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SINTERED SILICON CARBIDE VARISTORS

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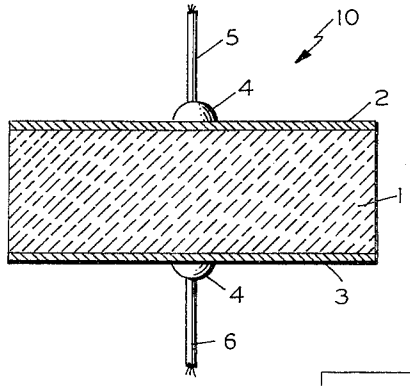


FIG.1

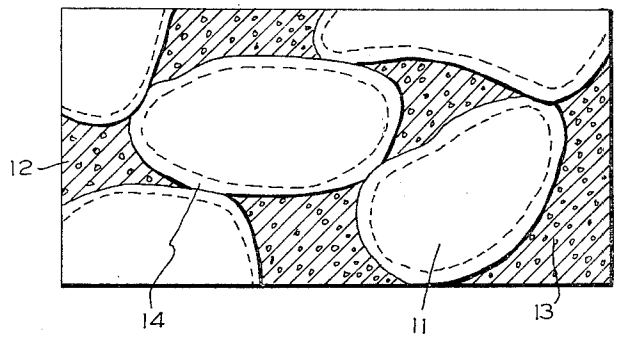


FIG.2

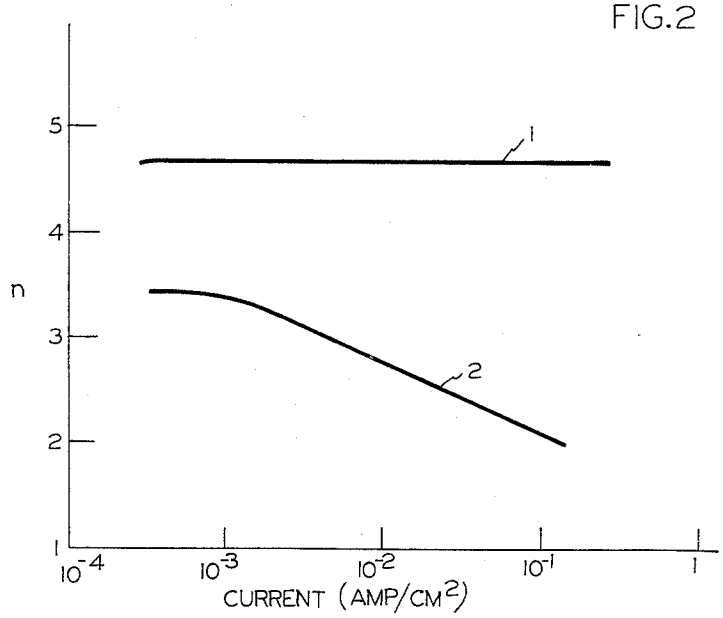


FIG.3

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SINTERED SILICON CARBIDE VARISTORS

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5 Claims

ABSTRACT OF THE DISCLOSURE

A silicon carbide varistor having a low varistor voltage C and a high *n*-value which does not decrease with increase in current flow is made by mixing fine particles of silicon carbide with water, ceramic binder and pulverulent copper carbonate, and then drying and firing the pressed body at 1080° C. to 1400° in an inert gas or in hydrogen, the proportions of ingredients being such that the final product contains 5 to 9 weight parts of silicon carbide, 1 to 5 weight parts of ceramic binder and 0.1 to 1 weight part of copper, the latter being partly dispersed in said ceramic binder and partly diffused in the surface layer of said silicon carbide particles. Such varistor is useful in electronic equipment such as transistor radio and transistor TV. Graphite may be added.

This invention relates to silicon carbide varistors having non-ohmic resistance and to a method for making the same.

Silicon carbide varistors are ordinarily manufactured by mixing fine particles of silicon carbide with water and ceramic binder, pressing the mixture in a mold to the desired shape, and then drying and firing the pressed body. The electrical characteristics of such a varistor are expressed by the relation:

$$I=(V/C)^n$$

where V is the voltage across the varistor, I is the current flowing through the varistor, C is a constant which is named conveniently varistor voltage and is equivalent to a voltage at a given current, and 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.

