(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 686 983 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **95105045.9**

(51) Int. Cl.^{6}: **H01C 17/06**

(22) Date of filing: **04.04.95**

(30) Priority: **06.06.94 JP 123853/94**

(43) Date of publication of application:
13.12.95 Bulletin 95/50

(84) Designated Contracting States:
DE FR GB

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(54) Resistive paste

(57) A resistive paste comprising (a) a solid content comprising (a1) a resistive material having a composition of $Nb_xLa_{1-x}B_{6-4x}$, wherein x is from 0.1 to 0.9 mol, and (a2) non-reducing glass frit, (b) from 1 to 10% by weight, based on the solid content, of TiO_2 as a first additive, (c) from 1 to 10% by weight, based on the solid content, of at least one second additive selected from the group consisting of Co_3O_4, CoO, and Fe_2O_3, and (d) an organic vehicle.

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(3.10/3.09/3.3.4)

FIELD OF THE INVENTION

This invention relates to a resistive paste which can be baked in a neutral or reducing atmosphere and has improved temperature coefficient of resistivity.

BACKGROUND OF THE INVENTION

A circuit pattern composed of electrodes, resistors, etc., on which various electronic parts are mounted, has been generally formed on a ceramic base made of alumina, etc., and the electrodes are generally formed by screen printing a paste comprising a noble metal, e.g., silver or a silver-palladium alloy, on the ceramic base followed by baking in air.

However, because not only of expensiveness of the noble metallic paste but also of the demand for sufficient migration resistance of a resistive paste to cope with the decreasing electrode distance due to size reduction of electronic equipment and parts, the noble metallic paste has recently been displaced with a paste of a base metal, e.g., copper, nickel or aluminum. Such a base metallic paste is screen-printed on a ceramic base and baked in a neutral or reducing atmosphere to form an inexpensive electrode pattern having excellent characteristics.

When electrodes are formed by using such a base metallic paste, resistors which are arranged to bridge over the electrodes should also be formed by using a resistive paste which can be baked in a neutral or reducing atmosphere. Examples of known resistive pastes which can be baked in a neutral or reducing atmosphere include LaB_6-based pastes (as described in JP-B-59-6481, the term "JP-B" as used herein means an "examined published Japanese patent application"), NbB_2-based pastes (as described in JP-A-63-224301, the term "JP-A" as used herein means an "unexamined published Japanese patent application"), and Nb-La-B-based pastes (as described in JP-A-2-249203).

A desired surface resistivity over a broad range has been obtained by varying the mixing ratio of a resistive material and glass frit. In using the LaB_6-based or NbB_2-based resistive pastes, however, the surface resistivity suffers drastic changes with a slight variation in glass frit amount due to poor affinity between the resistive material and glass frit. Therefore, the range of surface resistivity in which satisfactory reproducibility can be assured has been limited.

On the other hand, resistors formed of the $Nb_xLa_{1-x}B_{6-4x}$-based paste show a milder increase in surface resistivity than with those formed of the LaB_6-based pastes or NbB_2-based pastes. Accordingly, the $Nb_xLa_{1-x}B_{6-4x}$-based paste has an advantage of a broadened surface resistivity range of from 10 Ω/square to 10 MΩ/square by varying the mixing ratio of resistive material to glass frit. However, the resistors formed of the $Nb_xLa_{1-x}B_{6-4x}$-based paste, particularly those adjusted to have a low surface resistivity (e.g., from about 10 Ω/square to 100 Ω/square), show a tendency that the temperature coefficient of resistivity (hereinafter abbreviated as "TCR") shifts to the plus (+) direction with its absolute value getting far from zero. In this point, they do not always satisfy the characteristics required for practical use.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an $Nb_xLa_{1-x}B_{6-4x}$-based resistive paste which can be baked in a neutral or reducing atmosphere and whose TCR in a low surface resistivity range can be shifted to the minus (-) direction so as to get close to zero in its absolute value.

Other objects and effects of the present invention will be apparent from the following description.

