Base metal resistive paints.

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Description

Technical field

The present invention relates to base metal resistive paints, resistors made from the resistive paint, and a method for making the resistive paint. More particularly, this invention relates to thick film base metal resistive paints comprising a mixture of 75 to 95 percent by weight glass frit, well blended with from 5 to 25 percent by weight of a tantalum oxide, the mixture being melted and reground to form a tantalum glass frit therefrom with a melting temperature of less than 800°C; a tin oxide in the ratio of 75 to 80 percent by weight tin oxide to 20 to 25 percent by weight tantalum glass frit; and a screening agent selected to be substantially vaporized during firing, wherein the resistive paint made therefrom is suitable for screening and firing in an inert atmosphere at a peak temperature of 900°C±20°C. The tin oxide is preferably preheated at 450 to 600°C in the absence of a reducing gas, prior to mixing with the tantalum glass frit. The screening agent preferably forms no carbon residue when pyrolytically decomposed in an inert atmosphere.

Background art

Tin oxide compounds have been used as a major conductive material in resistors for many years. Tin oxide films may be processed by spraying and heating a tin chloride solution; by evaporation or sputtering technology; by chemical vapor disposition, or by thick film technology.

Thick film technology has been used in the electronics industry for more than 25 years. Thick film technology includes printing and firing a resistive paint in a desired pattern upon a suitable substrate. Resistive paints used in thick film technology typically include a conductive material, a glas frit, and a screening agent.

Early thick film resistive paint patterns varied only in the composition of the conductive materials. The glass frit, after melting, was used primarily as a bonding agent to bond the conductive material to the substrate. The chemical composition of the glass frit was considered important only in regard to its melting point which was required to be below the melting point of the conductive material used. The screening agent was selected for consistency and ease of printing. Commercially available glass frits and screening agents were typically used.

Certain materials were typically mixed with tin oxide powder to obtain the wide range of resistivity and low TCR (temperature coefficient of resistance) desired.

Dearden, in an article published in Electronic Components Magazine in March, 1967, entitled High Value, High Voltage Resistors discloses the use of doped antimony oxide with tin oxide to make a binary resistive paint, but the best TCR obtained was −1500 ppm/°C. Kamigaito (U.S. Patent No. 3,915,721) patented a ternary conduc-
tive paint material including powders of 2% tantalum oxide, antimony oxide and tin oxide. Kuden et al. (U.S. Patent No. 3,928,242) discloses the use of tantalum glass frit for use with ruthenium oxide resistors. Moriguchi et al. (U.S. Patent 3,900,330) patented a zinc-sealing glass containing 0.1 to 25% Ta₂O₅ to improve surface charge density. Wahlers et al. (U.S. Patent 4,065,743) patented the use of binary conductive materials of tin oxide and tantalum oxide powders for use with standardized glass frit. Wahlers et al. (U.S. Patent 4,215,020) also patented ternary conductive materials for use with tin oxide resistors. Recently Wahlers et al. (U.S. Patents 4,378,409 and 4,397,915) claimed a tin oxide material for use with a 30 to 40% barium oxide glass frit, and a glass frit with more than 20% silicon oxide.

Chemical compounds found in a typical glass frit are mineral and inorganic. These chemicals typically exhibit a number of undesirable properties, such as: high TCR; widely variable thermal stability; poor short time overload characteristics; variable resistance values due to uneven mixing; and visible cracks and fissures. A base metal resistive paint is a resistive paint having no noble metals included in its composition.

Disclosure of the invention

The present invention discloses a tantalum glass frit, preferably a tantalum strontium glass frit, for use in mixing with tin oxide and a screening agent, preferably a non-carbon residue organic compound screening agent to form a base metal resistive paint for screening upon a substrate for subsequent firing in an inert atmosphere at a peak temperature of approximately 900°C. The tantalum glass frit and tin oxide are preferably ground to a particle size of 10 microns or less prior to mixing.

