

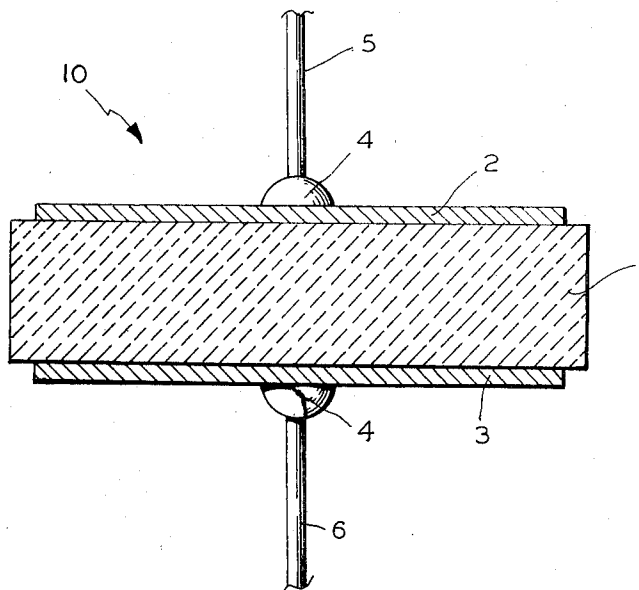
Aug. 10, 1971

MICHIO MATSUOKA ET AL

3,598,763

MANGANESE-MODIFIED ZINC OXIDE VOLTAGE VARIABLE RESISTOR

Filed Oct. 30, 1969



INVENTORS

MICHIO MATSUOKA
TAKESHI MASUYAMA
YOSHIO IIDA

BY

Wendroth, Rind & Ponack
ATTORNEYS

1

3,598,763

MANGANESE-MODIFIED ZINC OXIDE VOLTAGE VARIABLE RESISTOR

Michio Matsuoka, Takeshi Masuyama, and Yoshio Iida, Osaka-fu, Japan, assignors to Matsushita Electric Industrial Co., Ltd., Kadoma, Osaka, Japan

Filed Oct. 30, 1969, Ser. No. 872,590

Claims priority, application Japan, Nov. 8, 1968, 43/82,125

Int. Cl. H01b 1/06

U.S. Cl. 252—518

10 Claims

ABSTRACT OF THE DISCLOSURE

A voltage variable resistor ceramic composition consisting essentially of zinc oxide and, as an additive, manganese oxide. The manganese-modified zinc oxide voltage variable resistor has improved voltage nonlinear properties due to the further addition of barium oxide, strontium oxide, lead oxide, uranium oxide, cobalt oxide, bismuth oxide and calcium oxide.

This invention relates to compositions of ceramic voltage variable resistors having non-ohmic resistance, and more particularly to compositions of varistors comprising zinc oxide having non-ohmic resistance due to the bulk thereof.

Various voltage variable 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 variable resistor are expressed by the relation:

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

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 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 V₁ and V₂ are the voltages at given currents I₁ and I₂, 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.

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

An object of the present invention is to provide a composition of a voltage variable resistor having non-ohmic properties due to the bulk thereof and having a controllable C-value.

2

Another object of the present invention is to provide a composition of a voltage variable resistor characterized by a high n-value.

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 variable resistor according to 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 of the drawing wherein reference character 10 designates, as a whole, a voltage variable 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 is 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 voltage variable resistor according to the invention comprises a sintered body of a composition consisting essentially of 90.0 to 99.95 mole percent of zinc oxide and 0.05 to 10.0 mole percent of manganese oxide. Such a voltage variable 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 said opposite surfaces. The shorter distance results in the lower C-value.

The higher n-value can be obtained when said sintered body consists essentially of 97.0 to 99.9 mole percent of zinc oxide and 0.1 to 3.0 mole percent of manganese oxide in accordance with the invention.