The present invention relates to a resistive paste comprising:

(a) a solid content comprising (a1) a resistive material having a composition of $Nb_xLa_{1-x}B_{6-4x}$, wherein x is from 0.1 to 0.9 mol, and (a2) non-reducing glass frit,

(b) from 1 to 10% by weight, based on the total amount of the solid content, of TiO_2 as a first additive,

(c) from 1 to 10% by weight, based on the total amount of the solid content, of at least one second additive selected from the group consisting of Co_3O_4, CoO, and Fe_2O_3, and

(d) an organic vehicle.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention, $Nb_xLa_{1-x}B_{6-4x}$, wherein x is from 0.1 to 0.9 mol, preferably from 0.2 to 0.8 mol, is used as a resistive material (a1). If x is less than 0.1 mol, it tends to be difficult to gradually increase the surface resistivity, while if x is more than 0.9 mol, the change rate of surface resistivity with the content of glass frit tends to become large, thus making it difficult to improve the reproducibility of the surface resistivity.

The grain size of the resistive material is generally from 0.1 to 5 µm. If the grain size is less than 0.1 µm, a prolonged period of grinding time is required to prepare the resistive material, and impurities introduced during the grinding tend to adversely affect the properties of the resistive material. If the grain size is more than 5 µm, it tends to be difficult to obtain a constant resistivity in a stable manner.

The resistive material can be prepared in any conventional manners, such as those described in U.S. Patent 5,036,027.

Examples of the non-reduced glass frit (a2) used in the present invention include alkali earth borosilicate, boroaluminosilicate, etc. The grain size of the non-reduced glass frit is generally from 1 to 10 µm. If the grain size is less than 1 µm, the change rate of surface resistivity tends to be too large, while if it is more than 10 µm, it tends to be difficult to obtain uniform resistors in a stable manner. The non-reduced glass frit can be prepared in any conventional manners, such as by mixing appropriate oxides followed by being fused.

The weight ratio of the resistive material (a1) to the non-reduced glass frit (a2) in the solid content (a) can be widely varied depending on the desired surface resistivity and the like, and is generally from 5/100 to 70/100 by weight in the present invention.

TiO_2 as the first additive (b) is added to the solid content comprising resistive material and glass frit in an amount of from 1 to 10% by weight, preferably from 2 to 7% by weight, based on the total amount of the solid content. At least one member selected from the group consisting of Co_3O_4,CoO, and Fe_2O_3 as the second additive (c) is also added to the solid content in an amount of from 1 to 10% by weight, preferably from 2 to 5% by weight, based on the total amount of the solid content. If the amount of at least one of the first and second additives is less than 1% by weight, the resulting resistor will have a TCR insufficiently shifted to the minus (-) direction. If the amount of at least one of the first and second additives is more than 10% by weight, the resulting resistor will have a TCR too largely shifted to the minus (-) direction.

In the present invention, it is preferred to use (1) a combination of from 2 to 7% by weight (particularly 5% by weight) of TiO_2 and from 2 to 5% by weight (particularly 5% by weight) of Co_3O_4 or (2) a combination of from 2 to 7% by weight (particularly 5% by weight) of TiO_2 and from 1 to 3% by weight (particularly 3% by weight) of Fe_2O_3.

An organic vehicle (d) is used for forming the resistive paste according to the present invention. Examples thereof include an acrylic resin and an ethylcellulose diluted with terpenes such as α-terpineol, β-terpineol or a mixture thereof with other solvents such as kerosine, butyl carbitol, butyl carbitol acetate and high boiling alcohols and alcohol esters. The organic vehicle should be thixotropic in order that it set up rapidly after being screened, thereby giving good resolution.

In the resistive paste of the present invention, the ratio of the amount of the organic vehicle (d) to the total amount of the solid content (a) and the additives (b) and (c) is generally from 20/80 to 60/40 by weight, and preferably from 30/70 to 50/50 by weight.

The resistive paste of the present invention can be produced in any conventional manner for preparing resistive pastes. For example, a resistive material and a glass frit, which have been separately prepared, are mixed with the first and second additives, and the resulting mixture is kneaded with an organic vehicle to form a resistive paste according to the present invention.