The tantalum glass frit powder is well mixed at a ratio of 20 to 25% with 75 to 80% tin oxide powder. A screening agent in the ratio of 25 to 35% is added to the tantalum glass frit and tin oxide powders, and well mixed to form a base metal resistive paint for subsequent screening and firing in an inert atmosphere at a peak temperature of 900°C±20°C to form a resistive pattern upon a substrate with a TCR within ±300 ppm/°C.

The disclosed resistive paint exhibits improved thermal stability and short time overload; maintains a tight resistance value due to improved homogeneous mixing of the chemical compounds; and improves physical appearance by reducing the observable cracks and fissures in the fired resistive paint screened upon a suitable substrate. Furthermore, a cost savings in energy, furnace life and maintenance is realized by firing at a peak temperature of 900°C, as compared with firing at peak temperatures of 1000°C to 1100°C, as currently practiced for firing most tin oxide resistive paints.

Therefore, one object is to provide an improved thick film resistive paint.

Another object is to provide a resistive paint mixed with tantalum glass frit, tin oxide powders,
and a screening agent to form a resistive paint whose TCR is within ±300 ppm/°C.

Another object is to provide a method for manufacturing a resistor made from tantalum glass frit and tin oxide powders.

Another object is to provide a screening agent having no carbon residue when pyrolytically decomposed in an inert atmosphere, for use with a base metal resistive paint.

Yet another object is to provide a tantalum glass frit and tin oxide resistive paint suitable for firing at a peak temperature of approximately 900°C.

Still another object is to provide a resistor made from a resistive paint embodying any of the objects previously disclosed.

The above-mentioned and other features and objects of the invention and the manner of attaining them will be best understood by reference to the following description of an embodiment of the invention, when considered in conjunction with the accompanying drawings.

Description of the drawings

Fig. 1 shows a partial sectional view of a resistor prior to firing made with the resistive paint of the present invention.

Fig. 1A is a graph comparing the effects of firing temperatures on TCR (SnO₂ reduced at 520°C).

Fig. 1B is a graph comparing the effects of firing temperatures on sheet resistance in ohms/square (SnO₂ reduced at 520°C).

Fig. 2A is a graph comparing the effects of firing temperatures on TCR (SnO₂ reduced at 450°C).

Fig. 2B is a graph comparing the effects of firing temperatures on sheet resistance in ohms/square (SnO₂ reduced at 450°C).

Fig. 3 is a graph comparing the ratios of SnO₂/tantalum glass on sheet resistance and TCR.

Fig. 4 is a table comparing properties of examples one through four disclosed in detail in the specification.

Fig. 5 is a flow chart showing the method of processing a resistor for tantalum glass frit, tin oxide, and a screening agent.

Best mode for carrying out the invention

The subject matter which we regard as our invention is particularly pointed out and distinctly claimed in the Claims. The structure and operation of our invention, together with further objects and advantages, may be better understood from the following description given in connection with the accompanying drawings, in which:

Fig. 1 shows a base metal resistor of the present invention prior to firing, generally designated 10.

Resistor 10 comprises a substrate 12, such as a ceramic substrate, having a layer of the resistive paint 14 of the present invention screen-printed or otherwise coated thereon for subsequent firing.

The resistive paint 14 comprises a mixture of tantalum glass frit 16 and tin oxide 18 in a preferred ratio of 20 to 25% tantalum glass frit to 75 to 80% tin oxide. Note: all compositions disclosed herein are based upon weight percentage.

The tantalum glass frit 16 preferably has a melting point of 800°C or less, and comprises from five to twenty-five percent tantalum oxide (TeO₂). The tantalum glass frit 16 preferably comprises, at least in part, strontium oxide (SrO), or strontium peroxide (SrO₂). The glass 17 and tantalum 19 are preferably ground to a particle size of ten micrometers or less, then well mixed, remelted and ground to form the tantalum glass frit 16 of the present invention.

