

Description

This invention relates to a novel electroconductive composition in paste form, and more specifically to such an electroconductive paste to be baked or fired on ceramic bodies for use as conductors or electrodes of ceramic capacitors, varistors or the like.

Further the invention relates to a method of forming conductors or electrodes on a ceramic substrate to provide a capacitor, varistor or the like, whereby the electroconductive paste according to the invention is baked on the ceramic substrate.

US-A-3 784 407 describes an electroconductive paste comprising zinc powder, a glass frit, an additive, e.g. Cu or Pb, and a vehicle for pasting the mixture of the zinc powder, the glass frit and the additive. This paste, however, is used in the fabrication of resistors. Moreover, US-A-4 168 519 describes an electroconductive paste comprising zinc powder, tin powder, a frit and a vehicle for pasting the mixture of zinc powder, tin powder and frit.

As is well known in the fabrication of ceramic capacitors or ceramic varistors, the conductors or electrodes are formed by baking the coatings of electroconductive pastes on ceramic bodies. Typical of such pastes as heretofore used is what is known as a silver paste, composed of powdered silver, a glass frit, and a vehicle or the liquid ingredient or ingredients of the paste. The silver paste is itself an excellent material for the purposes. When used for the conductors of ceramic capacitors, for example, it can provide desired capacitance, dielectric loss tangent (the tangent of the dielectric loss angle), and a firm bond between the conductors and ceramic bodies of the capacitors. Offsetting all these advantages, however, is the expensiveness of silver, a precious metal, which adds considerably to the costs of the electrical components.

The present invention solves the problem of the prior art by providing a materially less expensive substitute for the silver paste. Although inexpensive, the electroconductive paste in accordance with the invention provides the desired electrical properties in its intended use as conductors or electrodes of ceramic capacitors, variators or the like. Further the conductors or electrodes made from the inventive paste adhere to the ceramic bodies with sufficient strength.

Stated broadly, the electroconductive paste in accordance with the invention is composed of 100 parts by weight of zinc powder in the form of spherical particles, from about 0.01 to 10.00 parts by weight of a glass frit, from about 0.01 to 5.00 parts by weight of an additive selected from the class consisting of Pb, Bi, Pr, Cu, Cd, and the compounds of the listed metallic elements, and a vehicle for pasting the mixture of the zinc powder, the glass frit and the additive.

The zinc paste, as the electroconductive paste of this invention will hereinafter be so called for simplicity, is not just a cheap substitute for the silver paste. When the zinc paste is used as the conductors of strontium titanate ceramic semiconductor capacitors, for example, by being fired on the ceramic bodies, the capacitance of the capacitors is even higher than that of conventional capacitors with their conductors made from the silver paste. Thus the zinc paste can reduce the size of capacitors of this class for a given capacitance. To give another example, titanium dioxide ceramic varistors having their electrodes made from the zinc paste are just as excellent in electrical and mechanical properties as those having the conventional silver electrodes. Both of these applications of the zinc paste will be discussed in more detail in the subsequent disclosure of specific Examples of the invention.

Among the advantages offered by the zinc paste is that it admits of baking or firing in atmosphere. This is because, filling the interstices of the zinc powder, the glass ingredients of the paste limits the oxidation of the individual zinc particles. For this reason the electrical ceramic components with the zinc conductors or electrodes are mass producible at reduced costs. As regards the inexpensiveness of the zinc paste itself, suffice it to say that powdered zinc is available at approximately 1/200 the cost of powdered silver.

The above and other features and advantages of this invention and the manner of attaining them will become more apparent, and the invention itself will best be understood, from a study of the following detailed description taken together with the attached drawings, in which:—

Figure 1 is a fragmentary sectional view diagrammatically illustrating, on a greatly magnified scale, a conductive region formed on a ceramic body from the zinc paste of this invention, the view being explanatory of the way in which the unoxidized interiors of the zinc particles become fused to each other on baking;

Figure 2 is a diametrical section through a ceramic capacitor having conductors made from the zinc paste;

Figure 3 is a plan view explanatory of the way in which the ceramic capacitor is tested as to the strength with which the conductors adhere to the ceramic body against tensile stress;

Figure 4 is a diametrical section through another example of ceramic capacitor having conductors made from the zinc paste; and

Zinc powder constituting the principal ingredient of the zinc paste of this invention is in the form of spherical particles with preferably a size of not more than about 15 μm . In practice, however, the particle size can average from about 0.1 to 30.0 μm .

From about 0.01 to 10.00 parts by weight, preferably from one to five parts by weight, of a glass frit or frits is added to 100 parts by weight of zinc powder. The glass frit is intended to function as inorganic binder and oxidation inhibitor. Should the proportion of the glass frit be less than about 0.01 part by weight, it

would hardly perform these functions and would give rise to fluctuations in some physical properties of the ceramic components concerned on mass production. If the glass frit content of the zinc paste were more than about 10 parts by weight, on the other hand, then the conductors or electrodes made from the paste would offer too much electrical resistance and would make the dielectric loss tangent of the capacitors too high.

Preferred examples of glass frits include those composed of litharge (PbO), boric oxide (B_2O_3) and silica (SiO_2), of PbO and B_2O_3 , and of zinc oxide (ZnO), B_2O_3 and SiO_2 , all with a softening point ranging from about 415° to 625°C . and with about 0.043 mm (325-mesh) particles. Other frit compositions are adoptable as well, such as those comprising any two or more of such metal oxides as PbO , B_2O_3 , SiO_2 , ZnO , red lead oxide (Pb_3O_4), barium oxide (BaO), zirconium oxide (ZrO_2), calcium carbonate (CaCO_3), aluminum oxide (Al_2O_3), and bismuth trioxide (Bi_2O_3). The softening points of such adoptable glass frits can be in the range of about 400° — 800°C .

A preferred example of the vehicle for pasting the mixture of zinc powder and a glass frit or frits is alpha-terpineol containing from two to 20% by weight ethylcellulose as an organic binder, or that containing from two to 20% by weight nitrocellulose or polyvinyl alcohol. Instead of alpha-terpineol as a solvent there may be employed butyl "Carbitol" (trademark for diethylene glycol mono-n-butyl ether), butyl "Carbitol" acetate (trademark for diethylene glycol mono-n-butyl ether acetate), or dioctyl phthalate.

