

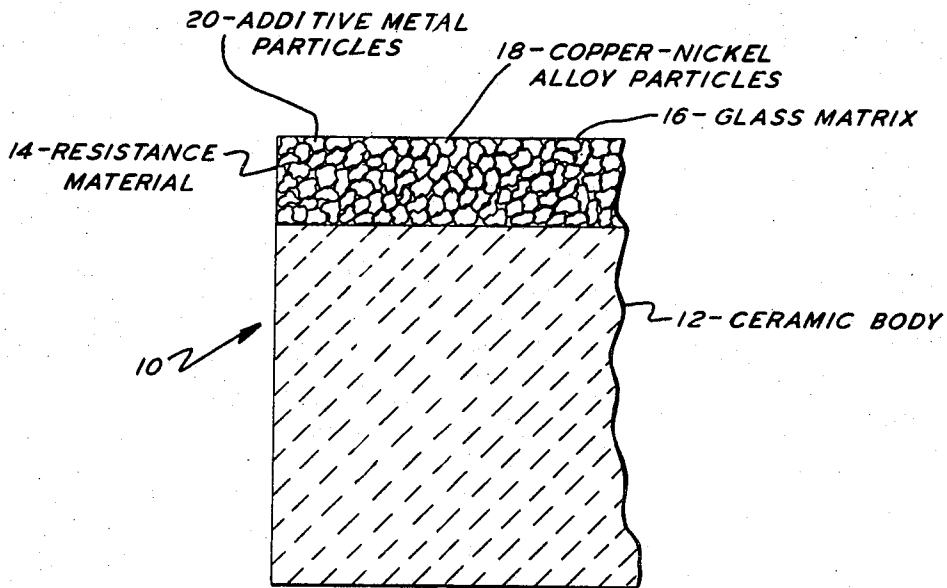
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ELECTRICAL RESISTANCE MATERIAL AND METHOD OF MAKING THE SAME

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ELECTRICAL RESISTANCE MATERIAL AND METHOD OF MAKING THE SAME

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16 Claims

ABSTRACT OF THE DISCLOSURE

An electrical resistance material comprising a mixture of a glass frit and finely divided particles of an alloy of copper and nickel. The resistance material may also include finely divided particles of an additional metal having a positive temperature coefficient of resistance and which may readily oxidize at high temperatures. The resistance material is adapted to be applied to and fixed on a substrate to form an electrical resistor which will readily fuse or open when subjected to an overload to prevent excessive overheating of the resistor.

This is a continuation-in-part of my copending application Ser. No. 8,941 filed Feb. 5, 1970 and entitled Electrical Resistance Material and Method of Making the Same, now abandoned.

The present invention relates to an electrical resistance material, a method of making the material and an electrical resistor made from the material.

A type of resistance material which has recently come into use is the vitreous enamel resistance material which comprises a mixture of a glass frit and finely divided particles of a conductive material. The mixture is applied to the surface of a ceramic substrate and fired at the melting temperature of the glass. When cooled there is provided a film of glass having the particles of the conductive material dispersed throughout the glass film. The conductive material used must not only provide a wide range of resistance values, but also must provide a stable resistor, i.e., a resistor whose resistance value does not change during use. Another characteristic which may be desirable in a resistor is a low temperature coefficient for resistance, i.e., a resistor providing a small change in resistance when subjected to a change in temperature.

Heretofore, the conductive material which has been used to obtain a vitreous enamel resistor having satisfactory electrical characteristics generally includes one or more noble metals. However, since the noble metals are expensive, the resistance materials made with them are also expensive. Therefore, it would be desirable to have a conductive material which can be used in a vitreous enamel resistance material which is inexpensive and still provides a resistor having satisfactory electrical characteristics.

Another desirable characteristic in a resistor is that it be self-limiting as to the amount of heat generated when subject to overload conditions.

It is an object of the present invention to provide a novel vitreous enamel resistance material and a method of making the same.

It is another object of the present invention to provide a vitreous enamel resistance material and a resistor made therefrom which utilizes an inexpensive conductive material.

It is a further object of the present invention to provide a vitreous enamel resistance material which utilizes an inexpensive conductive material and which will provide electrical resistors having a desired range of resistance values and which are relatively stable.

It is a further object of the present invention to provide a vitreous enamel resistance material and a resistor made

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therefrom which will fuse or open to a high resistance condition when subjected to an overload condition, so as to prevent excessive overheating of the resistor.

These objects are achieved by a vitreous enamel resistance material comprising a mixture of a glass frit and finely divided particles of an alloy of copper and nickel. Finely divided particles of an additional metal which has a positive temperature coefficient of resistance may also be included. Such particles are preferably of a metal which is easily oxidized at elevated temperatures. The conductive material is present in the amount of 25% to 75% by weight, and the additional metal can be present in the amount of not more than 20% by weight.