The desired value of C depends upon the particular use to which the varistor is to be put. It is ordinarily desirable that the value of n be as large as possible since this exponent determines the degree to which the varistor departs from ohmic characteristics.

Recent progress in electronic equipment such as transistor TV has required a varistor having a varistor voltage as low as C_{10}=30 v. and an n-value as high as possible. The notation C_{10}=30 v. means that a current of 10 ma. produces a voltage of 30 v. across the two ends of the varistor. Such requirement has been partly satisfied by a silicon carbide varistor which includes graphite powder. However, it has been difficult for the conventional silicon carbide varistor to achieve a low varistor voltage C and a high n-value. In addition, the n-value of a conventional silicon carbide varistor is apt to decrease with an increase in the current flowing through the varistor.

An object of the present invention is to provide a silicon carbide varistor having a low varistor voltage C and a high n-value.

A further object of the present invention is to provide a silicon carbide varistor having a high n-value which does not decrease with an increase in the current flowing through the varistor.

A further object of the present invention is to provide a method for making a varistor characterized by a low varistor voltage and a high n-value which does not decrease with an increase in the current flowing through the varistor.

The objects are achieved according to the present invention, presently-preferred embodiments of which are set forth in the following detailed description, with reference to the accompanying drawings, of which:

FIG. 1 shows a cross-sectional view of a varistor according to the present invention.

FIG. 2 shows an enlarged cross-section of a varistor element according to the present invention.

FIG. 3 shows a graphical illustration of a comparison of I–n curves between a conventional varistor and a varistor according to the present invention.

Before proceeding with a detailed description of the nature of a varistor embodying the invention, the construction of a form of a varistor will be described with reference to the drawing of FIG. 1, wherein **10** indicates generally a varistor having, as its active element, a sintered body **1** composed of a composition contemplated by the present invention.

The sintered body **1** is provided on two opposite surfaces with electrodes **2** and **3**. The sintered body **1** has any suitable shape, for example, disc, square, plate or bar in a cylinder 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. The relationship of these parts is per se conventional.

The sintered body **1** comprises 5 to 9 weight parts of silicon carbide particles, 0.1 to 1 weight part of copper and 1 to 5 weight parts of ceramic binder which bonds said silicon carbide particles together. Said ceramic binder is composed of any ceramic material inert to silicon carbide particles at high temperature in non-oxidizing ambient, such as clay, pottery stone, refractory oxide and their combinations. A high amount of ceramic binder results in a high-electrical resistivity of the varistors and a low amount thereof produces poorly sintered varistors. Desirable proportions of the ceramic binder to silicon carbide are 1 to 5 weight parts of ceramic binder to 5 to 9 weight parts of silicon carbide particles.

Referring to FIG. 2, silicon carbide particles **11** are bonded together by means of ceramic binder **12** surrounding said silicon carbide particles **11**. Finely divided copper powder **13** is dispersed in said ceramic binder **12**. The surface layer **14** of said silicon carbide particles **11** has copper atoms diffused therein.

According to the present invention, a varistor element having such a structure shows a low varistor voltage C

and a high n-value which does not decrease with an increase in the current flowing through the varistor element.

Referring to FIG. 3, curve **1** is an I–n curve of a varistor comprising copper partly dispersed in the ceramic binder and partly diffused into the surface layer of silicon carbide particles and curve **2** is an I–n curve of a conventional varistor comprising no copper. For easy comparison, the two varistors are similar to each other in the weight proportion of silicon carbide particles to the ceramic binder. The weight proportion is 5.0 weight parts of silicon carbide particles to 4.0 weight parts of the ceramic binder. The varistor according to the present invention includes 0.5 weight parts of copper. The two varistor voltages C are $V_{10}=24$ and $V_{10}=80$ for the novel varistor and the conventional varistor, respectively. It will be readily understood that the novel varistor having the structure of FIG. 2 has the low varistor voltage and the high n-value which does not decrease with increase in the current.