Whichever substance is employed, the vehicle will evaporate when the zinc paste is baked on ceramic bodies, and so will be substantially absent from the completed conductive regions on the ceramic bodies. Thus a wide variety of well known organic vehicles find use as a pasting agent within the scope of this invention.

Any selected vehicle is to be used in an amount suitable for pasting the zinc mixture. The amount of the vehicle normally ranges from 10 to 50% by weight, preferably from 15 to 25% by weight, and most desirably from 19 to 21% by weight, of the combined weight of zinc powder and a glass frit or frits, together with an additive or additives to be referred to subsequently. The viscosity of the paste would become too high if the amount of the vehicle were less than 10% by weight, and too low if the amount of the vehicle were more than 50% by weight.

Such being the basic composition of the zinc paste in accordance with the invention, it will now be discussed how it forms conductive regions on ceramic bodies when fired. The discussion will make clear that the use of zinc powder as the main ingredient of the paste is no arbitrary choice but an outcome of extensive experimentation.

Figure 1 is explanatory of the unique behavior of the zinc paste on firing. This figure is a greatly enlarged, fragmentary section through, for instance, a ceramic capacitor comprising a conductor 10 and a ceramic body 12. The conductor 10 is made from the zinc paste, coated on the ceramic body 12 and baked for several tens of minutes at a temperature above the melting point (419.5°C .) of the zinc powder. When so treated, each zinc particle 14 is oxidized and bears an oxide cladding 16. The oxidation of the zinc powder does not proceed deep into each particle 14 as the glass 18 fills the interstices of the zinc powder. Further, while being baked, the unoxidized interiors 20 of the zinc particles 14 melt and expand at a greater rate than their oxide claddings 16, until the zinc interiors disrupt the oxide claddings and become fused to each other to form the conductor 10. Thus the zinc paste is well suited as a material for conductors or electrodes of some electrical ceramic components. It may be noted that the fusion of the unoxidized interiors of zinc particles to each other on baking involves a process different from the cohesion of metal particles by sintering.

As had been mentioned, the zinc paste of this invention additionally comprise from about 0.01 to 5.00 parts by weight of one or more of the additives lead (Pb), bismuth (Bi), praseodymium (Pr), copper (Cu), cadmium (Cd), and the compounds of each of these metallic elements. The zinc paste containing such an additive or additives, when baked on ceramic bodies, will adhere thereto more firmly. If used for the conductors of ceramic capacitors, moreover, the zinc paste with such an additive or additives will afford higher capacitance and smaller dielectric loss tangent.

More specific, preferred examples of the additives are the oxides of the listed metallic elements such as Pb_3O_4 , Bi_2O_3 , praseodymia (Pr_6O_{11}), black copper oxide (CuO), and cadmium oxide (CdO), with a particle size ranging from about 0.1 to $15.0\ \mu\text{m}$. Uncompounded metals such as those enumerated above are adoptable as well, however. The metals will be converted into oxides upon baking of the zinc paste. Additional examples of additives are PbO , lead dioxide (PbO_2), lead tetraacetate ($\text{Pb}(\text{CH}_3\text{COO})_4$), $\text{Pr}_2(\text{C}_2\text{H}_4\text{O}_2)_3$, red copper oxide (Cu_2O), and bismuth citrate ($\text{BiC}_6\text{H}_5\text{O}_7$). The hydroxides, salts such as carbonates and oxalates, and peroxides of the metals may also be employed.

Experiment has proved that if the proportion of the additive or additives is less than about 0.01 part by weight, no substantial improvements result in such properties of the electrical components as capacitance, dielectric loss tangent, and the strength with which the conductive regions adhere to the ceramic bodies against tensile loading. Such properties may also fluctuate considerably from component to component on mass production if the additive content of the paste is insufficient. If the amount of the additive or additives exceeds about five parts by weight, on the other hand, then the tensile strength will decrease, and the dielectric loss tangent in particular will deteriorate.

Described hereinbelow are Examples of the invention, dealing with specific examples of the zinc paste as actually produced in accordance with the principles of the invention, and the physical properties of the

ceramic capacitors and varistors having conductors or electrodes made from the zinc paste examples. These Examples, however, are meant purely to illustrate or explain and not to impose limitations upon the invention.

5 Examples 1—20

As specified in Table 1, various proportions of $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ glass frit, ranging from 0.01 to 10.00 parts by weight, and various proportions of powdered Pb_3O_4 as an additive, ranging from 0.01 to 5.00 parts by weight, were added to 100 parts by weight of zinc powder. The Pb_3O_4 powder had a particle size from 0.1 to 15.0 μm . About 20% by weight of the vehicle set forth below was admixed with the various mixtures of the noted ingredients. The admixtures were agitated for 15 hours thereby preparing the twenty zinc pastes of Examples 1—20. Capacitors were produced by use of these zinc pastes through the procedure as given below and their capacitance, dielectric loss tangent, and tensile strength were measured by the below mentioned methods Table 1 represents the results.

The zinc powder in use was of spherical particles with diameters up to 15 μm and was of such purity as to contain about 0.01% by weight of impurities such as cadmium and iron. (The zinc powder used in all the other Examples presented subsequently was of the same grade). The glass frit in use was the mixture of six parts by weight PbO , two parts by weight B_2O_3 , and two parts by weight SiO_2 , having a softening point of 500°C. and 0.043 mm (325-mesh) particles. As the vehicle there was employed alpha-terpineol admixed with 5% by weight ethylcellulose as an organic binder. (The same vehicle was used in all the following Examples).

The above prepared examples of the zinc paste were each coated on opposite faces of each of several discs of ceramic semiconductor material composed principally of strontium titanate, SrTiO_3 , and were baked thereon. Figure 2 is a section through each ceramic capacitor 22 thus fabricated, showing the ceramic disc 24 and the pair of zinc conductors 26 on its opposite faces. A more detailed discussion of the ceramic capacitors and the method of their fabrication follows.

The ceramic discs 24 of the capacitors 22 were prepared from a mixture of 98.8 mole% SrTiO_3 , 0.8 mole% germanium dioxide, GeO_2 , and 0.4 mole% niobium oxide, Nb_2O_5 , admixed with polyvinyl alcohol as an organic binder. After having been agitated, the mixture was molded into discs at a pressure of approximately one ton per square centimeter. The disc-like moldings were baked for three hours at a temperature of 1420°C. in a furnace, in which there was a gaseous atmosphere of 98% by capacity of molecular nitrogen (N_2) and 2% by capacity of molecular hydrogen (H_2). The ceramic discs thus formed had each a diameter of eight millimeters (mm) and a thickness of 0.4 mm. The discs were then coated with a $\text{PbO-B}_2\text{O}_3\text{-Bi}_2\text{O}_3$ glass paste. The coated ceramic discs were heated and held at a temperature of 1200°C. for three hours, thereby causing diffusion of the glass ingredients into the ceramic to insulate its particles.

