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RESISTANCE MATERIAL AND RESISTOR MADE THEREFROM

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The present invention relates to a resistance material and a resistor made therefrom. More particularly, the present invention relates to a vitreous enamel resistance material and a resistor made therefrom.

One common type of electrical resistor comprises a ceramic dielectric body having a film of a resistance material coated on the surface thereof. The resistance material used must not only be capable of providing a desired range of resistance values, but also should be stable with respect to changes in temperature, moisture, applied voltage and other conditions which the resistor may be subjected to during use. Heretofore attempts have been made to produce a vitreous enamel resistance material comprising an enamel containing an electrically conductive material. Such enamel type resistance materials are coated on a ceramic dielectric body and fired to fuse and mature the enamel composition. The most satisfactory enamel type resistance material heretofore produced utilizes a noble metal or mixtures of noble metals as the electrically conductive material. However, the use of the noble metals as the conductive material in an enamel type resistance material has a major disadvantage in that the noble metals are relatively expensive so that the resistors formed therewith are expensive to manufacture.

It is an object of the present invention to provide a novel resistance material.

It is another object of the present invention to provide a novel vitreous enamel resistance material.

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

It is a further object of the present invention to provide an electrical resistor utilizing a novel vitreous enamel resistance material.

It is a still further object of the present invention to provide a vitreous enamel electrical resistor having a desired range of resistance values, which is relatively stable, and which is inexpensive to manufacture.

Other objects will appear hereinafter.

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

In general, the vitreous enamel resistance material of the present invention comprises a mixture of a vitreous frit or enamel and finely divided tungsten carbide. The mixture may be applied to a ceramic dielectric body, and then fired to fuse the enamel frit and bond the tungsten carbide and frit to the dielectric body. Further, it has been found that by the addition of finely divided tungsten metal to the resistance material of the present invention, the temperature coefficient of resistance of the resistance material is improved.

More specifically, the vitreous enamel resistance material of the present invention comprises a mixture of a vitreous frit or enamel and finely divided tungsten carbide in the proportion, by weight, of 25% to 90% tungsten carbide and 75% to 10% enamel frit. When including tungsten metal in the vitreous enamel resistance material of the present invention to improve the temperature coefficient of resistance of the resistance materials, the resistance material comprises 25% to 90% tungsten carbide plus tungsten metal, and 75% to 10% enamel frit. Although any amount of tungsten metal included in the resistance material of the present invention will improve its temperature coefficient of resistance, it has been found that a ratio of 4 parts of tungsten carbide to 1 part tungsten metal provides the best and most uniform improvement in the temperature coefficient of resistance throughout all ranges of resistance values.

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The vitreous enamel frit used in the resistance material of the present invention may be composed of any glass frit, such as a borosilicate frit, lead borosilicate frit, bismuth, cadmium, barium, calcium or other alkaline earth borosilicate frits. The preparation of such frits is well known and consists, for example, in melting together boric oxide, silicon dioxide, barium oxide and calcium oxide 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 coarse frit is preferably milled in a ball-mill with water to reduce the particle size of the frit.

To make the resistance material of the present invention, the glass frit, tungsten carbide and tungsten metal, when used, are broken down, such as by ball milling, to a particle size of preferably 1 to 2 microns average size. The glass frit and tungsten carbide powder, with or without tungsten metal 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 ceramic body 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 in a uniform thickness on the surface of a ceramic body. The ceramic body may be comprised of any ceramic material which can withstand the firing temperature of the resistance material composition. For example, the ceramic body may be glass, porcelain, refractory, barium titinate, or the like. The resistance material may be coated on the ceramic body by brushing, dipping, spraying, or screen stencil application. The ceramic body and resistance material coating is then fired in a conventional furnace at a temperature at which the glass frit is molten, between 750° C. and 1000° C. The resistance material is preferably fired in an inert atmosphere, such as argon, helium, nitrogen or a mixture of nitrogen and hydrogen. When the ceramic body and resistance material is cooled, the vitreous enamel hardens to bond the resistance material to the ceramic body.

Table I shows the resistance and temperature coefficient of resistance of a number of resistors of the present invention using various compositions of the resistance material of the present invention. For the resistors of Table I, the conductor of the resistance material was tungsten carbide and the glass frit consisted of 48% BaO, 8% CaO, 23% B_2O_3 and 21% SiO_2. The mixture of the conductor and the glass frit in the proportions shown in Table I was mixed together in a ball-mill in butyl Carbitol acetate. The resistance material was then coated on a steatite ceramic body. The ceramic body and resistance material coating were fired in a furnace containing an atmosphere of 15% hydrogen and 85% nitrogen at a temperature of 950° C. The resulting resistors had the resistance values and temperature coefficients of resistance shown in Table I.

Table I

Percent Glass Frit	Percent Tungsten Carbide Conductor	Resistance Ω/□	Temp. Coef. of Resistor, Percent per ° C.
70	30	270	+.03
60	40	180	+.06
50	50	100	+.09
40	60	14	+.12
30	70	7	+.13
10	90	2	+.13

Table II shows the resistance and temperature coefficient of resistance of a number of resistors using various compositions of the resistance material of the present invention in which the conductor of the resistance material comprised a mixture of tungsten carbide and tungsten metal. The ratio of tungsten carbide and tungsten metal was 4 parts tungsten carbide to 1 part tungsten metal. The glass frit was of the same composition as the glass frit used in the resistors of Table I. The resistors of Table II were made by the same method and under the same conditions as the resistors of Table I. It can be seen by comparing Table II with Table I that the addition of tungsten metal to the resistance material of the present invention reduces the temperature coefficient of resistance of the resistors.

Table II

Percent Glass Frit	Percent Tungsten Metal and Tungsten Carbide Conductor	Resistance Ω/□	Temp. Coef. of Resistor, Percent per ° C.
70	30	1,400	±.005
60	40	310	+.02
50	50	320	+.007
40	60	110	+.02
30	70	60	+.03

It should be understood that the examples of the resistors and resistance materials of the present invention shown in Table I and Table II are given merely to illustrate certain preferred 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 ceramic body to form an electrical resistor consisting essentially of by weight 25% to 90% a mixture of finely divided tungsten carbide and finely divided tungsten metal and 75% to 10% glass frit.

2. A vitreous enamel resistor composition adapted to be applied to and fired on a ceramic body to form an electrical resistor consisting essentially of by weight 25% to 90% a mixture of finely divided tungsten carbide and finely divided tungsten metal with the ratio of tungsten carbide to tungsten metal being 4 parts tungsten carbide to 1 part tungsten metal, and 75% to 10% glass frit.

3. An electrical resistor comprising a ceramic body containing on the surface thereof a coating of a vitreous enamel resistor composition consisting essentially of by weight 25% to 90% a mixture of finely divided tungsten carbide and finely divided tungsten metal embedded in a glass matrix.

4. An electrical resistor comprising a ceramic body containing on the surface thereof a coating of a vitreous enamel resistor composition consisting essentially of by weight 25% to 90% a mixture of finely divided tungsten carbide and finely divided tungsten metal with the ratio of tungsten carbide to tungsten metal being 4 parts tungsten carbide to 1 part tungsten metal, said tungsten carbide and tungsten metal being embedded in a glass matrix.

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