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Brady et al.

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[54] **RESISTANCE COMPOSITION AND METHOD OF MAKING ELECTRICAL RESISTANCE ELEMENTS**

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[52] **U.S. Cl.** **427/101;** 427/102; 427/103; 427/376; 252/514; 252/518

[51] **Int. Cl.**[2] **H01B 1/02;** H01B 1/06

[58] **Field of Search** 117/227, 201; 252/514, 252/518; 338/308; 427/101, 102, 103, 376

[56] **References Cited**

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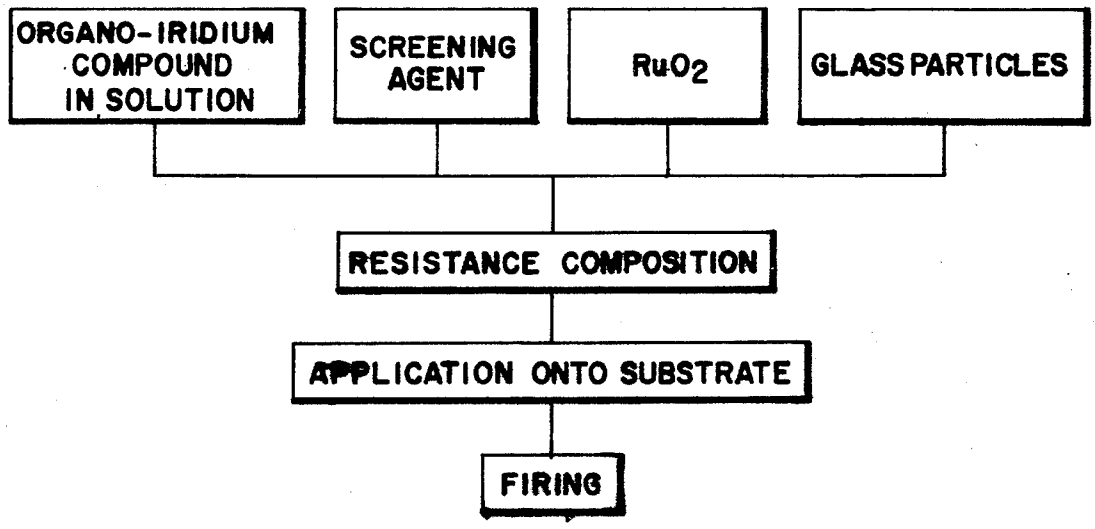
Primary Examiner—Michael F. Esposito

[57] **ABSTRACT**

An improved resistance composition and method of making electrical resistance elements comprising a glass frit and a conductive phase containing ruthenium dioxide and iridium. The ingredients are measured and mixed with a screening agent to produce a resistance composition, the iridium being present in the composition as an organometallic compound in solution.