For the fabrication of the conductors on the opposite faces of each ceramic disc the zinc paste of the above specified composition was first "printed" on one face of the disc through a 0.074 mm (200-mesh) Teflon (trademark) screen. The coated discs were placed in a drying furnace for drying the coatings at 150°C. for 10 minutes. Then the zinc paste was coated on the other face of each disc, and the coatings were dried in the same manner. Then, placed on an iron net, the ceramic discs with the dried coatings were introduced into a tunnel-shaped heater, in which the coatings were baked at approximately 700°C., above the melting point of zinc, for 10 minutes in exposure to atmosphere. The coated ceramic discs were held in the heater for a total of 40 minutes including the time for raising and lowering its temperature. There were thus completed the conductors 26 of Figure 2, each having a diameter of 7.8 mm and a thickness of 15 μm .

As has been explained in conjunction with Figure 1, the heating of the zinc paste coatings in atmosphere, as above, causes oxidation of the zinc particles. Being surrounded by the glass, however, each zinc particle undergoes oxidation only to a limited depth from its surface. It has also been mentioned that the zinc paste of this invention is baked at a temperature above the melting point of zinc, unlike the conventional silver paste which is fired at a temperature below the melting point of silver. Thus the unoxidized interiors of the zinc particles melt and, disrupting the oxide claddings, become bridged to each other.

During such baking of the coatings the vehicle of the zinc paste evaporates. The zinc powder and the glass frit, on the other hand, combine as in Figure 1 by the baking to make up the conductors.

The ceramic capacitors with the zinc conductors prepared as above were tested as to capacitance, dielectric loss tangent, and the strength with which the conductors were bonded to the ceramic discs against pulling stress. Table 1 gives the results. In this and all the succeeding tables each listed value is the average of ten samples. Also, in all the tables given herein, the capacitance of the capacitors represents the values measured at a frequency of 1 kHz, in nanofarads (nF), and the dielectric loss tangent represents 100 times the values measured at 1 kHz. For the actual values of dielectric loss tangent, therefore, the tabulated figures should be multiplied by 10^{-2} .

Figure 3 explains the method adopted for measurement of the strength with which the zinc conductors 26 adhere to the ceramic disc 24 of each capacitor. There were first prepared two annealed copper wires 28 and 30 for each capacitor, each wire having a diameter of 0.6 mm and a length of 35.0 mm. Each wire was bent at a point approximately 4 mm from one end, as shown. The bent end of each wire was soldered to one of the conductors 26 of each capacitor with application of ultrasonic vibration. Then, with one wire 28 held against movement, the other was pulled slowly via a spring scale in the arrow marked direction, until

either of the conductors came off the ceramic disc 24. The reading in kilograms (kg) of the spring scale at that moment is given as the tensile strength of each capacitor.

The tabulated results indicate that the addition of Pb_3O_4 improves all the three properties in question of the capacitors, and in particular their dielectric loss tangent and tensile strength. The reason for this seems to be the improved state of the interfaces between the ceramic bodies and conductors of the capacitors due to the addition of Pb_3O_4 . Particular attention is directed to Example 11, which represents the zinc paste containing one part by weight of the glass frit and one part by weight of Pb_3O_4 . The properties of the capacitors formed by use of this zinc paste are better than those of the conventional capacitors with the silver conductors.

The proportion of Pb_3O_4 should range from about 0.01 to 5.00 parts by weight, preferably from 0.1 to 1.0 part by weight. Should the additive be used in an amount outside the range of 0.01 to 5.00 parts by weight, the dielectric loss tangent of the resulting capacitors would exceed the acceptable maximum of 1.5×10^{-2} .

TABLE 1

Examples	Paste ingredients		Capacitor properties		
	PbO-B ₂ O ₃ -SiO ₂ glass frit, weight part	Pb ₃ O ₄ (additive), weight part	Capacitance, nF	Dielectric loss tangent, $\times 10^{-2}$	Tensile strength, kg
1	0.01	0.01	55	1.40	1.1
2	0.01	0.10	56	1.32	1.2
3	0.01	1.00	61	0.88	1.3
4	0.01	5.00	55	1.44	1.1
5	0.10	0.01	59	1.03	1.8
6	0.10	0.10	60	0.98	1.9
7	0.10	1.00	63	0.65	2.0
8	0.10	5.00	58	1.07	1.7
9	1.00	0.01	61	0.86	2.0
10	1.00	0.10	61	0.82	2.0
11	1.00	1.00	64	0.55	2.1
12	1.00	5.00	60	0.89	1.6
13	5.00	0.01	58	1.12	1.6
14	5.00	0.10	58	1.06	1.7
15	5.00	1.00	62	0.71	1.7
16	5.00	5.00	57	1.16	1.4
17	10.00	0.01	56	1.39	1.1
18	10.00	0.10	56	1.31	1.2
19	10.00	1.00	61	0.88	1.2
20	10.00	5.00	54	1.43	1.0

Examples 24—40

As specified in Table 2, various proportions of $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ glass frit of Examples 1—20, ranging from 0.01 to 10.00 parts by weight, and various proportions of powdered Bi_2O_3 , an additive, ranging from 0.01 to 5.00 parts by weight, were added to 100 parts by weight of zinc powder. The Bi_2O_3 powder had a particle size ranging from 0.1 to 15.0 microns. About 20% by weight of the same vehicle as in Examples 1—20 was admixed with the various mixtures of the above ingredients. The admixtures were agitated for 15 hours to prepare the twenty different zinc pastes of Examples 21—40. Capacitors were fabricated by use of these zinc pastes through the same procedure as in Examples 1—20, and their capacitance, dielectric loss tangent, and tensile strength were measured by the same methods as in Examples 1—20. Table 2 represents the results. It will be observed from this table that the addition of Bi_2O_3 in the specified range of proportions gives just as favorable results as does the addition of Pb_3O_4 as in Examples 1—20.

