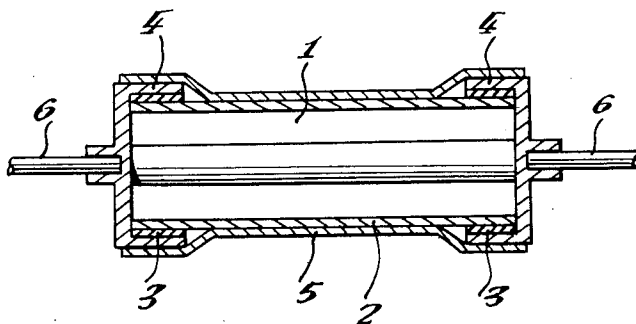


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PROCESS FOR THE PRODUCTION OF ELECTRICAL  
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## PROCESS FOR THE PRODUCTION OF ELECTRICAL RESISTORS AND RESULTING ARTICLE

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This invention relates to an electrical resistor comprising an electrically conductive fired on layer consisting of oxides and having a body composed of a vitrified or sintered inorganic material selected from e.g. glass, ceramic materials and like insulating materials (e.g. porcelain and refractories); these electrical resistors are referred to herein as resistors of the type described. It must be understood that the term "electrical resistor" is not limited to so-called precision resistors for use in radio, wireless and electronic or other electrical apparatus, but includes also electrical heating elements and devices for removing or conducting electric charges.

In United Kingdom patent specification No. 803,885 there is described and claimed an electrical resistor having a body of insulating material provided with an electrically conductive coating consisting of oxides, characterized in that said coating comprises tin, antimony and boron in the form of oxides, the amount of antimony expressed as antimony pentoxide being at most 10% and the amount of boron expressed as boric oxide being at most 2.5%, both percentages being based on the total weight of the electrically conductive coating, said coating being in the form of a film of which the surface resistivity is 1 ohm to 10,000 ohms per square centimetre. In said prior U.K. specification there is also described and claimed a process for the production of an electrical resistor having a body of insulating material provided with an electrically conductive coating consisting of oxides, which process comprises depositing under oxidizing conditions a fluid coating medium comprising a volatile or steam volatile tin compound, antimony compound and boron compound on the resistor body in a furnace, and furnace temperature being 500 to 1,000° C., said coating being in the form of a film of which the surface resistivity is 1 ohm to 10,000 ohms per square centimetre.

In U.K. patent specification No. 814,674 (application No. 17,408/56) there is described and claimed an electrical resistor having a body of a vitrified material selected from glass, ceramic material and similar insulating material, and provided with an electrically conductive coating consisting of oxides, characterized in that said coating comprises tin and boron in the form of oxides, said resistance coating being present as a film of which the surface resistivity is 1 ohm to 10,000 ohms per square centimetre. In said last mentioned prior U.K. specification there is also described and claimed a process for the production of an electrical resistor having a body of a vitrified material selected from glass, ceramic material and similar insulating material, and provided with an electrically conductive coating consisting of oxides which process comprises depositing under oxidizing conditions a fluid coating medium comprising a volatile tin compound and boron compound on the resistor body in a furnace to form a film, the furnace temperature being 600 to 1,000° C., said film having a surface resistivity of 1 ohm to 10,000 ohms per square centimetre.

Electrical resistors which are suitable for use in precision components often require a high electrical resistance coupled with other properties required of resistors for use in precision instruments, e.g. temperature coefficient of resistance.

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It has now been found that resistors of the type described and having an electrically conductive coating similar to that described in the above two prior U.K. specifications may be produced with high resistivities, e.g. under certain circumstances a surface resistivity of up to  $10^7$  (in some cases  $10^8$  and even  $10^{13}$ ) ohms per square, by applying the oxides intended to form the electrically conductive coating in a certain manner as described hereinafter. It must be understood that the oxides in the resistive film on the resistors of the present invention are (i) tin oxide and (ii) boron oxide or antimony oxide or both antimony and boron oxides; optionally there may be present a further oxide, for example titanium oxide, aluminum oxide, beryllium oxide, magnesium oxide, silicon oxide, zinc oxide, manganese oxide and cobalt oxide or an admixture thereof.