For convenience, a current coefficient of n-value will be defined as

$$\frac{n_1-n_2}{n_1}\times 100\%$$

wherein n_1 and n_2 are n-values 1 ma. and 100 ma. of current respectively.

The thickness of said surface layer **14** varies with heating temperature and heating time. It is not easy to measure the exact thickness of said surface layer **14**. When the sintered body is immersed in HF solution, the SiC particles **11** do not dissolve in the HF solution but the ceramic binder **12** and dispersed copper **13** dissolve into the HF solution. A chemical analysis of SiC particles separated from the ceramic binder indicates that copper diffuses into the SiC particles. There is a difference in the n-value and varistor voltage C between aggregate of original SiC particles and that of the SiC particles separated from the ceramic binder. Such difference further supports the diffusion of copper into the SiC particles. When the SiC particles separated from the ceramic binder are heated at 1000° C. in air, they are covered at the surface thereof with SiO_2 film formed by partial oxidation of SiC. The SiO_2 film dissolves into the HF solution. A repetition of air-heating and HF treatment removes the surfaces layer of the SiC particles. The removal of the surface layer of SiC particles which are separated from the ceramic matrix causes the SiC particles to have an n-value and a varistor-voltage C similar to those of the original SiC particles.

According to the present invention, an addition of graphite powders dispersed in the ceramic binder causes the varistor element to have a lower varistor voltage C without degrading the n-value in association with the copper dispersed in the ceramic matrix and diffused in the surface layer. Operable particle size of said graphite particles ranges from 0.1μ to 50μ. Operable weight proportion of said graphite powder to said ceramic matrix is 4 to 14 wt. percent of graphite powder to 86 to 96 wt. percent of ceramic matrix in accordance with the present invention.

Operable particle size of said silicon carbide particles ranges from 30 to 200μ. Any available silicon carbide particles can be used as the starting raw materials.

The best results are obtained with the varistor element comprising 6 to 8 weight parts of silicon carbide particles, 2 to 4 weight parts of ceramic matrix and 0.1 to 0.5 weight part of copper, part of which disperses in said ceramic matrix and another part of which diffuses in the surface layer of said silicon carbide particles. It is advantageous for achievement of lower varistor voltage C that said ceramic matrix has 4 to 14 wt. percent of graphite powder dispersed therein.

The varistor element having a structure shown in FIG. 2 is prepared by pressing a mixture of silicon carbide particles, ceramic binder, copper powder and, if necessary, graphite powder in a weight proportion described above, into desired shape; heating the pressed body for 30 minutes to 2 hours in non-oxidizing atmosphere such as nitrogen, argon, helium or hydrogen at a temperature higher than the melting point of copper, i.e. 1080° C. A heating temperature higher than 1080° C. is necessary to effect the surface layer of silicon carbide particles having copper diffused therein as shown in FIG. 2. The upper limit of the heating temperature is 1400° C. because a heating temperature higher than 1400° C. results in a low C varistor but in a poor n-value.

The starting copper powders have a particle size ranging preferably from 1 to 20μ. The starting copper powders can be replaced with any copper compounds which are converted into copper when heated together with the SiC particles in a nonoxidizing atmosphere at a temperature higher than 1080° C. Operable copper compounds are copper oxide (Cu_2O, and CuO), copper hydroxide [$Cu(OH)_2$] and copper carbonate ($CuCO_3$) in a finely divided powder form of 1 to 20μ.

According to the present invention, a varistor element heated in an inert gas such as nitrogen, argon or helium gas having an oxygen partial pressure of 1 to 20 mm. Hg produces a varistor voltage C lower than that of a varistor element heated in hydrogen or pure nitrogen. The n-value in the inert gas having an oxygen partial pressure of 1 to 20 mm. Hg is essentially the same as that in hydrogen or pure nitrogen.

Presently preferred illustrative embodiments of the invention are described in the following examples.