According to the present invention, the n-value can be elevated when said sintered body is of a composition consisting essentially of 82.0 to 99.9 mole percent of zinc oxide, 0.05 to 10.0 mole percent of manganese oxide and 0.05 to 0.8 mole percent of one oxide selected from the group consisting of barium oxide and cobalt oxide.

The higher n-value can be obtained when said sintered body consists essentially of 94.0 to 99.8 mole percent of zinc oxide, 0.1 to 3.0 mole percent of manganese oxide and 0.1 to 3.0 mole percent of one oxide selected from the group consisting of barium oxide and cobalt oxide.

According to the present invention, the stability for ambient temperature and the electric load life test can be improved when said sintered body consists essentially of 82.0 to 99.9 mole percent of zinc oxide, 0.05 to 10.0 mole percent of manganese oxide and 0.05 to 8.0 mole percent of calcium oxide.

Further, the stability for ambient temperature and the electric load life test is extremely improved when said sintered body consists essentially of 94.0 to 99.8 mole percent of zinc oxide, 0.1 to 3.0 mole percent of manganese oxide and 0.1 to 3.0 mole percent of calcium oxide.

According to the present invention, the n-value is elevated when said sintered body consists essentially of 82.0 to 99.9 mole percent of zinc oxide, 0.05 to 10.0 mole percent of manganese oxide and 0.05 to 8.0 mole percent of one oxide selected from the group consisting of strontium oxide, lead oxide and uranium oxide.

The n-value is further elevated when said sintered body is of a composition consisting essentially of 94.0 to 99.8 mole percent of zinc oxide, 0.1 to 3.0 mole percent of manganese oxide and 0.1 to 3.0 mole percent of one oxide selected from the group consisting of strontium oxide, lead oxide and uranium oxide.

According to the present invention, a combination of a high n-value and a low C-value can be obtained when said sintered body is of a composition consisting essen-

tially of 74.0 to 99.85 mole percent of zinc oxide, 0.05 to 10.0 mole percent of manganese oxide, 0.05 to 8.0 mole percent of bisumuth oxide and 0.05 to 8.0 mole percent of one oxide selected from the group consisting of strontium oxide, lead oxide and uranium oxide.

Further, the C-value is lowered and the *n*-value is extremely elevated when said sintered body is of a composition consisting essentially of 91.0 to 99.7 mole percent of zinc oxide, 0.1 to 3.0 mole percent of manganese oxide, 0.1 to 3.0 mole percent of bismuth oxide and 0.1 to 3.0 mole percent of one oxide selected from the group consisting of strontium oxide, lead oxide and uranium oxide.

Accordingly to the present invention, the high *n*-value also can be obtained when said sintered body is of a composition consisting essentially of 74.0 to 99.85 mole percent of zinc oxide, 0.05 to 10.0 mole percent of manganese oxide, 0.05 to 8.0 mole percent of lead oxide, and 0.05 to 8.0 mole percent of one oxide selected from the group consisting of strontium oxide, cobalt oxide and barium oxide.

Further, the extremely high *n*-value and the low C-value also can be obtained when said sintered body is of a composition consisting essentially of 91.0 to 99.7 mole percent of zinc oxide and 0.1 to 3.0 mole percent of manganese oxide, 0.1 to 3.0 mole percent of lead oxide and 0.1 to 3.0 mole percent of one oxide selected from the group consisting of strontium oxide, cobalt oxide and barium oxide.

According to the present invention, a combination of a high *n*-value and a high stability can be obtained when said sintered body is of a composition consisting essentially of 74.0 to 99.85 mole percent of zinc oxide, 0.05 to 10.0 mole percent of manganese oxide, 0.05 to 8.0 mole percent of lead oxide and 0.05 to 8.0 mole percent of calcium oxide. Further, a combination a high *n*-value and a high stability can be extremely promoted when said sintered body is of a composition consisting essentially of 91.0 to 99.7 mole percent of zinc oxide, 0.1 to 3.0 mole percent of manganese oxide, 0.1 to 3.0 mole percent of lead oxide and 0.1 to 3.0 mole percent of calcium oxide.