In the accompanying drawing reference numeral 1 relates to the ceramic substrate which, in this case, is in the form of a tube. Reference numeral 2 denotes the resistive film. Reference numeral 3 indicates a conducting compound applied to the ends of the resistive film. Reference numeral 4 designates caps which are a force fit on the ends of the resistor. Reference numeral 5 denotes an insulating layer of lacquer or other suitable material. Reference numeral 6 indicates the terminal wires by which the current is applied.

According to the present invention there is provided a process for the production of a resistor of the type described which includes applying a suspension of a flux and a powdered oxide mixture in a liquid, said powdered oxide mixture comprising tin oxide and boron oxide and/or antimony oxide, and said liquid being inert to the flux and to the powdered oxide mixture, to a resistor body composed of a vitrified or sintered inorganic material to form a coating thereon, then drying the resultant coated body and thereafter firing it under neutral or oxidizing conditions according to requirements to produce a resistive film on the body which resistive film is in the form of a fired on layer, the proportions and amounts of said powdered oxide and flux and the thickness of the coating applied to said body before firing being such as to produce a film after firing having a surface resistivity greater than 1,000 ohms per square. It must be understood that the suspension with which the resistor body is to be coated may also contain as a further constituent one or more of the oxides mentioned above as being optional.

The flux, e.g. ground glass in the suspension may be present in an amount from a few percent up to 50% or more by weight based on the total oxides present, the lower limit of the proportion of glass being that which is sufficient to bond the tin oxide and other oxides firmly to the surface of the substrate. This minimum amount depends on, inter alia, the nature of the glass, the firing temperature and the degree of subdivision. Under the most favourable conditions an amount of approximately 10% by weight would be sufficient.

The nature of the glass as flux to be incorporated in the suspension is not critical. Commercially used lead glass has been found to be as effective as specially prepared borosilicate glasses. Glass and like materials which have been used are as follows: A commercial lead glass containing 56 parts by weight silica, 30 parts by weight lead oxide, 5 parts by weight soda, 7 parts by weight potash and minor quantities of alumina and magnesia; another suitable commercial glass had the composition silica 54.25 parts by weight, alumina 22 parts by weight, boric oxide 7.5 parts by weight, calcium oxide 13.25 parts by weight, barium oxide 3 parts by weight; another glass which was used consisted of 88 parts by weight silica and 12 parts by weight boric oxide.

Generally speaking, as flux a high melting point glass

such as borosilicate glass would be used where the resistor is to be used at high temperatures, whereas a lead glass could be used where such high temperatures are not required.

The resistor body is composed of a vitrified or sintered inorganic material, which is preferably glass or a ceramic material.

The liquid in which the glass and oxides are to be suspended is for example an aqueous or alcoholic medium containing a suspending agent. For example, where water is used as suspension medium 0.5% by weight of ammonium alginate was found to be a useful suspending agent, whereas 5% by weight of colophony resin was used with industrial alcohol.

It must be understood that the flux need not necessarily be added to the suspension as such but it is also within the scope of the present invention to melt together the ingredients of the final resistive film together, then to grind the solidified melt and suspend the resulting ground mass. For example, silica, boric oxide and tin oxide in the required proportions may be melted together and the resulting solidified mass ground and suspended in the suspension medium after grinding it.

The fineness to which the material to be suspended is to be ground is of some importance as it is necessary for the ground material to remain in suspension during its application to the resistor body, e.g. of the order of a particle size of 1 to 10 microns. Suitably the ground particles should pass a 250 or 300 mesh sieve, preferably 350 mesh sieve. Advantageously the powdered oxide mixture is sufficiently finely divided as to pass through a 350 British Standard mesh sieve with a maximum of 1% residue.

The amounts of tin oxide, boron oxide and/or antimony oxide in the resistive film are as set forth in the above two prior U.K. specifications.

The process of this invention also includes the further step, if required, of applying electrical contacts to the fired resistor. The electrical contacts may be sprayed-on metal or electrolytically deposited metal. Alternatively the electrical contacts may be applied to the resistor body by applying a suitable liquid suspension of silver oxide or other metallic oxide to the resistor body and firing said body at a suitably high temperature.

The following examples illustrate the present invention without, however, limiting it.