TABLE 2

15	Paste ingredients			Capacitor properties		
	Examples	PbO-B ₂ O ₃ -SiO ₂ glass frit, weight part	Bi ₂ O ₃ (additive), weight part	Capacitance, nF	Dielectric loss tangent, ×10 ⁻²	Tensile strength, kg
20	21	0.01	0.01	55	1.41	1.1
	22	0.01	0.10	57	1.29	1.2
25	23	0.01	1.00	61	0.84	1.2
	24	0.01	5.00	55	1.45	1.1
	25	0.10	0.01	59	1.05	1.7
30	26	0.10	0.10	60	0.96	1.8
	27	0.10	1.00	63	0.62	1.9
35	28	0.10	5.00	58	1.08	1.7
	29	1.00	0.01	60	0.87	1.9
	30	1.00	0.10	59	0.80	2.0
40	31	1.00	1.00	64	0.52	2.1
	32	1.00	5.00	60	0.90	1.9
45	33	5.00	0.01	58	1.13	1.9
	34	5.00	0.10	58	1.04	1.5
	35	5.00	1.00	63	0.67	1.6
50	36	5.00	5.00	57	1.17	1.5
	37	10.00	0.01	55	1.40	1.1
55	38	10.00	0.10	57	1.28	1.2
	39	10.00	1.00	61	0.83	1.3
	40	10.00	5.00	54	1.47	1.1
60						

Examples 41—60

To 100 parts by weight of zinc powder there were added $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ glass frit of Examples 1—20 in various proportions ranging from 0.01 to 10.00 parts by weight, and powdered Pr_6O_{11} , an additive, in various proportions ranging from 0.01 to 5.00 parts by weight, as specified in Table 3. The Pr_6O_{11} powder

had a particle size from 0.1 to 15.0 microns. The various mixtures of the noted ingredients were admixed with about 20% by weight of the same vehicle as used in Examples 1—20. The admixtures were agitated for 15 hours to prepare the twenty different zinc pastes of Examples 41—60. Capacitors were fabricated by use of these zinc pastes through the same procedure as in Examples 1—20, and their capacitance, dielectric loss tangent, and tensile strength were measured also by the same methods as in Examples 1—20. Table 3 represents the results. It will be seen from this table that the addition of Pr_6O_{11} in the range of 0.01—5.00 parts by weight provides just as favorable results as does the addition of Pb_3O_4 as in Examples 1—20.

TABLE 3

Examples	Paste ingredients		Capacitor properties		
	$\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ glass frit, weight part	Pr_6O_{11} (additive), weight part	Capacitance, nF	Dielectric loss tangent, $\times 10^{-2}$	Tensile strength, kg
41	0.01	0.01	55	1.42	1.1
42	0.01	0.10	56	1.28	1.2
43	0.01	1.00	60	0.86	1.8
44	0.01	5.00	54	1.48	1.2
45	0.10	0.01	58	1.07	1.7
46	0.10	0.10	60	0.99	1.8
47	0.10	1.00	62	0.68	1.8
48	0.10	5.00	58	1.10	1.4
49	1.00	0.01	61	0.89	1.9
50	1.00	0.10	61	0.85	2.0
51	1.00	1.00	63	0.60	2.1
52	1.00	5.00	60	0.93	1.8
53	5.00	0.01	57	1.16	1.5
54	5.00	0.10	58	1.09	1.6
55	5.00	1.00	62	0.73	1.7
56	5.00	5.00	57	1.20	1.5
57	10.00	0.01	55	1.42	1.1
58	10.00	0.10	56	1.29	1.2
59	10.00	1.00	61	0.84	1.3
60	10.00	5.00	54	1.49	1.1

Examples 61—80

To 100 parts by weight of zinc powder there were added $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ glass frit of Examples 1—20 in various proportions ranging from 0.01 to 10.00 parts by weight, and powdered CuO , an additive, in various proportions ranging from 0.01 to 5.00 parts by weight, as listed in Table 4. The CuO powder had a particle size from 0.1 to 15.0 microns. The various mixtures of the zinc powder, glass frit and CuO powder were each admixed with about 20% by weight of the same vehicle as used in Examples 1—20. The admixtures were agitated for 15 hours thereby providing the twenty different zinc pastes of Examples 61—80.

Capacitors were fabricated by use of these zinc pastes through the same procedure as in Examples

1—20, and their capacitance, dielectric loss tangent, and tensile strength were measured also by the same methods as in Examples 1—20 Table V represents the results. It will be appreciated from the tabulated properties of the capacitors that the addition of CuO in the range of 0.01 to 5.00 parts by weight provides just as favorable results as does the addition of Pb₃O₄ as in Examples 1—20.

TABLE 4

10	Paste ingredients			Capacitor properties		
	Examples	PbO-B ₂ O ₃ -SiO ₂ glass frit, weight part	CuO (additive), weight part	Capacitance, nF	Dielectric loss tangent, ×10 ⁻²	Tensile strength, kg
15	61	0.01	0.01	55	1.43	1.1
	62	0.01	0.10	56	1.30	1.1
	63	0.01	1.00	61	0.87	1.2
20	64	0.01	5.00	55	1.43	1.1
	65	0.10	0.01	59	1.03	1.7
	66	0.10	0.10	60	0.99	1.7
25	67	0.10	1.00	63	0.66	1.8
	68	0.10	5.00	59	1.04	1.7
	69	1.00	0.01	60	0.90	1.8
30	70	1.00	0.10	61	0.84	2.1
	71	1.00	1.00	64	0.59	2.1
	72	1.00	5.00	60	0.92	1.9
35	73	5.00	0.01	58	1.16	1.6
	74	5.00	0.10	58	1.10	1.6
	75	5.00	1.00	60	0.90	1.7
40	76	5.00	5.00	57	1.21	1.5
	77	10.00	0.01	55	1.41	1.1
	78	10.00	0.10	56	1.30	1.2
45	79	10.00	1.00	60	0.95	1.3
	80	10.00	5.00	55	1.45	1.0

Examples 81—100

To 100 parts by weight of zinc powder there were added PbO-B₂O₃-SiO₂ glass frit of Examples 1—20 in various proportions ranging from 0.01 to 10.00 parts by weight, and powdered CdO, an additive, in various proportions ranging from 0.01 to 5.00 parts by weight, as set forth in Table 5. The CdO powder had a particle size from 0.1 to 15.0 microns. The various mixtures of the zinc powder, glass frit and CdO were each admixed with about 20% by weight of the same vehicle as used in Examples 1—20. The admixtures were agitated for 15 hours thereby providing the twenty different zinc pastes of Examples 81—100.

