1.4	-1.5	-1.2	-1.1
92.5	5	0.5	0.5	0.5	0.5	—	0.5	600	59	-1.3	-1.9	-1.1	-1.1	-1.0	-1.2
92.5	5	0.5	0.5	0.5	—	0.5	0.5	600	57	-1.2	-1.9	-1.8	-1.2	-1.1	-1.1
92.0	5	0.5	0.5	0.5	0.5	0.5	0.5	660	65	-0.5	-0.5	-0.4	-0.5	-0.8	-0.9

WHAT WE CLAIM IS:—

1. A sintered body consisting essentially of a major proportion of ZnO and a minor proportion of an additive which is from 0.05 to 20.0 mole percent SiO₂ and from 0.05 to 18.0 mole percent, in total, of one or more of the oxides Bi₂O₃, CoO, MnO, BaO, SrO, PbO, Sb₂O₃, Cr₂O₃ and NiO, each of the latter oxides not being present in an amount of more than 10.0 mole percent.
2. A sintered body according to claim 1 wherein Sb₂O₃, Cr₂O₃ or NiO or a mixture of two or more thereof are present only when Bi₂O₃ is present.
3. A sintered body according to claim 1, wherein the additive is SiO₂ and one or more of Bi₂O₃, CoO, MnO, BaO, SrO and PbO.
4. A sintered body according to claim 3, wherein the additive consists essentially of 0.1 to 10.0 mole percent SiO₂ and one or more of the oxides Bi₂O₃, CoO, MnO, BaO, SrO and PbO, the amount of each of the latter oxides present being from 0.1 to 3.0 mole percent.
5. A sintered body according to claim 2, wherein the additive consists essentially of 0.1 to 10.0 mole percent SiO₂, 0.1 to 3.0 mole percent Bi₂O₃ and one or more of 0.1 to 3.0 mole percent Sb₂O₃, 0.1 to 3.0 mole percent Cr₂O₃ and 0.1 to 3.0 mole percent NiO.

wherein the additive is SiO₂ and one or more of Bi₂O₃, CoO, MnO, BaO, SrO and PbO.

4. A sintered body according to claim 3, wherein the additive consists essentially of 0.1 to 10.0 mole percent SiO₂ and one or more of the oxides Bi₂O₃, CoO, MnO, BaO, SrO and PbO, the amount of each of the latter oxides present being from 0.1 to 3.0 mole percent.

5. A sintered body according to claim 2, wherein the additive consists essentially of 0.1 to 10.0 mole percent SiO₂, 0.1 to 3.0 mole percent Bi₂O₃ and one or more of 0.1 to 3.0 mole percent Sb₂O₃, 0.1 to 3.0 mole percent Cr₂O₃ and 0.1 to 3.0 mole percent NiO.



6. A sintered body according to claim 2, wherein the additive consists essentially of 0.1 to 10.0 mole percent SiO_2 , 0.1 to 3.0 mole percent Bi_2O_3 , 0.1 to 3.0 mole percent CoO and one or more of 0.1 to 3.0 mole percent Sb_2O_3 , 0.1 to 3.0 mole percent Cr_2O_3 and 0.1 to 3.0 mole percent NiO .
7. A sintered body according to claim 2, wherein the additive consists essentially of 0.1 to 10.0 mole percent SiO_2 , 0.1 to 3.0 mole percent Bi_2O_3 , 0.1 to 3.0 mole percent MnO and one or more of 0.1 to 3.0 mole percent Sb_2O_3 , 0.1 to 3.0 mole percent Cr_2O_3 , and 0.1 to 3.0 mole percent NiO .
8. A sintered body according to claim 1, wherein the additive consists essentially of 0.1 to 10.0 mole percent SiO_2 , 0.1 to 3.0 mole percent Bi_2O_3 , 0.1 to 3.0 mole percent CoO , 0.1 to 3.0 mole percent MnO and one or more of 0.1 to 3.0 mole percent Sb_2O_3 , 0.1 to 3.0 mole percent Cr_2O_3 , and 0.1 to 3.0 mole percent NiO .
9. A sintered body of the composition herein specified in Table 1.
10. A sintered body of the composition herein specified in Table 2, 3 or 4.
11. A voltage dependent resistor which comprises a body as defined in any of claims 1 to 10 and a pair of electrodes in contact with said body.
12. A resistor according to claim 11, wherein the electrodes comprise a film of aluminium and/or copper on opposite surfaces of said body.
13. A voltage dependent resistor substantially as herein described with reference to the accompanying drawing.
14. A voltage dependent resistor substantially as herein described in any of the Examples.
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