The resistive paste of the present invention can be used in the similar manner as in conventional resistive pastes. For example, the resistive paste can be printed on a suitable base, such as a ceramic base, by screen printing, dried at 150 °C for 10 minutes, and then baked at a peak temperature at 900 °C for 10 minutes in a nitrogen atmosphere.

The surface resistivity of the resistor, which is formed from the resistive paste of the present invention, is not particularly limited and is generally from 10 Ω/square to 200 Ω/square, and preferably from 20 Ω/square to 100 Ω/square.

The present invention will be illustrated in greater detail with reference to Example, but it should be understood that the present invention is not construed as being limited thereto. All the percents are by weight unless otherwise indicated.

EXAMPLE

Preparation of Electrodes:

A conductive paste containing Cu as a base metal was screen printed on an alumina ceramic base and baked in a nitrogen atmosphere to form electrodes.

Preparation of Resistive Paste:

Powdered NbB_2 and LaB_6 were weighed and mixed to provide a composition of $Nb_xLa_{1-x}B_{6-4x}$, with x being varied between 0.1 mol and 0.9 mol as shown in Table 1 below. The mixture was calcined in a nitrogen atmosphere for 2 hours at a temperature increase rate of 3 ° C/min with the peak temperature set at 1,000 ° C to prepare a solid solution of LaB_6 in NbB_2. The resulting mixture was ground in a vibration mill to an average particle size of 1 μm and dried to obtain a resistive material having a composition of $Nb_xLa_{1-x}B_{6-4x}$ (where x is 0.1 to 0.9 mol).

Separately, B_2O_3, SiO_2, BaO, CaO, Nb_2O_5, and K_2O were mixed at a molar ratio of 35.56/31.24/17.78/10.04/2.41/2.97 and fused at a temperature of from 1,200 to 1,350 ° C to prepare fused glass. The fused glass was quenched in pure water and ground in a vibration mill to an average particle size of 5 μm or smaller to prepare non-reducing glass frit.

The resulting mixture was kneaded with an organic vehicle composed of an acrylic resin diluted with α-terpineol to prepare a resistive paste.

TABLE 1

Sample No.	x^{*1} (mol)	Resistive Material (wt%)	Glass Frit (wt%)	First Additive (TiO_2) (wt%^{*2})	Second Additive (wt%^{*2})		
					CoO	Co_3O_4	Fe_2O_3
1^{*3}	0.50	40	60	0	5	0	0
2	0.50	40	60	2	5	0	0
3	0.50	40	60	5	5	0	0
4	0.50	40	60	9	5	0	0
5^{*3}	0.50	40	60	11	5	0	0
6^{*3}	0.25	40	60	0	0	0	0
7^{*3}	0.25	40	60	5	0	0	0
8	0.25	40	60	5	2	0	0
9	0.25	40	60	5	5	0	0
10	0.25	40	60	5	9	0	0
11^{*3}	0.25	40	60	5	11	0	0
12	0.25	40	60	5	0	2	0
13	0.25	40	60	5	0	5	0
14	0.25	40	60	5	0	9	0
15^{*3}	0.25	40	60	5	0	11	0
16	0.25	40	60	5	0	0	2
17	0.25	40	60	5	0	0	5
18	0.25	40	60	5	0	0	9
19^{*3}	0.25	40	60	5	0	0	11
20^{*3}	0.75	40	60	0	0	0	0
21^{*3}	0.75	40	60	5	0	0	0

(continued)

TABLE 1 (continued)

Sample No.	x^{*1} (mol)	Resistive Material (wt%)	Glass Frit (wt%)	First Additive (TiO_2) (wt%^{*2})	Second Additive (wt%^{*2}) CoO	Co_3O_4	Fe_2O_3
22	0.75	40	60	5	2	0	0
23	0.75	40	60	5	5	0	0
24	0.75	40	60	5	9	0	0
25^{*3}	0.75	40	60	5	11	0	0
26	0.75	40	60	5	0	2	0
27	0.75	40	60	5	0	5	0
28	0.75	40	60	5	0	9	0
29^{*3}	0.75	40	60	5	0	11	0
30	0.75	40	60	5	0	0	2
31	0.75	40	60	5	0	0	5
32	0.75	40	60	5	0	0	9
33^{*3}	0.75	40	60	5	0	0	11
34	0.50	40	60	5	3	3	0
35	0.50	40	60	5	0	3	3
36	0.50	40	60	5	3	0	3
37	0.50	40	60	5	2	2	2

Note: *1: x in $Nb_xLa_{1-x}B_{6-4x}$

*2: Based on the resistive material/glass frit mixture.