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 from 100 kg./cm.² to 1000 kg./cm.². The pressed bodies are sintered in air at a given temperature for 1 to 3 hours, and then furnace-cooled to room temperature (about 15° to about 30° C.).

The available sintering temperature is determined in view of electrical resistivity, non-linearity and stability and ranges from 1000° to 1450° C.

The pressed bodies are preferably sintered in a non-oxidizing atmosphere such as nitrogen and argon when it is desired to reduce the electrical resistivity.

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 be admixed with a suitable binder such as water, polyvinyl alcohol, etc.

It is advantageous that the sintered body be lapped at the opposite surfaces by abrasive powder such as silicon carbide in a particle size of 300 meshes to 1500 meshes.

The sintered bodies are provided, at the opposite surfaces therefore, with electrodes in any available and suitable method such as electroplating method, vacuum evaporation method, metallizing method by spraying or silver painting method.

The voltage variable properties are not practically affected by the kinds of electrodes used, but are affected by the thickness of the sintered bodies. Particularly, the C-value varies in proportion to the thickness of the sintered bodies, while the *n*-value is almost independent of

the thickness. This surely means that the voltage variable property is due to the bulk itself, but not to the electrodes.

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.

Voltage variable 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 rating power for 500 hours. The *n*-value and C-value do not change remarkably after heating cycles and load life test. It is advantageous for achievement of a high stability to humidity that the resultant voltage variable resistors are embedded in a humidity proof resin such as epoxy resin and phenol resin in a per se well known manner.

Presently preferred illustrative embodiments of the invention are as follows.

EXAMPLE 1

A mixture of zinc oxide and manganese oxide in a composition of Table 1 are mixed in a wet mill for 3 hours. The mixture is dried and then calcined at 700° C. for 1 hour. The calcined mixture is pulverized by the motor-driven ceramic mortar for 30 minutes and then pressed in a mold into a disc of 17.5 mm. in diameter and 2.5 mm. in thickness at the pressure of 500 kg./cm.².

The pressed body is sintered in air at 1150° 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 by silicon carbide in a particle size of 600 meshes. The resulting sintered disc has a size of 14 mm. in diameter and 1.5 mm. in thickness. Silver point electrodes commercially available are attached to the opposite surfaces of the sintered disc by painting. Then lead wires are attached to the silver electrodes by soldering. The electric characteristics of the resultant resistors are shown in Table 1. It will be readily understood that the zinc oxide sintered body incorporated with manganese oxide in an amount of 0.05 to 10.0 mole percent is available for the voltage variable resistor. Particularly, the addition of manganese oxide in an amount of 0.1 to 3.0 mole percent makes the voltage nonlinear property more excellent.

TABLE 1

MnO (mol. percent)	C (at 1 ma.)	<i>n</i>	MnO (mol. percent)	C (at 1 ma.)	<i>n</i>
0.05-----	305	3.0	2-----	180	3.6
0.1-----	200	3.5	3-----	205	3.5
0.2-----	170	3.7	5-----	230	3.3
0.5-----	150	3.9	8-----	280	3.2
1-----	165	3.8	10-----	350	3.1

EXAMPLE 2

Starting materials composed of 99.5 mole percent of zinc oxide and 0.5 mole percent of manganese oxide is mixed, dried, calcined and pulverized in the same manner as those of Example 1. The pulverized mixture is pressed in a mold into a disc of 17.5 mm. in diameter and 5 mm. in thickness at a pressure of 500 kg./cm.².