The invention accordingly comprises a composition of matter and the 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.

The drawing is a cross-sectional view, on a highly exaggerated scale, of a portion of a resistor made from the resistance material of the present invention.

In general the vitreous enamel resistance material of the present invention comprises a mixture of a glass frit and finely divided particles of an alloy of copper and nickel. By "finely divided particles" it is meant an average particle size of not greater than 5 microns. The alloy of copper and nickel is present in the resistance material in the amount of 25% to 75% by weight. The ratio of the copper to nickel in the alloy may be between 78% copper and 22% nickel and 35% copper and 65% nickel. However, an alloy having a copper to nickel ratio in the range of 74% copper and 26% nickel and 42% copper and 58% nickel is preferred to provide a resistance material having a low temperature coefficient of resistance. Furthermore, it has been found that the addition to the resistance material of a small amount of finely divided particles of an additive metal which has a positive temperature coefficient of resistance and which will readily oxidize at elevated temperature will not only improve the temperature coefficient of resistance of the resistance material, but also prevents blistered and rough surfaces when the resistance material is fired to fuse the material on a substrate. Such an additive metal may be a refractory metal, such as tungsten, molybdenum, zirconium, hafnium, vanadium, niobium, titanium, chromium or tantalum. The additive metal may be present in the resistance material in the amount of up to 20% by weight. However, from 3% to 7% by weight is preferred.

The glass frit used in the resistance material of the present invention may be of any well-known composition which has a melting point below that of the copper-nickel alloy and the additive metal used. 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, of 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, 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 and to obtain a frit of substantially uniform size.

To make the resistance material of the present invention, commercially available copper-nickel alloy powder, which is generally of a particle size larger than 5 microns, is reduced in size to an average particle size less than 5 microns by dry milling in a pebble mill with a portion

of the glass frit which is to be included in the resistance material. If the copper-nickel alloy powder is dry milled by itself, the powder tends to agglomerate because of the ductility of the alloy, and it is not possible to properly reduce the size of the powder. However, it has been

peak temperature of between 750° C. and 900° C. The firing time from room temperature to peak temperature and back to room temperature was between 10 to 60 minutes. The resulting resistors had the resistance values and temperature coefficients of resistance shown in Table II.

TABLE I

	1	2	3	4	5	6	7	8	9	10
Copper to nickel ratio	78/22	55/45	50/50	40/60	50/50	50/50	50/50	50/50	48/52	48/52
Wt. percent of copper-nickel alloy	50	50	50	50	41.6	43.5	51.5	61.8	44	58.5
Wt. percent of tungsten	0	0	0	0	3.4	3.5	3.5	3.2	6.0	6.5
Wt. percent of glass frit	50	50	50	50	55	53	45	35	50	35

found that by including some of the glass frit with the alloy powder during the milling operation, agglomeration is prevented and the alloy powder can be reduced to the desired particle size.

The copper-nickel alloy powder and glass frit mixture is then mixed with additional glass frit and the finely divided particles of the additional metal, if used, in the desired proportions of the ingredients to achieve a resistance material of the desired resistance value and temperature coefficient of resistance. The ingredients are thoroughly mixed together, such as by ball milling in water or an organic medium such as butyl carbitol acetate. After the ingredients are blended, the viscosity of the mixture is adjusted, such as by removing or adding the liquid medium, to the proper viscosity for the desired manner of applying the resistance material to make a resistor.

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 titanate, 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 becomes molten but less than the melting temperature of the copper-nickel alloy or the additive metal. The resistance material is preferably fired in an inert atmosphere, such as argon, helium or nitrogen, or a reducing atmosphere, such as hydrogen 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.

Referring to the drawing, there is shown a resistor, generally designated as 10, made from the resistance material of the present invention. Resistor 10 comprises a ceramic body 12 having a layer 14 of the resistance material coated on the surface thereof. The resistance material layer 14 comprises a glass matrix 16 having the copper-nickel alloy particles 18 and the additive metal particles 20 embedded in and dispersed throughout the glass matrix 16.

Table I shows the composition of a number of resistors of the present invention in which the particles of the copper-nickel alloy in the amounts shown were mixed with a titanium, aluminum, barium borosilicate glass frit of the composition described in U.S. Pat. No. 3,277,020 to B. V. Janakirana-Rao, issued Oct. 4, 1966, entitled "Glass Composition and Electrical Resistance Material Made Therefrom." Resistors 5 through 10 included tungsten as an additive metal. The resistance materials shown in Table I were made by mixing together the glass frit and conductive materials in the proportions shown in a ball mill in butyl carbitol acetate. The resistance materials were coated on cylindrical ceramic bodies by dipping the bodies in the resistance materials. The bodies were allowed to dry to remove the butyl carbitol acetate, and were then fired in a furnace containing a nitrogen atmosphere. The furnace was a conveyor kiln having a