The tantalum glass frit 16 and tin oxide 18 are preferably ground to a particle size of ten micrometers or less, and the resulting powders are added to a screening agent 20 in a ratio of 65 to 97% tantalum glass frit and tin oxide powders to 25 to 35% screening agent. The screening agent 20 preferably forms no carbon residue when pyrolytically decomposed in an inert atmosphere, such as 10% butyl-methacrylate dissolved into 90% pine oil.

The solvent used for making the screening agent can be pine oil, terpineol, an ester alcohol of Texanol from Texas Eastman Company, butyl carbitol acetate or the like. The resins used for binders can be polyalkylmethacrylate available from DuPont or Rohm and Haas; or polybutenes available as Amoco® H-25, Amoco® H-50, and Amoco® L-100 from Amoco Chemicals Corporation. A wetting agent may be added to wet the solid powders for good paint rheology.

Some commercially available screening agents after firing in an inert atmosphere at high temperature contain carbon residue, which is conductive. Such carbon residue is not combined with oxygen to form a carbon oxide during heating in an inert atmosphere, therefore the carbon in the screening agent remains in the resistive paint, adversely affecting the controlled performance characteristics of the resistor 10.

As shown in Fig. 1, the tantalum glass frit 16 contains a well blended mixture of tantalum 18 and glass 17, which has been remelted and ground to form the tantalum glass frit 16 of the present invention. The tantalum glass frit 16 when mixed with tin oxide 18 provides a more homogeneous mixture than can be readily obtained by admixing tantalum oxide to the resistive paint 14 during the mixing operation. Thus, as shown in Fig. 1, the tantalum glass frit 16 and tin oxide 18 are well dispersed within the layer of resistive paint 14.

The resulting resistive characteristics are thereby improved resulting in a more homogeneous mixture of resistive paint 14, which provides improved and more controllable conductive characteristics, as will hereinafter be disclosed.

As shown in Fig. 5, the tin oxide 18 is preferably preheated 22 in a reducing gas to a temperature of from 450°C to 600°C, for a time sufficient to reduce the oxide to a desired level. When preheating 22 is done in a tube furnace, the tin oxide 18 is preheated for about 10 minutes to one hour in a forming gas such as 2 to 7% H₂ and 93 to 98% N₂ atmosphere. The preheated tin oxide 18 is then mixed 24 with the tantalum glass frit 16 and the screening agent 20, preferably in a three roll mill
(not shown) to yield a consistent resistive paint 14 having uniform dispersions of tantalum 19 and tin oxide 18 throughout, in the desired proportions previously disclosed.

The screening agent 20 is preferably an organic compound which is free of carbon residue when pyrolytically decomposed in an inert atmosphere. A binding resin 21 may be incorporated into the screening agent 20 to improve the screening properties of the mixed resistive paint 14, prior to firing 28. Once the tantalum glass slit 16, tin oxide 18, and screening agent 20 are mixed 24 into a homogeneous resistive paint material 14, they are subsequently screened 26, preferably through a silk or stainless steel screen, onto a substrate 12. Substrate 12 is preferably an alumina substrate that has been pre-fired onto a thick film copper conductor in an inert atmosphere at about 900°C. The screen aperture size affects the resistive quality of the fired resistive paint, as will be subsequently disclosed. The preferred screen aperture size is from 185 to 325 mesh.

After screening, the resistive paint 14 disposed upon substrate 12 is preferably allowed to dry prior to firing 28. The resistive paint and substrate are subsequently fired 28 at a peak temperature of 900°C±20°C, in an inert atmosphere such as nitrogen, to form a vitreous enameled base metal resistor material fused to the substrate.

As shown in the following examples the glass frit of Example No. 1 through No. 4 will demonstrate the advantages of the addition of Ta₂O₅ (tantalum oxide) to the glass frit by comparison of 0%, 2%, 5% and 20% Ta₂O₅. Each example was tested to determine the ohms/square; Hot and Cold TCR; Thermal Stability and STOL.

