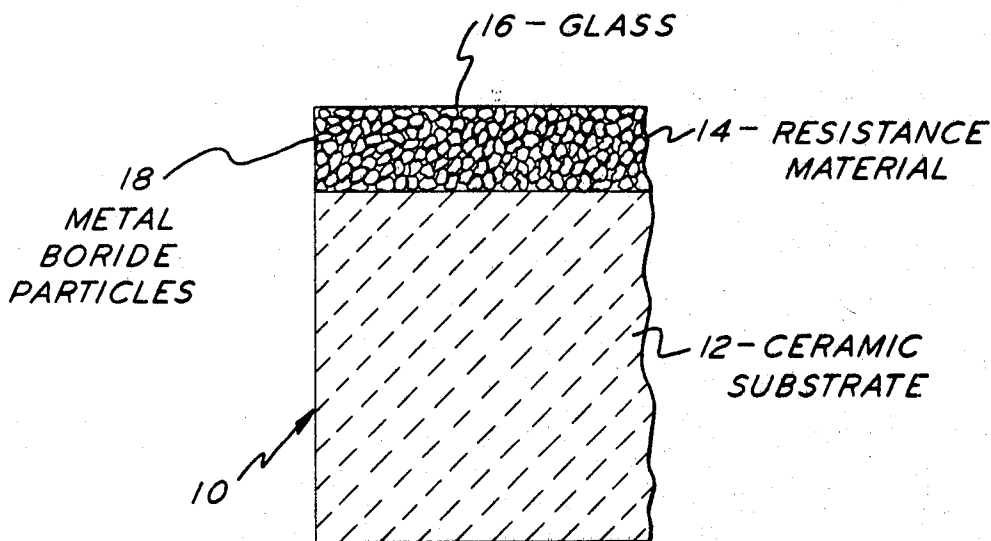


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VITREOUS ENAMEL RESISTANCE MATERIAL AND
RESISTOR MADE THEREFROM
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VITREOUS ENAMEL RESISTANCE MATERIAL AND RESISTOR MADE THEREFROM

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2 Claims

ABSTRACT OF THE DISCLOSURE

A vitreous enamel resistance material comprising a mixture of a vitreous glass frit and fine particles of a metal boride of the transition elements of Groups IV, V and VI of the periodic chart. The metal boride may be chromium boride (CrB_2), zirconium boride (ZrB_2), molybdenum boride (MoB_2), tantalum boride (TaB_2) or titanium boride (TiB_2). The metal boride is present in the vitreous enamel resistance material in the proportions of, by weight, 10% to 35% for chromium boride, 20% to 50% for zirconium boride, 20% to 50% for molybdenum boride, 35% to 65% for tantalum boride and 20% to 50% for titanium boride. An electrical resistor is made with the vitreous enamel resistor material of the present invention by coating a ceramic substrate with the vitreous enamel resistance material and firing the coated substrate at a temperature sufficient to melt the glass frit of the vitreous enamel resistance material. Upon cooling, the glass hardens so that the resultant resistor comprises the substrate having on the surface thereof a film of glass with the metal boride particles embedded in and dispersed throughout the glass film.

BACKGROUND

A type of electrical resistance material which has recently come into commercial use is a vitreous enamel resistance material which comprises a mixture of a glass frit and finely divided particles of an electrical conductive material. The vitreous enamel resistance material is coated on the surface of a substrate of an electrical insulating material, usually a ceramic, and fired to melt the glass frit. When cooled, there is provided a film of glass having the conductive particles dispersed therein. Terminations are connected to the film to permit the resultant resistor to be connected in the desired circuit.

The materials which have been generally used for the conductive particles are the noble metals. Although the noble metals provide vitreous enamel resistance materials which have satisfactory electrical characteristics, they have the disadvantage that they are expensive. Thus, the resistors made from the vitreous enamel resistance materials containing the noble metals are expensive to manufacture. Therefore, it would be desirable to have a vitreous enamel electrical resistance material which utilizes a relatively inexpensive conductive material so as to provide an electrical resistor which is relatively inexpensive to manufacture. In addition, the conductive material used must be capable of providing a resistance material having a wide range of resistance values and which has relatively good electrical characteristics over the entire range of the resistance values. Such electrical characteristics include temperature coefficient of resistance, voltage coefficient, stability under load, etc.

SUMMARY

It is an object of the present invention to provide a novel vitreous enamel resistance material utilizing a relatively inexpensive conductive material.

It is another object of the present invention to provide

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an electrical resistor utilizing a novel vitreous enamel resistance material.

It is a further object of the present invention to provide a vitreous enamel electrical resistor having a relatively wide range of resistance values, which has relatively good electrical characteristics over the entire range of resistance values and which is relatively inexpensive to manufacture.

