A method of making a resistor termination comprising the steps of applying to the surface of a substrate and firing a mixture of glass frit and particles of a compound taken from the group consisting of ruthenium oxide, iridium oxide, and rhodium oxide and mixtures thereof, until the compound dissociates to form and sinter the metal. The mixture is fired at a temperature of at least 900°C and preferably at 1,150°C in a reducing or non-oxidizing atmosphere such as that provided by nitrogen. When cooled there is provided a glass film with metal particles therein strongly bonded to the substrate.

7 Claims, 1 Drawing Figure
14-TERMINATION (METAL GLAZE)

16-RESISTANCE FILM

12-CERAMIC
TERMINATION FOR RESISTOR AND METHOD OF MAKING THE SAME

The present invention relates to a method of making a resistor termination and the termination produced thereby, and more particularly to a method of making a conductive termination for a vitreous enamel resistor.

Vitreous enamel resistors include a substrate having on a surface thereof, a film of glass and particles of a conductive material embedded in and dispersed throughout the glass film. The resistor is made by first forming a mixture of a glass frit and particles of the conductive material. The mixture is applied to the substrate and fired at a temperature at which the glass melts. Certain vitreous resistors such as those utilizing the precious metal and precious metal oxides are fired in oxidizing atmospheres, while other vitreous resistors such as those using refractory metals, and refractory metal borides, and nitrides, have been fired in non-oxidizing environments. When the resistor is cooled, the glass solidifies to form the glass film with the conductive particles therein.

In order to provide an electrical connection to the resistor, it is desirable to provide on the substrate at each end of the resistance film a conductive termination. Hereinafter, the termination generally used for resistors of the type produced in a non-oxidizing atmosphere, was a film of a metal, such as nickel or copper. However, it has been found that such metal film terminations are not suitable for many vitreous enamel resistance products.

Therefore, it is an object of the present invention to provide a novel method of making a termination for a vitreous enamel resistor.

It is another object of the present invention to provide a novel termination for a vitreous enamel resistor.

It is still another object of the present invention to provide a novel resistor termination.

These objects are achieved by applying to a substrate a mixture of a glass frit and particles of ruthenium oxide, iridium oxide, rhodium oxide or mixtures thereof. The substrate and coating are then heated in a nitrogen atmosphere at a temperature at which the glass frit melts and the metal oxide dissociates to the metal form and the metal sinters to a dense film which is strongly bonded to the substrate.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the composition possessing the features, properties, and the relation of constituents which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawing in which:

The FIGURE of the drawing is a sectional view of a resistor having the termination of the present invention.

Referring to the drawing there is shown a resistor which comprises a substrate of an electrical insulating material, such as a ceramic, a termination film on a surface of the substrate, and a resistance film on the surface of the substrate and contacting the termination film. The resistance film is a vitreous enamel resistance film which comprises a film of glass having particles of a conductive material embedded therein and dispersed therethrough. The conductive material may be any of the well known materials used in vitreous enamel resistors.

The termination film comprises a layer of glass having particles of either ruthenium, iridium, rhodium or mixtures thereof, embedded in and dispersed therethrough. The amount of the metal present in the termination film is preferably between 60% and 92% by volume or 79% to 99% by weight. The glass may be any glass having a suitable melting temperature, i.e., a melting temperature below that of the metal. The glasses most preferable are the borosilicate glasses, such as lead borosilicate, bismuth, cadmium, barium, calcium, or other alkaline earth borosilicates. If desired, up to 5% of the metal can be replaced by copper particles to improve the solderability of the termination film.

To make the termination film, a termination material is first formed. The termination material comprises a mixture of a glass frit and particles of either ruthenium oxide, iridium oxide, rhodium oxide or mixtures of the oxides. The amount of the oxide included is dependent on the volume percent of the metal desired in the termination film. The following table shows the amount of the oxide by weight percent needed to achieve 60% and 92% by volume of the metal in the termination film.