In each of the following examples the Cold TCR was tested at −5°C to +25°C; the Hot TCR was tested at +25°C to +125°C; Thermal Stability was tested at 150°C for 48 hours; the STOL was tested at 500 volts or 5 watts maximum; and the resistor size tested was 1,575×3,962 mm (0.062×0.156 inches), and 2.5 squares.

Example No. 1 comprises a glass frit, having no (0%) Ta₂O₅, with (5%) SiO₂(35%) SrO(60%) B₂O₃. These materials were heated to 1200°C to form a homogeneous glass frit. This glass frit was then ground into a fine powder having a particle size of ten micrometers or less. SnO₂ (tin oxide) was then added to the glass frit in a ratio of (75%) SnO₂+(25%) glass frit. No Ta₂O₅ was present in Example No. 1. The materials were well mixed with (30%) no carbon residue screening agent to yield a resistive paint, which was subsequently screened and fired at 900°C in an inert atmosphere, as previously disclosed.

Example No. 2 comprises the glass frit of Example No. 1, wherein (2%) Ta₂O₅ was added to the glass frit prior to heating. After heating and grinding, SnO₂ was added to the glass frit in a ratio of (75%) SnO₂+(25%) glass frit having (5%) Ta₂O₅ therein. These materials were well mixed with (30%) no carbon residue, screening agent to yield a resistive paint, which was subsequently screened and fired at 900°C in an inert atmosphere, as previously disclosed. As shown in Fig. 4, Example No. 2, the ohms/square was 31K; the cold TCR was −2270; the Hot TCR was −1074; the thermal stability was 3%; and the STOL was 4%.

Example No. 3 comprises the glass frit of Example No. 1, wherein (5%) Ta₂O₅ was added to the glass frit prior to heating. After heating and grinding, SnO₂ was added to the glass frit in a ratio of (75%) SnO₂+(25%) glass frit having (5%) Ta₂O₅ therein. These materials were well mixed with (30%) no carbon residue, screening agent to yield a resistive paint, which was subsequently screened and fired at 900°C in an inert atmosphere, as previously disclosed. As shown in Fig. 4, Example No. 3, the ohms/square was 9K; the Cold TCR was −268; the Hot TCR was −279; the thermal stability was 0.03%; and the STOL was 0.05%.

Example No. 4 comprises the glass frit of Example No. 1, wherein (20%) Ta₂O₅ was added to the glass frit prior to heating. After heating and grinding, SnO₂ was added to the glass frit in the ratio of (75%) SnO₂+(25%) glass frit having (20%) Ta₂O₅ therein. These materials were well mixed with (30%) no carbon residue, screening agent to yield a resistive paint, which was subsequently screened and fired at 900°C in an inert atmosphere, as previously disclosed. As shown in Fig. 4, Example No. 4, the ohms/square was 15K; the Cold TCR was −183; the Hot TCR was −187; the thermal stability was 0.3%; and the STOL was 0.01%.

As shown in Examples No. 1, through No. 4, the addition of Ta₂O₅ to the glass frit varies the TCR considerably. The addition of 5% Ta₂O₅ to the glass frit as shown in Example No. 3 brings the TCR to less than ±300 ppm/°C which is considered acceptable for most thick film applications. The addition of 20% Ta₂O₅ to the glass frit as shown in Example No. 4, brings the TCR to less than ±200 ppm/°C which is preferred.

Another significant improvement is in thermal stability. STOL 2 to 4% variation shown in Examples No. 1 and No. 2, is unacceptable for most applications. However, increasing the content of Ta₂O₅ to 5% or more brings the thermal stability and STOL to 0.3% or less, which is within the preferred range of less than 0.5% required for most stringent thick film resistor applications.