EXAMPLE 1

Mixtures of the composition listed in Table 1 are well mixed in a wet ball mill. The ceramic binder used is composed of crushed clay, crushed pottery stone and a small amount of flux. The total chemical ingredients in the binder are as follows: 72% SiO_2, 18% Al_2O_3, 0.50% Fe_2O_3, 1.0% CaO, 1.5% Mgo, 1.5% B_2O_3, 1.0% Na_2O and 1.0% K_2O, with 3.5% ignition loss by weight. The SiC particles are in a commercially available grade and include, as an impurity, 0.2 wt. percent of Al, 0.1 wt. percent of Fe and 0.02 wt. percent of nitrogen. The average grain size of the copper powder and Cu_2O is about 10μ and 2μ, respectively. The mixtures are dried and admixed with a small amount of water so as to be well compacted. The mixtures are pressed at 500 kg./cm.^{2} into discs. The pressed discs are heated in nitrogen gas having an oxygen partial pressure of about 1 mm. Hg at various temperatures for 1 hour as shown in Table 1.

The sintered discs are of a dimension of about 15 mm. in diameter and about 0.8 mm. thick. The sintered discs are provided on the opposite surfaces with zinc electrodes by the vacuum evaporation method. After completion by means of two lead wires, the varistors are tested for the n-value, varistor votlage C and the current dependence of I. The results are shown in Table 1.

EXAMPLE 2

Mixtures of compositions listed in Table 2 are prepared after the manner described in Example 1 and pressed at 500 kg./cm.^{2} into discs. The pressed discs are heated in H_2 at various temperatures for 1 hour as shown in Table 2. The sintered discs are of a dimension of about 15 mm. in diameter and about 0.8 mm. thick. The sintered discs are provided on the opposite surfaces with zinc electrodes by the vacuum evaporation method. After completion by addition of two lead wires, the varistors are tested for the n-value, varistor voltage C and the current dependence of I. The results are shown in Table 2.

EXAMPLE 3

Mixtures of compositions listed in Table 3 are prepared after the manner described in Example 1. Graphite powder used is of a commercially available grade. The other ingredients of the mixtures are similar to those of Example 1. The mixtures are pressed at 500 kg./cm.^{2} into discs. The pressed discs are heated in nitrogen gas having an oxygen partial pressure of about 1 mm. Hg. The sintered discs are provided on the opposite surfaces with zinc electrodes by the vacuum evaporation method. After completion by addition of two lead wires, the varistors are tested for the *n*-value, varistor voltage C and the current dependence of I. The results are shown in Table 3.

EXAMPLE 4

Mixtures of a composition similar ot that of No. 3 of Table 1 are pressed into discs in a way similar to that of Example 3. The pressed discs are heated for 1 hour at various temperatures in nitrogen gas having various oxygen partial pressures as shown in Table 4. The sintered discs are provided on the opposite surfaces with zinc electrodes by the vacuum evaporation method. After completion by addition of two lead wires, the varistors are tested for the *n*-value, varistor voltage C and the current dependence of I. The results are shown in Table 4.

TABLE 1

	Weight proportion				Heating temperature, ° C.	Electric characteristics of resultant resistor		
	Copper powder	Cu_2O	Ceramic binder	SiC particles		C at 10 mA	n	Current coefficient of n-value, percent
Sample No.:								
1			2.0	9.0	1,200	80	3.2	40
2		1.0	5.0	9.0	1,200	19	4.5	0
3		0.1	1.0	5.0	1,200	30	4.8	3
4		0.3	4.0	9.0	1,200	29	4.8	2
5		0.5	4.0	5.0	1,200	25	4.6	0
6		0.5	4.0	5.0	1,150	30	4.6	0
7		0.5	4.0	5.0	1,250	22	4.6	0
8		0.5	4.0	5.0	1,300	18	4.5	0
9	1.0		5.0	9.0	1,200	16	4.2	0
10	0.1		1.0	5.0	1,200	30	4.6	2
11	0.3		4.0	9.0	1,200	28	4.6	3
12	0.5		4.0	5.0	1,200	24	4.6	0
13	0.5		4.0	5.0	1,150	28	4.6	1
14	0.5		4.0	5.0	1,250	22	4.6	0
15	0.5		4.0	5.0	1,300	18	4.5	0