*3: Sample out of the scope of the present invention.

Preparation of Resistor:

Each of the resistive pastes of Table 1 was screen printed on the alumina base in a size of 1.5 mm long, 1.5 mm wide, and 20 µm thick (dry thickness), inclusive of a part of the electrodes, dried at 150 °C for 10 minutes, and baked in a nitrogen atmosphere with its peak temperature set at 900 °C for 10 minutes to form a resistor.

Evaluation:

The surface resistivity and TCR of each sample thus prepared were measured. The results obtained are shown in Table 2 below.

TABLE 2

Sample No.	Surface Resistivity (Ω/square)	TCR (ppm/°C)	
		-55°C	+150°C
1*	17	+478	+468
2	20	+216	+233
3	22	+157	+242
4	38	+121	+159
5*	78	-377	-414
6*	24	+488	+490
7*	34	+420	+367
8	32	+242	+157
9	35	+205	+201
10	40	+137	+105
11*	72	-240	-265
12	33	+107	-2
13	36	-197	-83
14	42	-398	-133
15*	86	-450	-511
16	40	+126	+13
17	46	-50	-48
18	51	-210	-254
19*	145	-450	-463
20*	140	+430	+390
21*	182	+355	+341

(continued)

TABLE 2 (continued)

Sample No.	Surface Resistivity (kΩ/square)	TCR (ppm/°C) -55°C	TCR (ppm/°C) +150°C
22	170	+150	+121
23	183	+63	+55
24	192	-142	-127
25*	255	-387	-368
26	172	+200	+187
27	179	+177	+150
28	189	+33	+21
29*	268	-391	-389
30	201	+125	+103
31	234	+58	+27
32	256	-154	-160
33*	305	-405	-413
34	115	+75	+81
35	122	+52	+59
36	128	+49	+55
37	108	+72	+83

Note: *: Samples out of the scope of the present invention.

It can be seen from Table 2 that Sample No. 1 (x=0.50 mol) containing only 5% CoO as a second additive with no first additive had a TCR of +478 ppm/°C at -55°C and +468 ppm/°C at +150°C, while samples containing 1 to 10% of TiO_2 as a first additive and 5% of CoO as a second additive had a TCR shifted to the minus (-) direction as compared with Sample No. 1. It is noted that Sample No. 5 containing more than 10% of the first additive (TiO_2) shows too a great shift of the TCR to the minus (-) direction, failing to exhibit satisfactory characteristics as a resistor.

It is also seen that Sample No. 7 containing only the first additive but no second additive had a TCR of +420 ppm/°C at -55°C and +367 ppm/°C at +150°C, whereas samples additionally containing from 1 to 10% of a second additive selected from CoO, Co_3O_4 and Fe_2O_3 had a TCR shifted to the minus (-) direction as compared with that of Sample No. 7, with the surface resistivity being substantially equal. To the contrary, Sample Nos. 11, 15, and 19 containing more than 10% of a second additive had a TCR too largely shifted to the minus (-) direction, thus failing to exhibit satisfactory characteristics as a resistor.

Similarly, Sample No. 21 (x = 0.75 mol) containing only a first additive but no second additive showed a TCR of +355 ppm/°C at -55°C and +341 ppm/°C at +150°C, while the samples additionally containing from 1 to 10% of a second additive selected from CoO, Co_3O_4, and Fe_2O_3 showed a shift of TCR to the minus (-) direction as compared with Sample No. 21, with the surface resistivity being substantially equal. Note that Sample Nos. 25, 29, and 33 containing more than 10% of a second additive showed too large a shift of TCR to the minus (-) direction, failing to exhibit satisfactory characteristics as a resistor.