The addition of Ta₂O₅ to the glass frit to form a tantalum glass frit provides a more homogeneous and uniform resistor paint, compared with the admixture of Ta₂O₅ particles, tin oxide, non-tantalum glass frit, and screening agent. Using the same percentage composition, the CV (coefficient of variance) of tantalum glass frit is 8 to 9% as compared to 13 to 14% for admixture compositions.

Any improvement in print technology and paint rheology will improve the CV in equal proportion. That is, an improvement in print-technology and
paint rheology reducing admixture compositions to a CV of 10 to 11%, will also reduce tantalum glass frit resistors to a CV of 5 to 6%, which remains a significant improvement.

Typically, thick film base metal resistors using tin oxide are fired at 1000°C or above (ref. US-patents 4,137,519 and 4,065,743) to improve thermal stability. At lower temperatures the glass frit is not well sintered, reducing thermal stability. By addition of 5% or more Ta₂O₅ to the glass frit, the frit is well sintered at 900°C ± 20°C.

Using the formulation disclosed in Fig. 4 Example No. 4 above, and varying the firing temperature in an inert atmosphere from 800°C to 1000°C, as shown in Fig. 1A and 1B, the most stable Hot and Cold TCR occur at approximately 900°C ± 20°C.

As shown in Fig. 1A, using a firing temperature of 900°C ± 20°C, both Hot and Cold TCR values are less than ±200 ppm/°C, which is desirable for high reliability resistor applications.

As shown in Figs. 2A and 2B, SnO₂ was pre-heated in a reducing atmosphere of 7% H₂ and 93% N₂ at a temperature of 450°C, prior to mixing the SnO₂ with the tantalum glass frit of Example No. 4 in a ratio of 3:1, (75%) SnO₂ + (25%) tantalum glass frit. These materials were well mixed with (30%) of a no carbon residue, screening agent to yield a resistive paint, which was subsequently screen upon a substrate and fired in an inert atmosphere at various temperatures from 800°C to 1000°C shown in Figs. 2A and 2B. As shown in Fig. 2A, the most stable Hot and Cold TCR values are obtained at a peak firing temperature of 900°C ± 20°C. These TCR values fall within ±100 ppm/°C, which is most desirable for the most stringent resistor applications.

Fig. 3 shows the effect on sheet resistance and Hot and Cold TCR when the ratios of SnO₂ to tantalum glass frit are varied, and the resulting mixture is screen printed in an inert atmosphere at a peak temperature of 900°C. At ratios between 3:1 and 4:1, the resulting Hot and Cold TCR are less than ±200 ppm/°C; and the sheet resistances in ohms/square are less than 10K.

Fig. 3 also shows the effect of screening through a 325 mesh screen in solid line; and the effect of screening through a 165 mesh screen in dashed line. Thus, it is noted that the larger the screen mesh size, the lower the resistance values and the more positive the TCR. However, as shown in Fig. 3, any screening size from 165 mesh to 325 mesh may be used to yield a TCR within ±200 ppm/°C, when the ratio of SnO₂ to tantalum glass frit is within the preferred range of from 3:1 to 4:1.

Thus, from Examples No. 1 through No. 4, and Figs. 1A through 4, it is disclosed that the preferred quantity of tantalum glass frit is from 20 to 25% and the preferred quantity of tin oxide is from 75 to 80% for best TCR results. If tin oxide is present in excess of 80%, the adhesion of the resistor paint to the substrate is weakened, and thermal stability is impaired. If more than 25% tantalum glass frit is present, the TCR becomes too negative.

Thus, a base metal resistor paint for firing on a substrate to form a controlled temperature coefficient of resistance within ±300 ppm/°C is disclosed for use with high reliability, thick film resistor applications.

Industrial applicability

This invention discloses a base metal resistive paint for subsequent screening and firing on a substrate to make a base metal thick film resistor for use in an electronic circuit.