The pressed body is sintered in air at 1150° C. for 1 hour, and then furnace-cooled to room temperature. The sintered disc is ground at the opposite surfaces thereof into the thickness shown in Table 2 by silicon carbide in a particle size of 600 meshes. The ground disc is provided with the electrodes and lead wires at the opposite surfaces in a manner similar to that of Example 1. The electric characteristics of the resultant resistors are shown in Table 2: the C-value varies approximately in proportion to the thickness of the sintered disc while the *n*-value

5

is essentially independent of the thickness. It will readily be realized that the voltage nonlinear property of the resistors are attributed to the sintered body itself.

Thickness (mm.)	C (at 1 ma.)	<i>n</i>
Initial (4.1)-----	403	4.0
3.5-----	350	3.9
3.0-----	300	3.8
2.5-----	246	3.9
2.0-----	203	4.0
1.5-----	150	3.9
1.0-----	98	4.0

EXAMPLE 3

Zinc oxide containing the additions of Tables 3 and 4 is fabricated into voltage variable resistors by the same process as that of Example 1. The *n*-values of the resulting resistors are shown in Tables 3 and 4. It will be readily seen that the combination of manganese oxide with one oxide selected from the group consisting of strontium oxide, lead oxide and uranium oxide as additives results in an excellent voltage-nonlinear property and a remarkably excellent *n*-value can be obtained by the additive combination of manganese oxide and lead oxide with one oxide selected from the group consisting of strontium oxide, cobalt oxide and barium oxide.

TABLE 3

Mole percent				C (at 1 ma.)	<i>n</i>
MnO	SrO	PbO	UO ₂		
0.05-----	0.05-----	-----	-----	900	4.5
0.05-----	0.5-----	-----	-----	450	9.0
0.05-----	8-----	-----	-----	890	4.3
0.5-----	0.05-----	-----	-----	450	6.0
0.5-----	8-----	-----	-----	445	5.8
10-----	0.05-----	-----	-----	1,000	4.5
10-----	0.5-----	-----	-----	500	9.0
10-----	8-----	-----	-----	700	4.6
0.1-----	0.1-----	-----	-----	400	7.0
0.1-----	0.5-----	-----	-----	300	10.5
0.1-----	3-----	-----	-----	390	6.9
0.5-----	0.1-----	-----	-----	300	7.9
0.5-----	3-----	-----	-----	305	8.0
3-----	0.1-----	-----	-----	410	7.0
3-----	0.5-----	-----	-----	300	10.5
3-----	3-----	-----	-----	400	6.9
0.5-----	0.5-----	-----	-----	220	12
0.05-----	-----	0.05-----	-----	870	4.1
0.05-----	-----	0.5-----	-----	460	8.8
0.05-----	-----	8-----	-----	900	4.5
0.5-----	-----	0.05-----	-----	450	6.1
0.5-----	-----	8-----	-----	420	5.7
10-----	-----	0.05-----	-----	950	4.5
10-----	-----	0.5-----	-----	520	9.2
10-----	-----	8-----	-----	680	4.6
0.1-----	-----	0.1-----	-----	420	7.2
0.1-----	-----	0.5-----	-----	310	11
0.1-----	-----	3-----	-----	375	7.0
0.5-----	-----	0.1-----	-----	380	7.8
0.5-----	-----	3-----	-----	300	8.1
3-----	-----	0.1-----	-----	405	7.0
3-----	-----	0.5-----	-----	300	11
3-----	-----	3-----	-----	395	7.0
0.5-----	-----	0.5-----	-----	200	13
0.05-----	-----	-----	0.05-----	780	6.0
0.05-----	-----	-----	0.5-----	390	9.3
0.05-----	-----	-----	8-----	800	4.5
0.5-----	-----	-----	0.05-----	420	6.2
0.5-----	-----	-----	8-----	400	6.0
10-----	-----	-----	0.05-----	1,000	4.7
10-----	-----	-----	0.5-----	450	9.1
10-----	-----	-----	8-----	600	4.8
0.1-----	-----	-----	0.1-----	400	7.2
0.1-----	-----	-----	0.5-----	265	12
0.1-----	-----	-----	3-----	350	8.0
0.5-----	-----	-----	0.1-----	270	7.9
0.5-----	-----	-----	3-----	275	8.4
3-----	-----	-----	0.1-----	400	7.2
3-----	-----	-----	0.5-----	275	12
3-----	-----	-----	3-----	380	7.6
0.5-----	-----	-----	0.5-----	190	13