#### Example 1

An intimate mixture in the proportions of 94 gms. of pure stannic oxide and 6 gms. of pure antimony trioxide was formed by wet milling these substances in a ball mill for 24 hours. The liquid used was industrial spirit but water could and has been used, and any suitably inert liquid would serve the purpose. The mixture was then dried at a suitable temperature to remove the industrial spirit, the powder was placed in a refractory crucible fitted with a cover or lid and the whole placed in an electrically heated furnace and fired to a peak temperature of 1300° C. for a period of 2 hours, the furnace atmosphere during this time being oxidizing. It should be noted that, whereas before this treatment the stannic oxide and antimony trioxide and the mixture formed therefrom was white and substantially a non-conductor of electricity, after this treatment the resultant powder was blue and a good conductor of electricity.

The powder so prepared was again wet milled in a ball mill for 24 hours and dried when it was found to be of such a fine state of division that it would all pass through a 350 mesh sieve.

100 gms. of this powder was added to 100 gms. of powdered glass, the glass being G.E.C. Lemington H.26.X., and the state of division of the glass being such that it would pass through a 350 mesh sieve; the mixture was then milled in a ball mill for 24 hours. This mixture was placed in a crucible and fired in an electric furnace to a

temperature greater than 850° C. but not exceeding 900° C. for a period of 1 hour, the furnace atmosphere during this time being oxidizing. The mixture was then broken down in a pestle and mortar until it would pass through a 20 mesh sieve. The resultant coarse powder was placed in a mill jar with 5% of its weight of colophony resin and 400 ccs. of industrial spirit and milled for 24 hours when it formed a suspension or slip.

This slip was applied to porcelain rods of dimensions 6.3 mm. x 50 mm. by holding one end of the porcelain rod in a chuck and rotating the rod axially at a few revolutions per second; whilst the rod was rotating the slip was sprayed on from a spray gun using compressed air at a pressure of 20 lbs./sq. in. The thickness of the film deposited on the rod was about 0.3 mm. The film dried within a few seconds after application and was then strong enough to stand handling. The rods were supported near the ends on a jig of nickel-chrome alloy and fired in an electrically heated furnace to a peak temperature of 900° C. for a period of 1 hour, the furnace atmosphere during this time being oxidizing.

In order to test the electrical properties of the resistors a contact material of sprayed zinc was applied to the ends of the rods and electrical contact was made by brass push-on caps with soldered leads. The surface resistivity of the film was  $10^8$  ohms per square and only varied slightly between specimens ( $3 \times 10^7$  to  $4 \times 10^8$  ohms per square). The temperature coefficients ranged from  $-0.13\%/^{\circ}\text{C.}$  to  $-0.21\%/^{\circ}\text{C.}$  (Load changes were about 2% after 100 hours D.C. load at 500 volts.)

#### Example 2

The preparation of the conductive stannic oxide and antimony oxide powder up to the grinding to pass a 350 mesh sieve was as in Example 1.

150 gms. of this powder was added to 50 gms. of powdered glass, the glass being G.E.C. Wembley L.I., and the state of division of the glass being such that it would all pass through a 350 mesh sieve; the mixture was then milled in a ball mill for 24 hours. This mixture was placed in a crucible and fired in an electric furnace to a temperature greater than 650° C. but not exceeding 700° C. for a period of 1 hour, the furnace atmosphere during this time being oxidizing. The mixture was then broken down in a pestle and mortar until it would pass through a 20 mesh sieve. The resultant coarse powder was placed in a mill jar with 5% of its weight of colophony resin and 400 ccs. of industrial spirit and milled for 24 hours when it formed a suspension or slip.

This slip was applied to porcelain rods of dimensions 6.3 mm. x 50 mm. by holding one end of the porcelain rod in a chuck and rotating the rod axially at a few revolutions per second; whilst the rod was rotating the slip was sprayed on from a spray gun using compressed air at a pressure of 20 lbs./sq. in. The thickness of the film deposited on the rod was about 0.3 mm. The film dried within a few seconds after application and was then strong enough to stand handling. The rods were supported near the ends on a jig of nickel chrome alloy and fired in an electrically heated furnace to a peak temperature of 900° C. for a period of 1 hour, the furnace atmosphere during this time being oxidizing.