Samples containing, in addition to a first additive, second additives in a total amount of 6% (Sample Nos. 34, 35, 36, and 37) also exhibit satisfactory characteristics as having a TCR of +49 to +75 ppm/°C at -55°C and +55 to +83 ppm/°C at +150°C.

In short, addition of the above-mentioned first and second additives to an $Nb_xLa_{1-x}B_{6-4x}$-based resistive paste (x is from 0.1 to 0.9) is effective to make the TCR of the resistor formed of that resistive paste get closer to zero, shifting the TCR to the minus (-) direction, without causing a substantial change in surface resistivity. If the amount either of first or second additive exceeds 10%, the surface resistivity increases, and the TCR is shifted to the minus direction too largely.

Incidentally, where x in an $Nb_xLa_{1-x}B_{6-4x}$-based paste is less than 0.1, the resistivity is significantly reduced, and if it exceeds 0.9, the resistivity markedly increases. In either case, such a resistive material cannot exhibit satisfactory performance as a resistor at any mixing ratio with glass frit.

As described and demonstrated above, the resistive paste according to the present invention comprises a solid content of a resistive material having a composition of $Nb_xLa_{1-x}B_{6-4x}$ (x = 0.1 to 0.9 mol) and non-reducing glass frit, from 1 to 10% by weight, based on the solid content, of TiO_2 as a first additive, and from 1 to 10% by weight, based on the solid content, of at least one second additive selected from the group consisting of Co_3O_4, CoO, and Fe_2O_3. According to the present invention, it is possible to shift the temperature coefficient of surface resistivity in a low resistivity range of a resistor formed by baking an $Nb_xLa_{1-x}B_{6-4x}$-based resistive paste to the minus (-) direction so that the resistive paste of the present invention sufficiently satisfies the characteristics required for a resistive paste to be baked in a neutral or reducing atmosphere.

While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A resistive paste comprising:
  (a) a solid content comprising (a1) a resistive material having a composition of $Nb_xLa_{1-x}B_{6-4x}$, wherein x is from 0.1 to 0.9 mol, and (a2) non-reducing glass frit,
  (b) from 1 to 10% by weight, based on the solid content, of TiO_2 as a first additive,
  (c) from 1 to 10% by weight, based on the solid content, of at least one second additive selected from the group consisting of Co_3O_4, CoO, and Fe_2O_3, and
  (d) an organic vehicle.

2. A resistive paste as claimed in claim 1, wherein the amount of said first additive (b) is from 2 to 7% by weight, based on the solid content, and the amount of said second additive (c) is from 2 to 5% by weight, based on the solid content.

3. A resistive paste as claimed in claim 2, wherein said first additive (b) is from 2 to 7% by weight, based on the solid content, of TiO_2 and said second additive (c) is from 2 to 5% by weight, based on the solid content, of Co_3O_4.

4. A resistive paste as claimed in claim 2, wherein said first additive (b) is from 2 to 7% by weight, based on the solid content, of TiO_2 and said second additive (c) is from 1 to 3% by weight, based on the solid content, of Fe_2O_3.

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EUROPEAN SEARCH REPORT

Application Number
EP 95 10 5045

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	PATENT ABSTRACTS OF JAPAN vol. 18 no. 158 (E-1525) ,16 March 1994 & JP-A-05 335106 (MURATA MFG CO LTD) 17 December 1993, * abstract * ---	1-4	H01C17/06
A	DATABASE WPI Section Ch, Week 944 Derwent Publications Ltd., London, GB; Class L03, AN 94-029246 & JP-A-05 335 107 (MURATA MFG CO LTD) , 17 December 1993 * abstract * ---	1	
A	US-A-5 036 027 (SHIZUHARU WATANABE) * the whole document *	1	
D,A	& JP-A-02 249 203 (MURATA MANUFACTURING CO LTD) -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	7 September 1995	Goossens, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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