TABLE 4

Mole percent					C (at 1 ma.)	<i>n</i>
MnO	PbO	SrO	CoO	BaO		
0.05-----	0.05-----	0.05-----	-----	-----	850	8.0
0.05-----	0.05-----	8-----	-----	-----	840	7.8
0.05-----	8-----	0.05-----	-----	-----	850	6.2
0.05-----	8-----	8-----	-----	-----	820	6.3
10-----	0.05-----	0.05-----	-----	-----	900	6.8
10-----	0.05-----	8-----	-----	-----	870	7.0
10-----	8-----	0.05-----	-----	-----	650	8.0
10-----	8-----	8-----	-----	-----	630	7.5
0.1-----	0.1-----	0.1-----	-----	-----	400	13
0.1-----	0.1-----	3-----	-----	-----	400	12

6

TABLE 4.—Continued

Mole percent					C (at 1 ma.)	<i>n</i>
MnO	PbO	SrO	CoO	BaO		
0.1-----	3-----	0.1-----	-----	-----	355	13
0.1-----	3-----	3-----	-----	-----	350	11
3-----	0.1-----	0.1-----	-----	-----	380	12
3-----	0.1-----	3-----	-----	-----	375	11
3-----	3-----	0.1-----	-----	-----	350	14
3-----	3-----	3-----	-----	-----	355	14
0.5-----	0.5-----	0.5-----	-----	-----	175	27
0.05-----	0.05-----	-----	0.05-----	-----	800	8.5
0.05-----	0.05-----	-----	8-----	-----	810	8.0
0.05-----	8-----	-----	0.05-----	-----	790	6.3
0.05-----	8-----	-----	8-----	-----	790	6.3
10-----	0.05-----	-----	0.05-----	-----	870	7.0
10-----	0.05-----	-----	8-----	-----	850	7.2
10-----	8-----	-----	0.05-----	-----	600	8.1
10-----	8-----	-----	8-----	-----	600	7.5
0.1-----	0.1-----	-----	0.1-----	-----	380	14
0.1-----	0.1-----	-----	3-----	-----	350	14
0.1-----	3-----	-----	0.1-----	-----	325	12
3-----	3-----	-----	3-----	-----	320	12
3-----	0.1-----	-----	0.1-----	-----	365	13
3-----	0.1-----	-----	3-----	-----	360	14
3-----	3-----	-----	0.1-----	-----	330	14
3-----	3-----	-----	3-----	-----	315	13
0.5-----	0.5-----	-----	0.5-----	-----	180	26
0.05-----	0.05-----	-----	-----	0.05-----	780	8.3
0.05-----	0.05-----	-----	-----	8-----	750	8.0
0.05-----	8-----	-----	-----	0.05-----	790	6.5
0.05-----	8-----	-----	-----	8-----	790	6.5
10-----	0.05-----	-----	-----	0.05-----	750	7.5
10-----	0.05-----	-----	-----	8-----	700	7.8
10-----	8-----	-----	-----	0.05-----	500	8.3
10-----	8-----	-----	-----	8-----	520	8.1
0.1-----	0.1-----	-----	-----	0.1-----	390	13
0.1-----	0.1-----	-----	-----	3-----	360	13
0.1-----	3-----	-----	-----	0.1-----	330	13
0.1-----	3-----	-----	-----	3-----	325	14
3-----	0.1-----	-----	-----	0.1-----	360	13
3-----	0.1-----	-----	-----	3-----	350	14
3-----	3-----	-----	-----	0.1-----	330	14
3-----	3-----	-----	-----	3-----	310	13
0.5-----	0.5-----	-----	-----	0.5-----	170	27

EXAMPLE 4

Zinc oxide containing the additions of Table 5 is fabricated into voltage variable resistors by the same process as that of Example 1. The *n*-values of the resulting resistors are shown in Table 5. It will be readily understood that the combination of manganese oxide with one oxide selected from the group consisting of barium oxide and cobalt oxide as additive results in an excellent voltage nonlinear property.