TABLE 2

	Weight proportion				Heating temperature, ° C.	Electric characteristics of resultant resistor		
	Copper powder	Cu_2O	Ceramic binder	SiC particles		C at 10 mA	n	Current coefficient of n-value, percent
Sample No.:								
16			2.0	9.0	1,200	96	3.4	40
17		1.0	5.0	9.0	1,200	23	4.8	0
18		0.1	1.0	5.0	1,200	36	5.5	2
19		0.3	4.0	9.0	1,200	34	5.4	3
20		0.5	4.0	5.0	1,200	30	5.1	0
21		0.5	4.0	5.0	1,150	32	5.1	1
22		0.5	4.0	5.0	1,250	27	5.1	0
23		0.5	4.0	5.0	1,300	22	4.9	0
24	1.0		5.0	9.0	1,200	18	4.8	0
25	0.1		1.0	5.0	1,200	33	5.1	1
26	0.3		4.0	9.0	1,200	30	5.1	3
27	0.5		4.0	5.0	1,200	28	5.1	0
28	0.5		4.0	5.0	1,150	33	5.1	1
29	0.5		4.0	5.0	1,250	24	5.0	0
30	0.5		4.0	5.0	1,300	22	4.9	0

TABLE 3

	Weight proportion				Heating temperature° C.	Electric characteristics of resultant resistor		
	Graphite	Cu_2O	Ceramic binder	SiC particles		C at 10 mA	n	Current coefficient of n-value, percent
Sample No.:								
31		1.0	4.0	9.0	1,200	21	4.8	0
32	0.16	1.0	4.0	9.0	1,200	18	5.2	0
33	0.30	1.0	4.0	9.0	1,200	12	5.2	0
34	0.16	0.5	4.0	5.0	1,200	24	5.5	0
35	0.30	0.5	4.0	5.0	1,200	20	5.3	0
36	0.45	0.5	4.0	5.0	1,200	15	5.3	0
37	0.56	0.5	4.0	5.0	1,200	10	4.8	0
38	0.30	0.3	3.0	7.0	1,200	16	5.3	0
39	0.30	0.3	2.0	7.0	1,200	15	5.2	0
40	0.30	0.3	2.0	7.0	1,150	15	5.2	0
41	0.30	0.3	2.0	7.0	1,250	15	5.2	0
42	0.30	0.3	2.0	7.0	1,300	15	5.1	0

TABLE 4

Sample No.	Oxygen partial pressure (mm. Hg)	Firing temperature, ° C.	Electric characteristics of resultant resistor: C at 10 mA	n	Current coefficient of n-value, percent
43	0.2	1,200	50	5.0	2
44	0.5	1,200	40	4.8	1
45	1	1,200	30	4.8	0
46	4	1,200	20	4.8	0
47	7	1,200	14	4.7	−1
48	10	1,200	20	4.8	0
49	20	1,200	28	4.8	0
50	50	1,200	70	5.0	5
51	1	1,300	25	4.8	0
52	4	1,300	18	4.8	0
53	7	1,300	13	4.7	−1
54	10	1,300	17	4.8	0
55	20	1,300	22	4.8	0
56	1	1,100	40	5.0	1
57	4	1,100	30	5.0	0
58	7	1,100	17	4.9	0
59	10	1,100	30	5.0	0
60	20	1,100	35	5.1	0
61	0.02	1,200	60	5.1	3

What is claimed is:

1. A sintered varistor element consisting essentially of 5 to 9 parts by weight of silicon carbide particles, 0.1 to 1 part by weight of copper and 1 to 5 parts by weight of a ceramic binder.

2. A sintered varistor element as defined by claim **1**, wherein said copper is partly dispersed in said ceramic matrix and partly diffused in the surface layer of said silicon carbide particles.

3. A sintered varistor element as defined by claim **2**, wherein said ceramic matrix has 4 to 14 wt. percent of graphite powder dispersed therein.

4. A sintered varistor consisting essentially of 6 to 8 parts by weight of silicon carbide particles, 2 to 4 by weight parts of a ceramic matrix and 0.1 to 0.5 part by weight of copper, part of which is dispersed in said ceramic matrix and part of which is diffused in the surface layer of said silicon carbide particles.

5. A sintered varistor element as defined by claim **4**, wherein said ceramic matrix has 4 to 14 wt. percent of graphite powder dispersed therein.

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