Capacitors were fabricated by use of these zinc pastes through the same procedure as in Examples 1—20, and their capacitance, dielectric loss tangent, and tensile strength were measured also by the same methods as in Examples 1—20. Table 5 represents the results. It will be seen from this table that the addition of CdO in the range of 0.01 to 5.00 parts by weight provides just as favorable results as does the addition of Pb₃O₄ as in Examples 1—20.

TABLE 5

5	Examples	Paste ingredients		Capacitor properties		
		PbO-B ₂ O ₃ -SiO ₂ glass frit, weight part	CdO (additive), weight part	Capacitance, nF	Dielectric loss tangent, ×10 ⁻²	Tensile strength, kg
	81	0.01	0.01	55	1.40	1.1
10	82	0.01	0.10	57	1.26	1.1
	83	0.01	1.00	61	0.84	1.2
15	84	0.01	5.00	55	1.42	1.1
	85	0.10	0.01	59	1.01	1.7
	86	0.10	0.10	60	0.92	1.9
20	87	0.10	1.00	63	0.64	2.0
	88	0.10	5.00	58	1.12	1.7
25	89	1.00	0.01	61	0.84	2.0
	90	1.00	0.10	61	0.79	2.1
	91	1.00	1.00	64	0.57	2.1
30	92	1.00	5.00	59	1.00	1.9
	93	5.00	0.01	57	1.14	1.6
35	94	5.00	0.10	58	1.05	1.7
	95	5.00	1.00	62	0.73	1.8
	96	5.00	5.00	57	1.20	1.7
40	97	10.00	0.01	55	1.41	1.1
	98	10.00	0.10	56	1.29	1.2
45	99	10.00	1.00	60	0.90	1.3
	100	10.00	5.00	55	1.44	1.2

50 Examples 101—112

These Examples were intended to ascertain the results of the use of two or more of the above enumerated additives in the zinc paste of this invention. Thus, to 100 parts by weight of zinc powder, there were added various proportions of PbO-B₂O₃-SiO₂ glass frit of Examples 1—20, ranging from 0.01 to 10.00 parts by weight, and 0.1 part by weight each of two or more of the powders of Pb₃O₄, Bi₂O₃, Pr₆O₁₁, CuO and CdO as additives, as specified in Table 6. The various mixtures of the zinc powder, glass frit and additives were each admixed with about 20% by weight of the same vehicle as used in Examples 1—20. The admixtures were agitated for 15 hours to prepare the twelve different zinc pastes of Examples 101—112.

Capacitors were made by use of these zinc pastes through the same procedure as in Examples 1—20, and their capacitance, dielectric loss tangent, and tensile strength were measured also by the same methods as in Examples 1—20. Table 6 represents the results. As will be understood from the tabulated results, the use of two or more of the above powdered metal oxides as additives provides just as favorable results as in the foregoing Examples. Although each zinc paste of Examples 101—112 contain 0.2—0.5 part by weight of the additives, experiment has proved that the total proportion of the additives can be anywhere between about 0.01 and 5.00 parts by weight. Such experiment is not presented here because the results are self-evident from the foregoing Examples 1—100.

TABLE 6

5	Examples	Paste ingredients		Capacitor properties		
		PbO-B ₂ O ₃ -SiO ₂ glass frit weight part	Additives (Each 0.1 weight part)	Capacitance, nF	Dielectric loss tangent, ×10 ⁻²	Tensile strength, kg
10	101	0.01	Pb ₃ O ₄ & Bi ₂ O ₃	59	0.96	1.2
	102	0.01	Bi ₂ O ₃ , Pr ₆ O ₁₁ & CuO	60	0.93	1.3
15	103	0.01	Bi ₂ O ₃ , Pr ₆ O ₁₁ & CuO	61	0.89	1.3
	104	0.01	Pb ₃ O ₄ , Bi ₂ O ₃ , Pr ₆ O ₁₁ , CuO & CdO	61	0.89	1.3
20	105	0.50	Bi ₂ O ₃ & Pr ₆ O ₁₁	61	0.85	1.8
	106	0.50	Pr ₆ O ₁₁ , CuO & CdO	62	0.80	1.8
25	107	5.00	Pb ₃ O ₄ , Pr ₆ O ₁₁ , CuO & CdO	63	0.74	1.8
	108	5.00	Pb ₃ O ₄ , Bi ₂ O ₃ , Pr ₆ O ₁₁ , CuO & CdO	63	0.69	1.9
30	109	10.00	Pr ₆ O ₁₁ & CuO	57	0.61	1.4
	110	10.00	Pb ₃ O ₄ , CuO & CdO	58	1.29	1.2
35	111	10.00	Pb ₃ O ₄ , Bi ₂ O ₃ , CuO & CdO	59	1.10	1.2
	112	10.00	Pb ₃ O ₄ , Bi ₂ O ₃ , Pr ₆ O ₁₁ , CuO & CdO	60	1.06	1.1

45 The foregoing Examples 1—112, concerning the zinc pastes containing additives in the form of metal oxides, all employ the PbO-B₂O₃-SiO₂ glass frit of the kind used in Examples 1—20, and do not deal with the glass frits of the other compositions, referenced B to H, listed below:

- 50 B PbO-B₂O₃-SiO₂; softening point (s.p.) 460°C.
 C: PbO-B₂O₃-SiO₂; s.p. 600°C.
 D: PbO-B₂O₃; s.p. 415°C.
 E: PbO-B₂O₃; s.p. 430°C.
 F: ZnO-B₂O₃-SiO₂; s.p. 560°C.
 65 G: ZnO-B₂O₃-SiO₂; s.p. 625°C.
 H: PbO-B₂O₃-SiO₂; s.p. 500°C.

As has been experimentally confirmed, however, the use of these glass frits B to H in combination with the metal oxides cited as preferred examples of additives provides results similar to those of Examples 1—112.