In order to test the electrical properties of the resistors a contact material of sprayed zinc was applied to the ends of the rods and electrical contact was made by brass push-on caps with soldered leads. The surface resistivity of the film was  $10^6$  ohms per square and only varied slightly between specimens ( $8 \times 10^5$  to  $2 \times 10^6$  ohms per square). The temperature coefficients ranged from  $-0.12\%/^{\circ}\text{C.}$  to  $-0.15\%/^{\circ}\text{C.}$

#### Example 3

The solid component of the coating slip was prepared as follows. A mixture was formed in the proportions of 61.7 gms. stannic oxide, 21.3 gms. antimony trioxide,

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66.0 gms. precipitated silica and 17 gms. boric acid, by mixing the components in a mechanical mortar for 2 hours. The mixture was placed in a refractory crucible fitted with a cover or lid and the whole placed in an electrically heated furnace and fired to a peak temperature of 1300° C. for a period of 2 hours, the furnace atmosphere during this time being oxidizing.

The resultant vitrified material was removed from the crucible and broken down in a pestle and mortar until it would all pass through a 20 mesh sieve. The coarse powder was then placed in a mill jar with 5% of its weight of colophony resin and 300 ccs. of industrial spirit and milled for 24 hours when it formed a suspension or slip.

This slip was applied to porcelain rods of dimensions 6.3 mm. x 50 mm. by holding one end of the porcelain rod in a chuck and rotating the rod axially at a few revolutions per second; whilst the rod was rotating the slip was sprayed on from a spray gun using compressed air at a pressure of 20 lbs./sq. in.

The thickness of the coating deposited was about 0.3 mm. The coating dried within a few seconds after application and was then strong enough to stand handling. The rods were supported near the ends on a jig of nickel chrome alloy and fired in an electrically heated furnace to a peak temperature of 1100° C. for a period of 10 minutes, the furnace atmosphere during this time being oxidizing.

A contact material of sprayed zinc was applied to the ends of the rods and electrical contact was made by brass push-on caps with soldered leads. The surface resistivity was  $8 \times 10^8$  ohms per square. The temperature coefficients range from  $-0.085\%/^{\circ}\text{C.}$  to  $-0.088\%/^{\circ}\text{C.}$  (Load change 0.05% after 100 hours A.C. load at 2 watts.)

What I claim and desire to secure by Letters Patent is:

1. A process for the production of an electrical resistor comprising a body composed of a vitrified or sintered inorganic material and an electrically conductive fired on layer consisting of oxides, which includes applying a suspension of a flux and a powdered oxide mixture in a liquid to said resistor body to form a coating thereon wherein the powdered oxide mixture is prepared separately and is mixed with the flux suspension to form a slip, said powdered oxide mixture comprising tin oxide and at least one of the oxides selected from the group consisting of boron oxide and antimony oxide, and said liquid being inert to the flux and to the powdered oxide mixture, then drying the resultant coated body and thereafter firing it under non-reducing conditions to produce a resistive film on said resistor body which resistive film is in the form of a fired on layer, the proportions and amounts of said powdered oxide and flux and the thickness of the coating applied to said resistor body before firing being such as to produce a film after firing having a surface resistivity greater than 1,000 ohms per square.

2. A process for the production of an electrical resistor comprising a body composed of a vitrified or sintered inorganic material and an electrically conductive fired on layer consisting of oxides, which includes applying a suspension of a flux and a powdered oxide mixture in a liquid to said resistor body to form a coating thereon wherein the powdered oxide mixture is prepared separately and is mixed with the flux suspension to form a slip, said powdered oxide mixture comprising tin oxide and at least one of the oxides selected from the group consisting of boron oxide and antimony oxide, and said liquid being inert to the flux and to the powdered oxide mixture, then drying the resultant coated body and thereafter firing it under oxidizing conditions to produce a resistive film on said resistor body which resistive film is in the form of a fired on layer, the proportions and amounts of said powdered oxide and flux and the thickness of the coating applied to said resistor body before firing being

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such as to produce a film after firing having a surface resistivity greater than 1,000 ohms per square.