Claims

1. A thick film base metal resistor paint for screening and firing onto a substrate to form a resistor with a controlled temperature coefficient of resistance within ±300 ppm/°C, which comprises:

   a mixture of 75 to 95 percent by weight glass frit, blended with from 5 to 25 percent by weight of a tantalum oxide, the mixture being melted and reground to form a tantalum glass frit therefrom with a melting temperature of less than 800°C;

   a tin oxide in the ratio of 75 to 80 percent by weight tin oxide to 20 to 25 percent by weight tantalum glass frit; and

   a screening agent selected to be substantially vaporized during firing, wherein the resistive paint made therefrom is suitable for screening and firing in an inert atmosphere at a peak temperature of 900°C ± 20°C.

2. The paint of Claim 1, characterised in that the tin oxide is preheated in a reducing atmosphere at a temperature of 450°C, to 800°C.

3. The paint of Claim 2, characterised in that the tin oxide is preheated in a reducing gas comprising from 2 to 7% H₂ and from 93 to 98% N₂, by weight.

4. The paint of Claim 1, characterised in that the tantalum glass frit and tin oxide are well mixed with 25 to 35%, by weight, screening agent to yield a consistent resistive paint for screen printing on a substrate prior to firing.

5. The paint of Claim 4, characterised in that the tantalum glass frit and tin oxide are reduced to a particle size of 10 micrometres or less prior to mixing with the screening agent.

6. The paint of Claim 4, characterised in that a binding resin is present in the screening agent.

7. The paint of Claim 4, characterised in that the screening agent forms no carbon residue when pyrolytically decomposed in an inert atmosphere.

8. The paint of Claim 7, characterised in that the screening agent which forms no carbon residue comprises 5 to 15% by weight of butyl-methacyrinate and 85 to 95% by weight of pine oil.

9. The paint of Claim 1, characterised in that the tantalum glass frit further comprises at least one additive selected from the group consisting of strontium oxide and strontium peroxide.

10. A method for preparing a thick film base metal resistor having a substrate with a resistive paint according to Claim 1 screened and fired thereon, characterized in that it comprises:

   (a) blending a tantalum glass frit with a tin oxide in the ratio of one part tantalum glass frit with three to
four parts tin oxide;
(b) mixing the combined tantala glass frit and
and tin oxide with a screening agent in the ratio of 25
to 35% by weight screening agent to 65 to 75% of
the blend of tantala glass frit and tin oxide to yield
a resistive paint;
(c) screening the resistive paint upon a sub-
strate, and
(d) subsequently firing the substrate with resis-
tive paint, thence in an inert atmos-
phere at a peak temperature of 900°C ± 20°C.
11. The method of Claim 10, characterised in
that the tantala glass frit and tin oxide are ground
to a particle size of ten micrometres or less.
12. The method of Claim 10, characterised in
that the tin oxide is preheated in a reducing gas at
a peak temperature of 450°C to 600°C.
13. The method of Claim 10, characterised in
that the screening agent forms no carbon residue
when pyrolytically decomposed in an inert atmos-
phere.
14. The method of Claim 10, characterised in
that the tantala glass frit contains from five
percent to twenty-five percent tantalum oxide of
the formula Ta₂O₅ by weight.