<table>
<thead>
<tr>
<th>Metal</th>
<th>60% by Vol.</th>
<th>92% by Vol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ruthenium Oxide</td>
<td>86.0 wt.%</td>
<td>98.0 wt.%</td>
</tr>
<tr>
<td>Iridium Oxide</td>
<td>91.0 wt.%</td>
<td>98.8 wt.%</td>
</tr>
<tr>
<td>Rhodium Oxide</td>
<td>79.0 wt.%</td>
<td>96.7 wt.%</td>
</tr>
</tbody>
</table>

The glass frit and the metal oxide particles are thoroughly mixed together, such as by milling, in a suitable vehicle, such as butyl carbital acetate, a mixture of butyl carbital acetate and toluol or any well known screening medium. The viscosity of the mixture is then adjusted for the desired manner of applying the material either by adding or removing some of the vehicle medium. If copper is to be included in the termination film, it is included in the termination material either as copper particles or copper oxide particles.

The termination material is then applied to the substrate by any desired technique, such as brushing, dipping, spraying or screen stencil application. The coated film is then preferably dried, such as by heating at a low temperature, such as 150°C for about 10 minutes. Next, the film is heated at a higher temperature, about 400°C or higher, to burn off the vehicle. Finally, the film is fired at a temperature at which the glass melts, generally at least 900°C and preferably 1,150°C, in an atmosphere, such as nitrogen, which allows dissociation of the metal oxide and sintering of the metal thus formed. After the termination film is applied to the substrate, the vitreous enamel resistance film can be applied to the substrate in the manner well known in the art.

The following table provides test results for resistors utilizing terminations produced in accordance with the present invention.
The change in resistance shown in the Table is for the application of 50 watts per square for a period of 100 hours. The small change in resistance from the power loading and the low value of current noise for the resistors indicate good electrical continuity between the resistor and the termination film.

The present invention may be carried out and embodied in other specific forms without departing from the spirit or essential attributes thereof, and, accordingly, references should be made to the appended claims, rather than the foregoing specification as indicating the scope of the invention.

What is claimed is:

1. A method of making a termination for refractory metal glaze resistors comprising the steps of:
   a. applying to the surface of a substrate a mixture of a glass frit and particles of a compound taken from the group consisting of ruthenium oxide, iridium oxide, rhodium oxide, and mixtures thereof, the metal oxide particles being present in the amount of 79% to 99% by weight and
   b. firing the mixture at a temperature of at least 900°C in a non-oxidizing atmosphere until the compound dissociates to form and sinter the metal.

2. The method in accordance with claim 1 in which the mixture is fired at a temperature of at least 900°C in a nitrogen atmosphere.

3. The method in accordance with claim 1 in which the mixture is fired at a temperature of between 1,100°C to 1,150°C.

4. The method in accordance with claim 2 in which the metal oxide particles are present in the mixture, such that the amount of metal in the termination is between 60% and 92% by volume.

5. The method in accordance with claim 4 in which copper particles are present in the mixture and in which the metal oxide and copper particles no greater than 5% are of the copper particles.

6. The method in accordance with claim 5 in which the copper particles include particles of copper and copper oxide.

7. A termination film for an electrical refractory metal glaze resistor consisting of a glass film bonded to the surface of an insulating substrate, and particles of metal from the group consisting of ruthenium, iridium and rhodium, and mixtures thereof, embedded within and dispersed throughout the glass film, the metal particles being present in the amount of 60% to 92% by volume.

* * * * *

<table>
<thead>
<tr>
<th>Compound Used</th>
<th>%ΔR</th>
<th>TCR ppm/°C</th>
<th>Noise μ V/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuO₂</td>
<td>+0.10</td>
<td>±7</td>
<td>-22</td>
</tr>
<tr>
<td>IrO₂</td>
<td>+0.07</td>
<td>±3</td>
<td>-27</td>
</tr>
<tr>
<td>Rh₂O₃</td>
<td>±3.24</td>
<td>±122</td>
<td>±80</td>
</tr>
</tbody>
</table>