3. A process for the production of an electrical resistor comprising a body composed of a vitrified or sintered inorganic material and an electrically conductive fired on layer consisting of oxides, which includes applying a suspension of a flux and a powdered oxide mixture in a liquid to said resistor body to form a coating thereon wherein the powdered oxide mixture is prepared separately and is mixed with the flux suspension to form a slip, said powdered oxide mixture comprising tin oxide and at least one of the oxides selected from the group consisting of boron oxide and antimony oxide and at least one further oxide selected from the group consisting of titanium oxide, aluminium oxide, beryllium oxide, magnesium oxide, silicon oxide, zinc oxide, manganese oxide and cobalt oxide, and said liquid being inert to the flux and to the powdered oxide mixture, then drying the resultant coated body and thereafter firing it under non-reducing conditions to produce a resistive film on said resistor body which resistive film is in the form of a fired on layer, the proportions and amounts of said powdered oxide and flux and the thickness of the coating applied to said resistor body before firing being such as to produce a film after firing having a surface resistivity greater than 1,000 ohms per square.

4. A process for the production of an electrical resistor comprising a body composed of a vitrified or sintered inorganic material and an electrically conductive fired on layer consisting of oxides, which includes applying a suspension of a ground glass and a powdered oxide mixture in a liquid to said resistor body to form a coating thereon wherein the powdered oxide mixture is prepared separately and is mixed with the flux suspension to form a slip, said powdered oxide mixture comprising tin oxide and at least one of the oxides selected from the group consisting of boron oxide and antimony oxide, and said liquid being inert to the ground glass and to the powdered oxide mixture, then drying the resultant coated body and thereafter firing it under non-reducing conditions to produce a resistive film on said resistor body which resistive film is in the form of a fired on layer, the proportions and amounts of said powdered oxide and ground glass and the thickness of the coating applied to said resistor body before firing being such as to produce a film after firing having a surface resistivity greater than 1,000 ohms per square.

5. A process according to claim 4, wherein the glass is selected from the group consisting of borosilicate glass and lead glass.

6. A process according to claim 1, wherein the resistor body is composed of glass or a ceramic material.

7. A process according to claim 1, wherein the powdered oxide mixture is sufficiently finely divided as to pass through a 350 British Standard mesh sieve with a maximum of 1% residue.

8. A process for the production of an electrical resistor comprising a body composed of a vitrified or sintered inorganic material and an electrically conductive fired on layer consisting of oxides, which includes applying a suspension of a flux and a powdered oxide mixture in a liquid to said resistor body to form a coating thereon wherein the powdered oxide mixture is prepared separately and is mixed with the flux suspension to form a slip, said powdered oxide mixture comprising tin oxide and at least one of the oxides selected from the group consisting of boron oxide and antimony oxide, and said liquid being inert to the flux and to the powdered oxide mixture, then drying the resultant coated body and thereafter firing it under non-reducing conditions to produce a resistive film on said resistor body which resistive film is in the form of a fired on layer, the proportions and amounts of said powdered oxide and flux and the thickness of the coating applied to said resistor body before firing being such as to produce a film after firing having

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a surface resistivity greater than 1,000 ohms per square, and finally applying electrical contacts to the fired resistor.

9. A process according to claim 8, wherein the electrical contacts are sprayed-on metal.

10. A process according to claim 8, wherein the electrical contacts are electrolytically deposited metal.

11. A process according to claim 8, wherein the electrical contacts are applied to the resistor body by applying a suitable liquid suspension of metallic oxide, for example silver oxide, to the resistor body and firing said body at a suitably high temperature.

12. A process according to claim 1, wherein said liquid inert to the flux and the powdered oxide mixture is an aqueous medium containing a suspending agent.

13. A process according to claim 1, wherein said liquid inert to the flux and the powdered oxide mixture is an alcoholic medium containing a suspending agent.

14. A process for the production of an electrical resistor comprising a body composed of a vitrified or sintered inorganic material and an electrically conductive fired on layer consisting of oxides, which includes applying a suspension of ground glass and a powdered oxide mixture in a liquid to said resistor body to form a coating thereon wherein the powdered oxide mixture is prepared

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separately and is mixed with the flux suspension to form a slip, said powdered oxide mixture comprising stannic oxide and antimony trioxide, and said liquid being inert to the ground glass and to the powdered oxide mixture, then drying the resultant coated body and thereafter firing it under oxidizing conditions to produce a resistive film on said resistor body which resistive film is in the form of a fired on layer, the proportions and amounts of said powdered oxide and ground glass and the thickness of the coating applied to said resistor body before firing being such as to produce a film after firing having a surface resistivity greater than 1,000 ohms per square.

15. A process according to claim 14, in which the powdered oxide mixture also comprises boron trioxide and silica.

16. An electrical resistor produced by the process of claim 1.

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