Patentansprüche

1. Auf Metall basierte Dickfilmwiderstands-
Paste zum Aufdrucken durch Siebdruck auf ein
Substrat und zum anschließenden Einbrennen
auf dem Substrat, um einen Widerstand mit
einem Widerstandskoeffizienten des
Widerstandes innerhalb von ±300 · 10⁻⁶°C zu
bilden, mit:
Einer Mischung aus 75—95 Gewichtsprozenten
Glas-Fritte und 5—25 Gewichtsprozenten eines
Tantaloxides, wobei diese Mischung geschmol-
en und feinzerkleinert wird, um hieraus eine
Tantal-Glas-Fritte mit einer Schmelztemperatur
von weniger als 800°C zu bilden;
einem Zinnoxid, wobei ein Verhältnis von
75—80 Gewichtsprozenten Zinnoxid zu 20—25
Gewichtsprozenten Tantal-Glas-Fritte vorgesehen
ist; und
einem Siebstoff, der so ausgewählt ist, daß er
während des Einbrennens i.w. verdampft, wobei
die aus diesen Komponenten hergestellte Wider-
stands-Paste für das Aufdrucken durch Siebdruck
und das Einbrennen in einer inerten Atmosphäre
bei einer Spitzen temperatur von 900°C±20°C ver-
wendbar ist.
2. Paste nach Anspruch 1, dadurch gekenn-
zeichnet, daß das Zinnoxid in einer reduzierenden
Atmosphäre bei einer Temperatur von 450°C bis
600°C voreingetäst wird.
3. Paste nach Anspruch 2, dadurch gekenn-
zeichnet, daß das Zinnoxid in einem reduzier-
den Gas voreingetäst wird, welches 2 bis 7 Gewichts-
prozenten H₂ und 93 bis 98 Gewichtsprozenten N₂
enthält.
4. Paste nach Anspruch 1, dadurch gekenn-
zeichnet, daß die Tantal-Glas-Fritte und das Zin-
noxid mit 25—35 Gewichtsprozenten des Sieb-
stoffes gut vermischt werden.
Revendications

1. Pâte résistante à base de métal pour couche épaisse, destinée à être appliquée par tamisage et cuite sur un substrat pour former une résistance dont le coefficient de résistance en fonction de la température est établi entre ± 300 ppm/°C, et comportant :

un mélange comprenant de 75 à 95 pour cent en poids de frite de verre mélangée avec de 5 à 25 pour cent en poids d’un oxyde de tantale, le mélange étant fondu et rebroyé de façon à produire, à partir de ce mélange, une frite de verre au tantale possédant une température de fusion inférieure à 800°C ;

un oxyde d’étain dans le rapport de 75 à 80 pour cent en poids d’oxyde d’étain pour de 20 à 25 pour cent en poids de frite de verre au tantale ; et

un agent de tamisage choisi pour être pratiquement vaporisé au cours de la cuisson, la pâte résistante résultante étant apte à être appliquée par tamisage et cuite en atmosphère inerte à une température maximum de 900°C ± 20°C.

2. Pâte selon la revendication 1, caractérisée en ce que l’oxyde d’étain est préchauffé en atmosphère réductrice à une température comprise entre 450°C et 600°C.

3. Pâte selon la revendication 2, caractérisée en ce que l’oxyde d’étain est préchauffé en présence d’un gaz réducteur comprenant de 2 à 7% en poids d’H₂ et de 93 à 98% en poids de N₂.

4. Pâte selon la revendication 1, caractérisée en ce que la frite de verre au tantale et l’oxyde d’étain sont mélangés soigneusement avec de 25 à 35% en poids d’agent de tamisage, de façon à produire une pâte résistive homogène destinée à être chargée au tamis sur un substrat avant la cuisson.

5. Pâte selon la revendication 4, caractérisée en ce que la frite de verre au tantale et l’oxyde d’étain sont réduits en particules de dimensions inférieures ou égales à 10 micromètres avant leur mélange avec l’agent de tamisage.

6. Pâte selon la revendication 4, caractérisée en ce qu’une résine de liaison est comprise dans l’agent de tamisage.

7. Pâte selon la revendication 4, caractérisée en ce que l’agent de tamisage ne donne pas de résidu carboné lorsqu’il est décomposé par pyrolyse en atmosphère inerte.

8. Pâte selon la revendication 1, caractérisée en ce que l’agent de tamisage qui ne forme pas de résidu carboné comprend de 5 à 15% en poids de méthacrylate de butyle et de 85 à 95% en poids d’huile de pin.

9. Pâte selon la revendication 1, caractérisée en ce que la frite de verre au tantale comprend en outre au moins un additif choisi parmi le groupe consistant en l’oxyde de strontium et le peroxyde de strontium.