Admittedly, the conductors formed on ceramic bodies by use of the zinc paste of this invention are less solderable than the conventional silver conductors. The solderability of the zinc conductors is easy to improve, however, by covering the zinc conductors with layers of a less ionizable metal such as copper or nickel by electroless plating. Figure 4 shows at 32 such platings of more solderable metal on the zinc conductors 26 of capacitors. Alternatively such solderable overlayers may be formed by the plating, vapor

deposition, or coating of gold or silver. The use of the precious metals will not significantly add to the cost of the capacitors because the overlayers can be of minimal thickness.

Examples 113—115

These Examples deal with the applicability of the zinc pastes in accordance with the invention to the electrodes of ceramic varistors. The zinc pastes tested were identical in composition with those of Examples 1—20, 41—60, and 81—100. First, for the preparation of varistors, there was formed a mixture of 99.6 mole% titanium dioxide, TiO_2 , 0.2 mole% niobium oxide Nb_2O_5 , and 0.2 mole% manganese dioxide, MnO_2 , to which was added a solution of polyvinyl alcohol as an organic binder. The mixture was molded into discs, and these were baked in a reductive atmosphere. Each ceramic disc thus fabricated had a diameter of 8 mm and a thickness of 0.8 mm.

Then the zinc pastes of Examples 1—20, 41—60 and 81—100 were coated on the ceramic discs, and the coatings were baked at 750°C. for ten minutes in a tunnel-shaped heater in exposure to atmosphere, thereby completing varistor electrodes on the ceramic discs. The coated ceramic discs were held in the heater for a total of 40 minutes including the time required for raising and lowering the temperature of the heater.

In order to ascertain the properties of the varistors thus prepared, there were measured the voltage E_{10} of each varistor when a current of 10 milliamperes (mA) flows therethrough, and the voltage E_1 when a current of a 1 mA flows therethrough. From these voltages E_{10} and E_1 the nonlinearity coefficient α was computed by the equation,

$$\alpha = 1/\log \frac{E_{10}}{E_1}$$

Also, in order to determine the strength with which the zinc electrodes of the varistors adhere to the ceramic discs, a copper wire of 60.0 mm in length and 0.6 mm in diameter was soldered perpendicularly to the center of one of the electrodes of each varistor, with use of approximately 50 mg of solder and by application of ultrasonic vibration. With the ceramic disc of each varistor held against movement, the wire was pulled via a spring scale until the electrode came off the disc. The reading in kg of the spring scale at that time was recorded as the tensile strength T . The results were as given in Table 7, wherein Examples 113 to 115 combinedly represent the values exhibited by the varistors using the zinc pastes of Examples 1—20, 41—60 and 81—100, respectively.

TABLE 7

Examples	Zinc pastes in use	Varistor properties		
		E_{10} , V	α	T , kg
113	Examples 1—20	9.8—10.5	3.1—3.3	1.0—2.0
114	Examples 41—60	9.8—10.4	3.0—3.3	1.0—2.0
115	Examples 81—100	9.7—10.5	3.1—3.4	1.0—2.0

By way of comparison a silver paste of the composition set forth in connection with Examples 1—20 was coated on ceramic discs, which had themselves been fabricated as in Examples 113—115. The coatings were baked at a temperature less than the melting point of silver. Measured by the same methods as above, the voltage E_{10} of the varistors averaged 10.5 V, their nonlinearity coefficient α 3.3, and their tensile strength T 1.8 kg. A comparison of these figures with those of Table 7 will show that the varistors with the zinc electrodes in accordance with the invention have approximately the same properties as do the varistors with the conventional silver electrodes.

Although the zinc paste of this invention is applied only to SrTiO_3 capacitors and TiO_2 varistors in the foregoing Examples, it also lends itself to use in TiO_2 ceramic capacitors, and BaTiO_3 ceramic capacitors, thermistors, and piezoelectric elements, as has been confirmed by experiment. It will of course be seen that the solderable overlayers 32 of Figure 4 can be formed not only on the zinc conductors of capacitors but also on the zinc electrodes of varistors.

Claims

1. An electroconductive paste to be baked on ceramic bodies to provide capacitors, varistors or the like, comprising 100 parts by weight of zinc powder in the form of spherical particles, from about 0.01 to 10.00 parts by weight of a glass frit, from about 0.01 to 5.00 parts by weight of an additive selected from the class

deposition, or coating of gold or silver. The use of the precious metals will not significantly add to the cost of the capacitors because the overlayers can be of minimal thickness.

Examples 113—115

These Examples deal with the applicability of the zinc pastes in accordance with the invention to the electrodes of ceramic varistors. The zinc pastes tested were identical in composition with those of Examples 1—20, 41—60, and 81—100. First, for the preparation of varistors, there was formed a mixture of 99.6 mole% titanium dioxide, TiO_2 , 0.2 mole% niobium oxide Nb_2O_5 , and 0.2 mole% manganese dioxide, MnO_2 , to which was added a solution of polyvinyl alcohol as an organic binder. The mixture was molded into discs, and these were baked in a reductive atmosphere. Each ceramic disc thus fabricated had a diameter of 8 mm and a thickness of 0.8 mm.

Then the zinc pastes of Examples 1—20, 41—60 and 81—100 were coated on the ceramic discs, and the coatings were baked at 750°C . for ten minutes in a tunnel-shaped heater in exposure to atmosphere, thereby completing varistor electrodes on the ceramic discs. The coated ceramic discs were held in the heater for a total of 40 minutes including the time required for raising and lowering the temperature of the heater.

In order to ascertain the properties of the varistors thus prepared, there were measured the voltage E_{10} of each varistor when a current of 10 milliamperes (mA) flows therethrough, and the voltage E_1 when a current of a 1 mA flows therethrough. From these voltages E_{10} and E_1 , the nonlinearity coefficient α was computed by the equation,

$$\alpha = 1/\log \frac{E_{10}}{E_1}$$

Also, in order to determine the strength with which the zinc electrodes of the varistors adhere to the ceramic discs, a copper wire of 60.0 mm in length and 0.6 mm in diameter was soldered perpendicularly to the center of one of the electrodes of each varistor, with use of approximately 50 mg of solder and by application of ultrasonic vibration. With the ceramic disc of each varistor held against movement, the wire was pulled via a spring scale until the electrode came off the disc. The reading in kg of the spring scale at that time was recorded as the tensile strength T . The results were as given in Table 7, wherein Examples 113 to 115 combinedly represent the values exhibited by the varistors using the zinc pastes of Examples 1—20, 41—60 and 81—100, respectively.