It is a still further object of the present invention to provide a vitreous enamel resistance material comprising a mixture of a glass frit and finely divided particles of a metal boride selected from the group consisting of molybdenum boride, titanium boride, zirconium boride, chromium boride and tantalum boride.

Other objects will appear hereinafter.

The invention accordingly comprises a composition of matter and product formed therewith possessing the characteristics, properties and relation of constituents which will be exemplified in the composition hereinafter described, and the scope of the invention will be indicated in the claims.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a cross-sectional view, on a highly exaggerated scale, of a resistor produced in accordance with the present invention.

DESCRIPTION OF INVENTION

In general, the vitreous enamel resistance material of the present invention comprises a mixture of a vitreous glass frit and fine particles of a metal boride of the transition elements of Groups IV, V and VI of the periodic chart. The metal boride can be molybdenum (MoB_2), titanium boride (TiB_2), zirconium boride (ZrB_2), chromium boride (CrB_2), or tantalum boride (TaB_2). In the vitreous enamel resistance material of the present invention, the metal boride of the above-stated group is present in the proportion of, by weight, 20% to 50% for molybdenum boride, 20% to 50% for titanium boride, 20% to 50% for zirconium boride, 10% to 35% for chromium boride, and 35% to 65% for tantalum boride.

The glass frit used in the resistance material of the present invention may be of any well-known composition which has a melting temperature below that of the refractory metal boride. The glass frits most preferably used are the borosilicate frits, such as lead borosilicate frit, bismuth, cadmium, barium, calcium or other alkaline earth borosilicate frits. The preparation of such glass frits is well-known and consists, for example, in melting together the constituents of the glass in the form of the oxides of the constituents, and pouring such molten composition into water to form the frit. The batch ingredients may, of course, be any compound that will yield the desired oxides under the usual conditions of frit production. For example, boric oxide will be obtained from boric acid, silicon dioxide will be produced from flint, barium oxide will be produced from barium carbonate, etc. The glass is preferably milled in a ball-mill with water to reduce the particle size of the frit and to obtain a frit of substantially uniform size.

To make the resistance material of the present invention, the glass frit and refractory metal boride are broken down, such as by ball-milling, to a substantially uniform particle size. An average particle size of between 1 to 2 microns has been found to be preferable. The glass frit and refractory metal boride powder are thoroughly mixed together, such as by ball-milling in water or an organic medium, such as butyl carbitol acetate or a mixture of butyl carbitol acetate and toluol. The mixture is then adjusted to the proper viscosity for the desired manner of applying the resistance material to a substrate by either adding or removing the liquid medium of the material.

To make a resistor with the resistance material of the present invention, the resistance material is applied to a uniform thickness on the surface of a substrate. The substrate may be a body of any material which can withstand the firing temperature of the resistance material composition. The substrate is generally a body of a ceramic, such as glass, porcelain, refractory, barium titanate, or the like. The resistance material may be applied on the substrate by brushing, dipping, spraying or screen stencil application. The substrate with the resistance material coating is then fired in a conventional furnace at a temperature at which the glass frit becomes molten. For resistance materials of the present invention, it has been found preferable to fire the coated substrate in an inert atmosphere, such as argon, helium, nitrogen or a mixture of nitrogen and hydrogen, to achieve a resistor of better stability. When the coated substrate is cooled, the vitreous enamel hardens to bond the resistance material to the substrate.

As shown in the drawing, the resultant resistor of the present invention is generally designated as 10. Resistor 10 comprises the ceramic substrate 12 having a layer 14 of the resistance material of the present invention coated and fixed thereon. The resistance material layer 14 comprises the glass 16 and the finely divided particles 18 of the metal boride embedded within and dispersed throughout the glass 16.

EXAMPLE I

A plurality of resistance materials of the present invention were made in which the conductive material was molybdenum boride in the various amounts shown in Table I and the glass frit was a barium, titanium, aluminum borosilicate glass. Each of the resistance materials was made by mixing together the glass frit and molybdenum boride particles in a ball-mill in butyl carbitol acetate. Resistors were made with each of the resistance materials by coating cylindrical ceramic bodies with the resistance material and firing the coated ceramic bodies in a furnace at approximately 900° C for thirty minutes. The resistors were fired in a nitrogen atmosphere. A number of resistors of each of the compositions were made, and the average resistance values and temperature coefficient of resistance of the resulting resistors of each group are shown in Table I.

TABLE I

Molybdenum boride (percent by weight)	Glass frit (percent by weight)	Resistance (ohms/□)	Temperature Coef. of resistance (percent per ° C.)	
			+25° C. to + 150° C.	+25° C. to -55° C.
20	80	125,000	-.1552	-.2210
25	75	275	-.0179	-.0280
30	70	250	+.0355	+.0353
35	65	190	+.0400	+.0408

EXAMPLE II

A plurality of resistance materials of the present invention were made in which the conductive material was zirconium boride in the various amounts shown in Table II and the glass frit was a barium, titanium, aluminum borosilicate glass. Each of the resistance materials was made in the same manner as the resistance materials of Example I, and resistors were made with each of the resistance materials in the same manner as described in Example I. The resistors were fired at 1050° C. in a nitrogen atmosphere for thirty minutes and the average resistance values and temperature coefficient of resistance for each group of the resultant resistors are indicated in Table II.