10. Procédé de préparation d’une résistance à couche épaisse à base de métal et comprenant un substrat sur lequel est appliquée par tamisage et cuite une pâte résistive selon la revendication 1, caractérisée en ce qu’il comprend :

(a) le mélange d’une frite de verre au tantale avec un oxyde d’étain dans le rapport d’une part de frite de verre au tantale pour trois à quatre parts d’oxyde d’étain ;

(b) le mélange de la frite de verre au tantale et de l’oxyde d’étain, combinés, avec un agent de tamisage dans le rapport de 25 à 35% en poids d’agent de tamisage pour de 65 à 75% du mélange de frite de verre au tantale et d’oxyde d’étain de façon à obtenir une pâte résistive ;

(c) l’application par tamisage de la pâte résistive sur le substrat, puis

(d) la cuisson du substrat portant la pâte résistive, en atmosphère inerte et à une température maximum de 900°C ± 20°C.

11. Procédé selon la revendication 10, caractérisé en ce que la frite de verre au tantale et l’oxyde d’étain sont broyés de façon à donner des particules de dimensions inférieures ou égales à 10 micromètres.

12. Procédé selon la revendication 10, caractérisé en ce que l’oxyde d’étain est préchauffé en présence de gaz réducteur à une température maximum comprise entre 450°C et 600°C.

13. Procédé selon la revendication 10, caractérisé en ce que l’agent de tamisage ne donne pas de résidu carboné lorsqu’il est décomposé par pyrolyse en atmosphère inerte.

14. Procédé selon la revendication 10, caractérisé en ce que la frite de verre au tantale contient de 5 pour cent à 25 pour cent en poids d’oxyde de tantale de formule Te₂O₅.
FIG. 1

<table>
<thead>
<tr>
<th>PROPERTIES</th>
<th>EXAMPLE 1</th>
<th>EXAMPLE 2</th>
<th>EXAMPLE 3</th>
<th>EXAMPLE 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>OHMS/SQ.</td>
<td>60K</td>
<td>31K</td>
<td>9K</td>
<td>15K</td>
</tr>
<tr>
<td>COLD TCR</td>
<td>-13900</td>
<td>-2270</td>
<td>-285</td>
<td>-183</td>
</tr>
<tr>
<td>HOT TCR</td>
<td>-6400</td>
<td>-1074</td>
<td>-279</td>
<td>-187</td>
</tr>
<tr>
<td>THERMAL STABILITY</td>
<td>2%</td>
<td>4%</td>
<td>0.3%</td>
<td>0.3%</td>
</tr>
<tr>
<td>STOL</td>
<td>3%</td>
<td>4%</td>
<td>0.05%</td>
<td>0.01%</td>
</tr>
</tbody>
</table>

FIG. 4
FIG. 1A

EFFECTS OF FIRING TEMPERATURES ON TCR (SnO₂ REDUCED AT 520°C)

FIG. 1B

EFFECTS OF FIRING TEMPERATURES ON SHEET RESISTANCE (SnO₂ REDUCED AT 520°C)
FIG. 2A  EFFECTS OF FIRING TEMPERATURES ON TCR (SnO$_2$ REDUCED AT 450°C)

- Cold TCR
- Hot TCR

FIG. 2B  EFFECTS OF FIRING TEMPERATURES ON SHEET RESISTANCE $\sigma/\square$
(SnO$_2$ REDUCED AT 450°C)
FIG. 3

RATIOS OF SnO₂ / TANTALA GLASS ON SHEET RESISTANCE & TCR

COLD TCR
HOT TCR
165 MESH SCREEN ——— 325 MESH SCREEN
TANTALA GLASS FRIT

TIN OXIDE

SCREENING AGENT

PREHEAT 450 TO 600°C IN REDUCING GAS

MIX RESISTIVE PAINT

SCREEN 165 TO 325 MESH

FIRE @ 900°C IN INERT ATMOSPHERE

FIG. 5