TABLE 7

Examples	Zinc pastes in use	Varistor properties		
		E_{10} , V	α	T , kg
113	Examples 1—20	9.8—10.5	3.1—3.3	1.0—2.0
114	Examples 41—60	9.8—10.4	3.0—3.3	1.0—2.0
115	Examples 81—100	9.7—10.5	3.1—3.4	1.0—2.0

By way of comparison a silver paste of the composition set forth in connection with Examples 1—20 was coated on ceramic discs, which had themselves been fabricated as in Examples 113—115. The coatings were baked at a temperature less than the melting point of silver. Measured by the same methods as above, the voltage E_{10} of the varistors averaged 10.5 V, their nonlinearity coefficient α 3.3, and their tensile strength T 1.8 kg. A comparison of these figures with those of Table 7 will show that the varistors with the zinc electrodes in accordance with the invention have approximately the same properties as do the varistors with the conventional silver electrodes.

Although the zinc paste of this invention is applied only to SrTiO_3 capacitors and TiO_2 varistors in the foregoing Examples, it also lends itself to use in TiO_2 ceramic capacitors, and BaTiO_3 ceramic capacitors, thermistors, and piezoelectric elements, as has been confirmed by experiment. It will of course be seen that the solderable overlayers 32 of Figure 4 can be formed not only on the zinc conductors of capacitors but also on the zinc electrodes of varistors.

Claims

1. An electroconductive paste to be baked on ceramic bodies to provide capacitors, varistors or the like, comprising 100 parts by weight of zinc powder in the form of spherical particles, from about 0.01 to 10.00 parts by weight of a glass frit, from about 0.01 to 5.00 parts by weight of an additive selected from the class



consisting of Pb, Bi, Pr, Cu, Cd, and the compounds of the listed metallic elements, and a vehicle for pasting the mixture of the zinc powder, the glass frit and the additive.

2. An electroconductive paste as claimed in claim 1, wherein the zinc powder has an average particle size ranging from about 0.1 to 30.0 μm .

3. An electroconductive paste as claimed in claim 1, wherein the glass frit is of about 0.043 mm (325-mesh) particles.

4. An electroconductive paste as claimed in claim 1 or 3, wherein the glass frit has a softening point ranging from about 400° to 800°C.

5. An electroconductive paste as claimed in claim 1 or 3, wherein the glass frit is selected from the class consisting of a $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ glass frit, a $\text{PbO-B}_2\text{O}_3$ glass frit, and a $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$ glass frit, all with a softening point ranging from about 415° to 625°C.

6. An electroconductive paste as claimed in claim 1, wherein the compounds are oxides.

7. An electroconductive paste as claimed in claim 6, wherein the oxides include Pb_3O_4 , Bi_2O_3 , Pr_6O_{11} , CuO , and CdO .

8. A method of forming conductors or electrodes on a ceramic substrate to provide a capacitor, varistor or the like, which comprises applying to the ceramic substrate an electroconductive paste comprising 100 parts by weight of zinc powder in the form of spherical particles, from about 0.01 to 10.00 parts by weight of a glass frit, from about 0.01 to 5.00 parts by weight of an additive selected from the class consisting of Pb, Bi, Pr, Cu, Cd and the compounds of the listed metallic elements, and an organic vehicle for pasting the mixture of the zinc powder and the glass frit and the additive, and baking the paste on the ceramic substrate at a temperature above the melting point of the zinc powder for a time sufficient to drive off the organic vehicle, with the glass frit serving to inhibit the complete oxidation of the zinc particles during the baking step, and for the unoxidized interiors of the zinc particles to expand and break the oxide claddings thereon and become fused to each other, with the consequent creation of electroconductive bodies on the ceramic substrate.

9. A method as claimed in claim 8, wherein the zinc powder has an average particle size ranging from about 0.1 to 30.0 μm .

10. A method as claimed in claim 8, wherein the glass frit is of about 0.043 mm (325-mesh) particles.

11. A method as claimed in claim 8 or 10 wherein the glass frit has a softening point ranging from about 400° to 800°C.

12. A method as claimed in claim 8 or 10 wherein the glass frit is selected from the class consisting of a $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ glass frit, a $\text{PbO-B}_2\text{O}_3$ glass frit, and a $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$ glass frit, all with a softening point ranging from about 415° to 625°C.

13. A method as claimed in claim 8 wherein the compounds are oxides.

14. A method as claimed in claim 13, wherein the oxides include Pb_3O_4 , Bi_2O_3 , Pr_6O_{11} , CuO , and CdO .

Patentansprüche

1. Elektrisch leitende Paste zum Einbrennen auf einem keramischen Körper zur Herstellung von Kondensatoren, Varistoren usw., bestehend aus 100 Gewichtsteilen Zinkpulver in Form von kugeligen Teilchen, aus etwa 0,01 bis 10,00 Gewichtsteilen einer Glasfritte, aus etwa 0,01 bis 5,00 Gewichtsteilen eines Zusatzstoffes der Gruppe Pb, Bi, Pr, Cu, Cd und der Verbindungen der genannten Metallelemente, sowie aus einem Träger zum Anteigen des Gemisches aus Zinkpulver, Glasfritte und dem Zusatzstoff.

2. Elektrisch leitende Paste nach Anspruch 1, bei der das Zinkpulver eine durchschnittliche Teilchengröße im Bereich von etwa 0,1 bis 30,0 μm hat.

3. Elektrisch leitende Paste nach Anspruch 1, bei der die Glasfritte aus etwa 0,043 mm (325-mesh) großen Teilchen besteht.

4. Elektrisch leitende Paste nach Anspruch 1 oder 3, bei der die Glasfritte einen Erweichungspunkt im Bereich von etwa 400° bis 800°C hat.

5. Elektrisch leitende Paste nach Anspruch 1 oder 3, bei der die Glasfritte aus der Gruppe $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ -Glasfritte, $\text{PbO-B}_2\text{O}_3$ -Glasfritte und $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$ -Glasfritte ausgewählt ist, die sämtlich einen Erweichungspunkt im Bereich von etwa 415° bis 625°C haben.