TABLE II

Zirconium boride (percent by weight)	Glass frit (percent by weight)	Resistance (ohms/□)	Temperature Coef. of resistance (percent per ° C.)	
			+25° C. to + 150° C.	+25° C. to -55° C.
20	80	50,000	-.0619	-.0764
25	75	2,300	-.0040	-.0112
30	70	500	+.0096	+.0054
35	65	112	+.0245	+.0154

EXAMPLE III

A plurality of resistance materials of the present invention were made in which the conductive material was chromium boride in the various amounts shown in Table III and the glass frit was a barium, titanium, aluminum borosilicate glass. Each of the resistance materials was made in the same manner as the resistance materials of Example I, and resistors were made with each of the resistance materials in the same manner as described in Example I. The resistors were fired at 850° C. in a nitrogen atmosphere for thirty minutes and the average resistance values and temperature coefficient of resistance for each group of the resultant resistors are indicated in Table III.

TABLE III

Chromium boride (percent by weight)	Glass frit (percent by weight)	Resistance (ohms/□)	Temperature Coef. of resistance (percent per ° C.)	
			+25° C. to + 150° C.	+25° C. to -55° C.
15	85	3,630	+.0115	+.0204
20	80	80	+.0792	+.0989
25	75	15	+.0856	+.1056
30	70	7.5	+.0865	+.1058

EXAMPLE IV

A plurality of resistance materials of the present invention were made in which the conductive material was tantalum boride in the various amounts shown in Table IV and the glass frit was a barium, titanium, aluminum borosilicate glass. Each of the resistance materials was made in the same manner as the resistance materials of Example I, and resistors were made with each of the resistance materials in the same manner as described in Example I. The resistors were fired at 1050° C. in a nitrogen atmosphere for thirty minutes and the average resistance values and temperature coefficient of resistance for each group of the resultant resistors are indicated in Table IV.

TABLE IV

Tantalum boride (percent by weight)	Glass frit (percent by weight)	Resistance (ohms/□)	Temperature Coef. of resistance (percent per ° C.)	
			+25° C. to + 150° C.	+25° C. to -55° C.
35	65	2,750	+.0035	±.0028
40	60	1,250	+.0127	+.0088
45	55	362	+.0291	+.0242
50	50	250	+.0289	+.0232

EXAMPLE V

A plurality of resistance materials of the present invention were made in which the conductive material was titanium boride in the various amounts shown in Table V and the glass frit was a barium, titanium, aluminum borosilicate glass. Each of the resistance materials was made in the same manner as the resistance materials of Example I, and resistors were made with each of the resistance materials in the same manner as described in Example I. The resistors were fired in a nitrogen atmosphere for thirty minutes with resistors containing 20% and 25% titanium boride being fired at a temperature of 1150° C. and the resistors containing 30% titanium boride being fired at 1100° C. The average resistance values and temperature coefficient of resistors for each group of the resultant resistors are indicated in Table V.

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TABLE V

Titanium boride (percent by weight)	Glass frit (percent by weight)	Resistance (ohms/□)	Temperature Coef. of resistance (percent per ° C.)	
			+25° C. to +150° C.	+25° C. to -55° C.
20	80	1,400,000	-.0737	-.1116
25	75	8,000	-.0548	-.0689
30	70	625	±.0047	-.0055

It should be understood that the examples of the resistors and resistance materials of the present invention shown in Tables I through V are given merely to illustrate certain details of the invention and are not to be taken as in any way limiting the invention thereto. The present invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof and, accordingly, reference should be made to the appending claims, rather than to the foregoing specification as indicating the scope of the invention.

We claim:

1. A vitreous enamel resistor composition adapted to be applied to and fired on a substrate to form an electrical resistor comprising a mixture of a glass frit and a

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finely divided metal boride selected from the group consisting of chromium boride, zirconium boride, molybdenum boride, tantalum boride and titanium boride, wherein the metal boride is present in the proportions of, by weight, 10% to 35% for chromium boride, 20% to 50% for zirconium boride, 20% to 50% for molybdenum boride, 35% to 65% for tantalum boride and 20% to 50% for titanium boride.

2. A vitreous enamel resistor composition in accordance with claim 1 in which the resistor composition is coated and fired on the surface of a ceramic body to provide a glass film having the metal boride particles embedded in and dispersed throughout the glass film.

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WILLIAM L. JARVIS, Primary Examiner

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