TABLE 5

Mole percent				C (at 1 ma.)	<i>n</i>
MnO	BaO	CoO	-----		
0.05-----	0.05-----	-----	-----	850	5.1
0.05-----	0.5-----	-----	-----	460	9.2
0.05-----	8-----	-----	-----	800	4.6
0.5-----	0.05-----	-----	-----	400	6.1
0.5-----	8-----	-----	-----	410	6.0
10-----	0.05-----	-----	-----	920	4.8
10-----	0.5-----	-----	-----	420	9.5
10-----	8-----	-----	-----	610	6.1
0.1-----	0.1-----	-----	-----	325	7.9
0.1-----	0.5-----	-----	-----	255	12
0.5-----	0.1-----	-----	-----	350	7.8
0.5-----	3-----	-----	-----	270	8.8
3-----	0.1-----	-----	-----	290	8.8
3-----	0.5-----	-----	-----	410	8.0
3-----	3-----	-----	-----	300	12
0.5-----	0.5-----	-----	-----	390	7.3
0.05-----	0.05-----	-----	-----	205	13
0.05-----	0.5-----	-----	-----	700	8.0
0.05-----	8-----	-----	-----	350	11
0.5-----	0.05-----	-----	-----	650	6.0
0.5-----	0.5-----	-----	-----	390	7.0
0.5-----	8-----	-----	-----	385	7.1
10-----	0.05-----	-----	-----	820	6.0
10-----	0.5-----	-----	-----	415	9.8
10-----	8-----	-----	-----	510	6.0
0.1-----	0.1-----	-----	-----	320	9.0
0.1-----	0.5-----	-----	-----	220	13
0.1-----	3-----	-----	-----	320	9.1
0.5-----	0.1-----	-----	-----	255	8.3
0.5-----	3-----	-----	-----	260	9.0
3-----	0.1-----	-----	-----	315	9.1
3-----	0.5-----	-----	-----	250	13
3-----	3-----	-----	-----	345	9.7
0.5-----	0.5-----	-----	-----	175	14

EXAMPLE 5

Zinc oxide incorporated with manganese oxide and calcium oxide in the compositions of Table 6 is fabricated into voltage variable resistors by the same process as that of Example 1. The resulting resistors are tested according to the methods used in the electronic components parts. The load life test is carried out at 70° C. ambient tempera-

ture at 0.5 watt rating power for 500 hours. The heating cycle test is carried out by repeating 5 times the 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. Table 6 shows a difference in the C-value and *n*-value between resistors before and after the load life test and the heating cycle test. It can be readily realized that the combination of manganese oxide and calcium oxide as an additive is effective for electrical and environmental stability.

TABLE 6

Mole percent		Load life test, percent		Heating cycle test, percent	
MnO	CaO	ΔC	Δ <i>n</i>	ΔC	Δ <i>n</i>
0.05	0.05	-8.6	-9.2	-8.5	-9.0
0.05	0.5	-6.2	-6.2	-7.2	-7.1
0.05	8	-5.9	-6.0	-7.1	-6.0
0.5	0.05	-8.7	-8.5	-6.3	-6.0
0.5	8	-8.9	-8.4	-7.2	-7.8
10	0.05	-7.3	-7.1	-6.9	-6.3
10	0.5	-6.0	-6.6	-6.8	-6.1
10	8	-9.0	-9.3	-9.1	-8.7
0.1	0.1	-4.2	-4.2	-4.2	-4.0
0.1	0.5	-2.8	-3.0	-3.8	-3.2
0.1	3	-4.0	-3.7	-4.1	-3.3
0.5	0.1	-3.0	-4.6	-2.6	-4.8
0.5	3	-2.6	-4.2	-2.7	-4.7
3	0.1	-2.8	-3.6	-3.0	-3.4
3	0.5	-3.0	-2.9	-3.7	-3.7
3	3	-3.7	-4.7	-4.9	-3.9
0.5	0.5	-1.5	-1.2	-1.2	-0.8