6. Elektrisch leitende Paste nach Anspruch 1, bei der die Verbindungen Oxide sind.

7. Elektrisch leitende Paste nach Anspruch 6, bei der die Oxide Pb_3O_4 , Bi_2O_3 , Pr_6O_{11} , CuO und CdO umfassen.

8. Verfahren zur Herstellung von Leiterzügen oder Elektroden auf einem keramischen Träger zur Erzeugung eines Kondensators, Varistors usw., bei dem auf den keramischen Träger eine elektrisch leitende Paste, bestehend aus 100 Gewichtsteilen Zinkpulver in Form von kugeligen Teilchen, aus etwa 0,01 bis 10,00 Gewichtsteilen einer Glasfritte, aus etwa 0,01 bis 5,00 Gewichtsteilen eines Zusatzstoffes der Gruppe Pb, Bi, Pr, Cu, Cd und den Verbindungen dieser Metallelemente und einem organischen Träger zum Anteigen des Gemisches aus Zinkpulver und der Glasfritte und dem Zusatzstoff aufgebracht wird, bei dem ferner die Paste auf dem keramischen Träger bei einer Temperatur oberhalb des Schmelzpunktes des Zinkpulvers für eine zum Austreiben des organischen Trägers, wobei die Glasfritte zum Unterbinden der vollständigen Oxidation der Zinkteilchen während der Brennstufe dient, und für eine zum Ausdehnen des nichtoxidierten Inneren der Zinkteilchen und Aufbrechen der Oxidhüllen darauf und zum miteinander





Verschmelzen ausreichende Zeit gebrannt wird, was die Bildung von elektrisch leitenden Körpern auf dem keramischen Träger zur Folge hat.

9. Verfahren nach Anspruch 8, bei dem das Zinkpulver eine durchschnittliche Teilchengröße im Bereich von etwa 0,1 bis 30,0 μm hat.

10. Verfahren nach Anspruch 8, bei dem die Glasfritte aus etwa 0,043 mm (325-mesh) großen Teilchen besteht.

11. Verfahren nach Anspruch 8 oder 10, bei dem die Glasfritte einen Erweichungspunkt im Bereich von etwa 400° bis 800°C hat.

12. Verfahren nach Anspruch 8 oder 10, bei dem die Glasfritte aus der Gruppe $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ -Glasfritte, $\text{PbO-B}_2\text{O}_3$ -Glasfritte und $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$ -Glasfritte ausgewählt ist, die sämtlich einen Erweichungspunkt im Bereich von etwa 415° bis 625°C haben.

13. Verfahren nach Anspruch 8, bei dem die Verbindungen Oxide sind.

14. Verfahren nach Anspruch 13, bei dem die Oxide Pb_3O_4 , Bi_2O_3 , Pr_6O_{11} , CuO und CdO umfassen.

15 Revendications

1. Pâte conductrice de l'électricité destinée à être cuite sur des corps en céramique pour former des condensateurs, des varistors ou analogue, comprenant 100 parties en poids de poudre de zinc sous forme de particules sphériques, entre environ 0,01 et 10,00 parties en poids de fritte de verre, entre environ 0,01 et 5,00 parties en poids d'un additif choisi dans le groupe constitué de Pb, Bi, Pr, Cu, Cd et les composés des éléments métalliques énumérés, et un véhicule pour l'empâtage du mélange de la poudre de zinc, de la fritte de verre et de l'additif.

2. Pâte conductrice de l'électricité selon la revendication 1, où la poudre de zinc a un diamètre moyen de particule compris entre environ 0,1 et 30,0 μm .

3. Pâte conductrice de l'électricité selon la revendication 1, où la fritte de verre a des particules d'environ 0,043 mm.

4. Pâte conductrice de l'électricité selon la revendication 1 ou la revendication 3, où la fritte de verre a un point de ramollissement compris entre environ 400° et 800°C.

5. Pâte conductrice de l'électricité selon la revendication 1 ou la revendication 3, caractérisée en ce que la fritte de verre est choisie dans le groupe constitué d'une fritte de verre de $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$, d'une fritte de verre de $\text{PbO-B}_2\text{O}_3$, et d'une fritte de verre de $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$, toutes avec un point de ramollissement compris entre environ 415°C et 625°C.

6. Pâte conductrice de l'électricité selon la revendication 1, caractérisée en ce que les composés sont des oxydes.

7. Pâte conductrice de l'électricité selon la revendication 6, caractérisée en ce que les oxydes comprennent Pb_3O_4 , Bi_2O_3 , Pr_6O_{11} , CuO , et CdO .

8. Procédé de formation de conducteurs ou d'électrodes sur un substrat en céramique de manière à former un condensateur, un varistor ou analogue, qui comprend l'application au substrat en céramique d'une pâte conductrice de l'électricité comportant 100 parties en poids de poudre de zinc sous forme de particules sphériques, entre environ 0,01 et 10,00 parties en poids d'une fritte de verre, entre environ 0,01 et 5,00 parties en poids d'un additif choisi dans le groupe constitué de Pb, Bi, Pr, Cu, Cd et les composés des éléments métalliques énumérés, et un véhicule organique pour l'empâtage du mélange de poudre de zinc et de la fritte de verre et de l'additif, et la cuisson de la pâte sur le substrat en céramique à une température supérieure au point de fusion de la poudre de zinc pendant un temps suffisant pour chasser le véhicule organique, avec la fritte de verre servant à inhiber l'oxydation complète des particules de zinc pendant l'étape de cuisson, et pour que les intérieurs non oxydés des particules de zinc dilantent et rompent les habillages en oxyde les recouvrant et les fassent fondre les une sur les autres, avec comme conséquence la création de corps conducteurs de l'électricité sur le substrat en céramique.

9. Procédé selon la revendication 8, où la poudre de zinc a une dimension moyenne de particule comprise entre environ 0,1 et 30,0 μm .

10. Procédé selon la revendication 8, où la fritte de verre a des particules d'environ 0,043 mm.

11. Procédé selon la revendication 8 ou la revendication 10, où la fritte de verre a un point de ramollissement compris entre environ 400 et 800°C.

12. Procédé selon la revendication 8 ou la revendication 10, caractérisé en ce que la fritte de verre est choisie dans le groupe constitué d'une fritte de verre en $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$, d'une fritte de verre en $\text{PbO-B}_2\text{O}_3$ et d'une fritte de verre en $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$, toutes ayant un point de ramollissement compris entre environ 415° et 625°C.

13. Procédé selon la revendication 8, où les composants sont des oxydes.

14. Procédé selon la revendication 13, caractérisé en ce que les oxydes comprennent Pb_3O_4 , Bi_2O_3 , Pr_6O_{11} , CuO et CdO .