TABLE II

Resistance (ohms/)	Temperature coefficient of resistance (percent per ° C.)	
	+25° C. to -55° C.	+25° C. to +150° C.
1-----	0.8	+ .0214
2-----	1.5	- .0106
3-----	1.5	- .0076
4-----	1.3	+ .0107
5-----	5.0	+ .0015
6-----	3.0	+ .0002
7-----	1.0	+ .0010
8-----	0.3	- .0045
9-----	1.6	+ .0020
10-----	0.3	0

The resistors of the present invention have very good flammability characteristics in that they do not excessively overheat when subject to an overload. This good flammability characteristic is the result of the resistors quickly converting to a high resistance condition when subjected to an overload. For example, resistors with a resistance value of 43 ohms and a rating of one-half (½) watt embodying the invention fused to an open circuit condition within approximately two seconds when subjected to an overload of 30 watts, and the fusing condition occurred more quickly as the overload wattage increased. On the other hand, prior art vitreous enamel resistors of the same resistance and wattage rating were found to flame and glow with intense heat within five seconds of such an overload. Thus, there is provided by the present invention, a vitreous enamel resistance material and resistor made therefrom which is relatively stable with regard to temperature, and has good flammability characteristics so that it will not catch fire when subjected to an overload.

It should be understood that the examples of the resistors and resistance materials of the present invention shown in Tables I and II 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.

What is claimed is:

1. A vitreous enamel resistance composition adapted to be applied to and fired on a substrate to form an electrical resistor consisting essentially of a glass frit and finely divided particles of an alloy of copper and nickel in which the alloy is present in the amount of 25% to 75% by weight.

2. A vitreous enamel resistance composition in accordance with claim 1 in which the ratio of the copper to nickel in the alloy is between 78% copper and 22% nickel and 35% copper and 65% nickel.

3. A vitreous enamel resistance composition in accordance with claim 2 in which the ratio of the copper to nickel in the alloy is between 74% copper and 26% nickel and 42% copper and 58% nickel.

4. A vitreous enamel resistance composition in accordance with claim 1 including up to 20% of finely divided particles of an additive metal having a positive temperature coefficient of resistance.

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5. A vitreous enamel resistance composition in accordance with claim 4 in which said additive metal is easily oxidized at elevated temperatures.

6. A vitreous enamel resistance composition in accordance with claim 4 in which the additive metal is present in the amount of 3% to 7% by weight.

7. A vitreous enamel resistance composition in accordance with claim 4 in which the additive metal is a refractory metal selected from the group consisting of tungsten, molybdenum, zirconium, hafnium, vanadium, niobium, titanium, chromium and tantalum.

8. An electrical resistor comprising a ceramic body containing on the surface thereof a coating of a vitreous enamel resistor composition consisting essentially of 25% to 75% by weight of finely divided particles of an alloy of copper and nickel embedded in a glass matrix.

9. An electrical resistor in accordance with claim 8 in which the alloy contains 78% to 35% copper and 22% to 65% nickel.

10. An electrical resistor in accordance with claim 9 in which the alloy contains 74% to 42% copper and 26% to 58% nickel.

11. An electrical resistor in accordance with claim 8 in which the vitreous enamel resistor composition includes up to 20% of finely divided particles of an additive metal having a positive temperature coefficient of resistance embedded in the glass matrix.

12. An electrical resistor in accordance with claim 11 in which said additive metal is easily oxidized at elevated temperatures.

13. An electrical resistor in accordance with claim 11 in which the additive metal is present in the amount of 3% to 7% by weight.

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14. An electrical resistor in accordance with claim 11 in which the additive metal is a refractory metal selected from the group consisting of tungsten, molybdenum, zirconium, hafnium, vanadium, niobium, titanium, chromium and tantalum.

15. A method of making an electrical resistor comprising the steps of reducing particles of an alloy of copper and nickel to an average particle size of not greater than 5 microns, mixing said alloy particles with a glass frit, applying said mixture to the surface of a ceramic body, and firing the coated body to a temperature at which the glass frit melts but below the melting temperature of the alloy.

16. A method in accordance with claim 15 in which the alloy is reduced in size by dry milling the alloy particles in a pebble mill with a portion of the glass frit.

References Cited

UNITED STATES PATENTS

20	3,180,841	4/1965	Murphy	252—515
	3,396,055	8/1968	Hedden	252—512 X
	2,696,544	12/1954	Poch	201—63
	2,679,568	5/1954	Smith	252—518 X
	2,863,840	12/1958	Bol	252—519 X
25	3,209,299	9/1965	Ganci	252—520 X
	3,441,516	4/1969	Mulligan	252—518 X
	3,551,195	12/1970	Wada	252—518 X

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