EXAMPLE 6

Zinc oxide containing the additions of Table 7 is fabricated into voltage variable resistors by the same process as that of Example 1. The electrical properties of the resulting resistors are shown in Table 7. It will be easily realized that the combination of manganese oxide and bismuth oxide with one oxide selected from the group consisting of strontium oxide, lead oxide and uranium oxide as additives results in a remarkably excellent *n*-value and at the same time in a lower C-value.

TABLE 7

Mole percent					C (at 1 ma.)	<i>n</i>
MnO	Bi ₂ O ₃	SrO	PbO	UO ₂		
0.05	0.05	0.05			600	4.6
0.05	0.05	8			590	4.7
0.05	8	0.05			575	4.3
0.05	8	8			560	4.2
10	0.05	0.05			700	4.5
10	0.05	8			450	4.6
10	8	0.05			480	4.5
10	8	8			470	4.6
0.1	0.1	0.1			200	7.1
0.1	0.1	3			205	7.0
0.1	3	0.1			205	6.9
0.1	3	3			195	7.0
3	0.1	0.1			220	7.0
3	0.1	3			200	7.0
3	3	0.1			210	7.1
3	3	3			200	7.1
0.5	0.5	0.5			75	12
0.05	0.05		0.05		600	4.1
0.05	0.05		8		600	4.4
0.05	8		0.05		620	4.1
0.05	8		8		605	4.5
10	0.05		0.05		620	4.5
10	0.05		8		600	4.7
10	8		0.05		550	4.5
10	8		8		420	4.7
0.1	0.1		0.1		210	7.3
0.1	0.1		3		200	7.1
0.1	3		0.1		200	7.0
0.1	3		3		210	7.4
3	0.1		0.1		200	7.0
3	0.1		3		200	7.1
3	3		0.1		205	7.1
3	3		3		195	7.3
0.5	0.5		0.5		65	14
0.05	0.05			0.05	520	6.1
0.05	0.05			8	550	4.5
0.05	8			0.05	530	6.0
0.05	8			8	560	4.6
10	0.05			0.05	700	4.7
10	0.05			8	400	4.8
10	8			0.05	680	4.5
10	8			8	395	4.7
0.1	0.1			0.1	200	7.3
0.1	0.1			3	180	8.0
0.1	3			0.1	205	7.5
0.1	3			3	175	7.8
3	0.1			0.1	200	7.3
3	0.1			3	190	7.6
3	3			0.1	205	7.3
3	3			3	200	7.7
0.5	0.5			0.5	85	14

EXAMPLE 7

Zinc oxide containing the additions of Table 8 is fabricated into voltage variable resistors by the same process as that of Example 1. The resulting resistors are tested under the same conditions as that of Example 5. The initial *n*-values and change rates of the C- and *n*-values of the resistors are shown in Table 8. It can be easily realized that the initial *n*-values of the resistors are elevated and at the same time stability for the electrical and environmental load tests is excellent by using manganese oxide, lead oxide and calcium oxide as additives.

TABLE 8

Mole percent				Load life test, percent		Heating cycle test, percent	
MnO	PbO	CaO	<i>n</i>	ΔC	Δ <i>n</i>	ΔC	Δ <i>n</i>
0.05	0.05	0.05	5.2	-7.8	-8.0	-8.1	-7.9
0.05	0.05	8	5.3	-6.8	-7.1	-7.4	-7.8
0.05	8	0.05	5.4	-6.7	-6.6	-6.2	-6.6
0.05	8	8	5.7	-6.0	-5.9	-7.8	-7.7
10	0.05	0.05	6.1	-6.8	-6.9	-6.5	-6.6
10	0.05	8	5.9	-6.2	-6.0	-8.1	-8.0
10	8	0.05	6.3	-5.7	-5.8	-7.4	-7.5
10	8	8	6.5	-6.3	-6.0	-8.3	-8.0
0.1	0.1	0.1	10	-4.2	-3.9	-4.2	-4.0
0.1	0.1	3	11	-3.9	-4.0	-4.1	-4.3
0.1	3	0.1	11	-3.4	-3.6	-3.9	-4.0
0.1	3	3	12	-3.7	-3.8	-3.6	-4.0
3	0.1	0.1	11	-2.9	-3.4	-3.4	-3.4
3	0.1	3	10	-3.6	-3.9	-2.8	-3.1
3	3	0.1	11	-3.2	-3.3	-3.1	-3.4
3	3	3	12	-2.8	-3.0	-2.2	-2.9
0.5	0.5	0.5	17	-1.4	-1.2	-0.9	-1.1

What is claimed is:

1. A voltage variable resistor ceramic composition consisting essentially of zinc oxide and 0.05 to 10.0 mole percent of manganese oxide.

2. A voltage variable resistor ceramic composition as claimed in claim 1, wherein said composition consists essentially of zinc oxide and 0.1 to 3.0 mole percent of manganese oxide.

3. A voltage variable resistor ceramic composition as claimed in claim 1, wherein said composition further includes 0.05 to 8.0 mole percent of one oxide selected from the group consisting of barium oxide and cobalt oxide.

4. A voltage variable resistor ceramic composition as claimed in claim 2, wherein said composition further includes 0.1 to 3.0 mole percent of one oxide selected from the group consisting of barium oxide and cobalt oxide.

5. A voltage variable resistor ceramic composition as claimed in claim 1, wherein said composition further includes 0.05 to 8.0 mole percent of one oxide selected from the group consisting of strontium oxide, lead oxide, uranium oxide and calcium oxide.

6. A voltage variable resistor ceramic composition as claimed in claim 2, wherein said composition further includes 0.1 to 3.0 mole percent of one oxide selected from the group consisting of strontium oxide, lead oxide, uranium oxide and calcium oxide.

7. A voltage variable resistor ceramic composition as claimed in claim 1, wherein said composition further includes 0.05 to 8.0 mole percent of bismuth oxide and 0.05 to 8.0 mole percent of one oxide selected from the group consisting of strontium oxide, lead oxide and uranium oxide.

8. A voltage variable resistor ceramic composition as claimed in claim 2, wherein said composition further includes 0.1 to 3.0 mole percent of bismuth oxide and 0.1 to 3.0 mole percent of one oxide selected from the group consisting of strontium oxide, lead oxide and uranium oxide.

9. A voltage variable resistor ceramic composition as claimed in claim 1, wherein said composition further in-

3,598,763

9

cludes 0.05 to 8.0 mole percent of lead oxide and 0.05 to 8.0 mole percent of one oxide selected from the group consisting of barium oxide, strontium oxide, cobalt oxide and calcium oxide.

10. A voltage variable resistor ceramic composition as claimed in claim 2, wherein said composition further includes 0.1 to 3.0 mole percent of lead oxide and 0.1 to 3.0 mole percent of one oxide selected from the group consisting of barium oxide, strontium oxide, cobalt oxide and calcium oxide.

5

10

10

References Cited

UNITED STATES PATENTS

2,258,646	10/1941	Grisdale	252—579
2,892,988	6/1959	Schusterius	252—520

DOUGLAS J. DRUMMOND, Primary Examiner

U.S. Cl. X.R.

252—521