14 Claims, 3 Drawing Figures



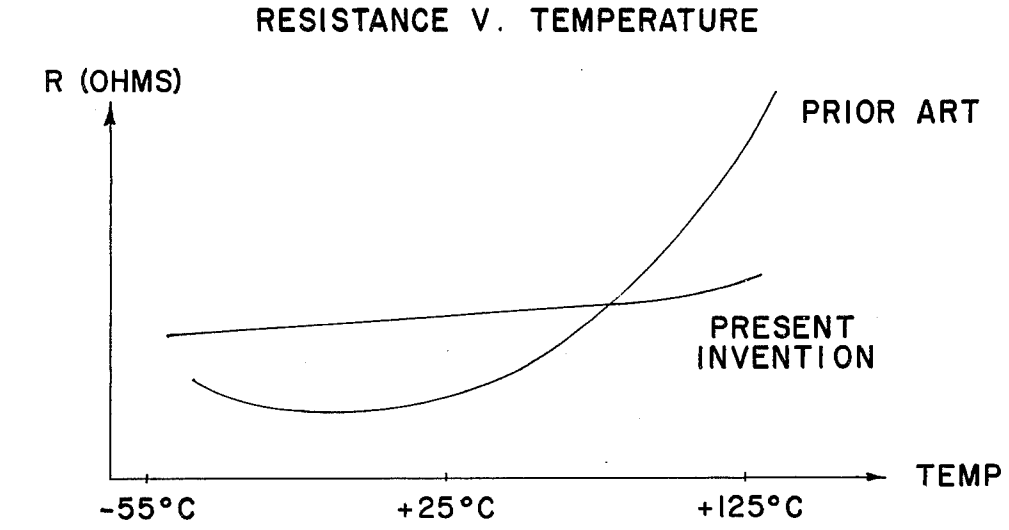


FIGURE 1

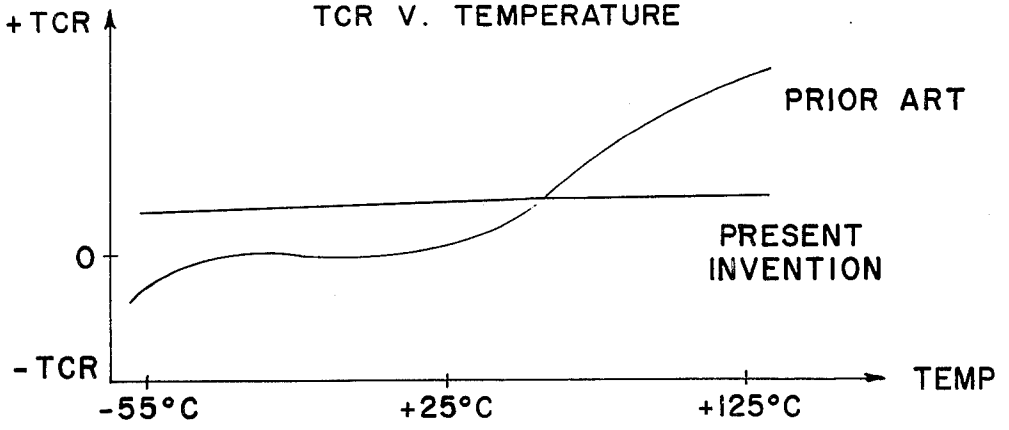


FIGURE 2

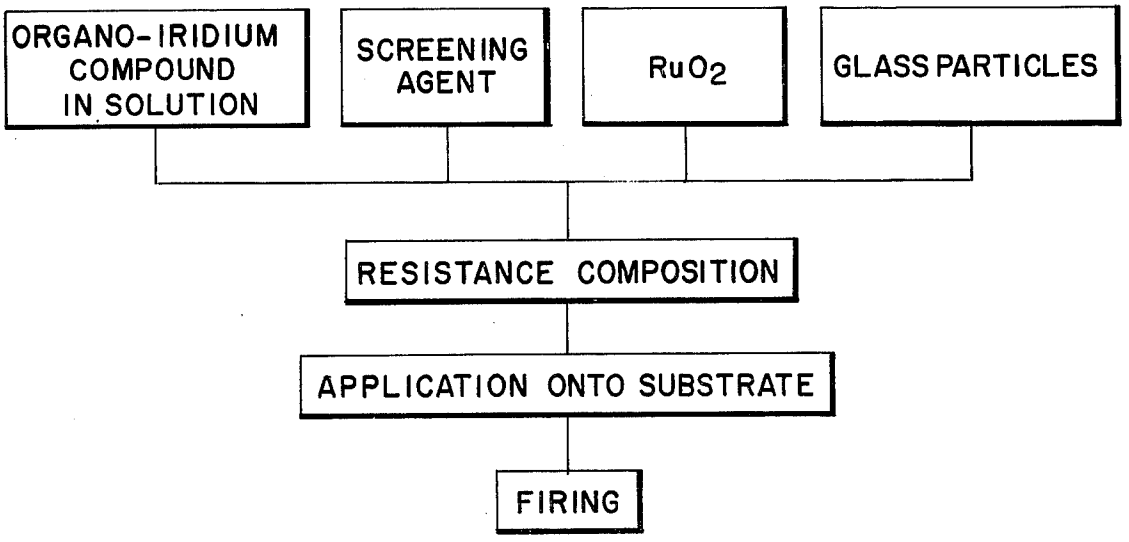


FIGURE 3

RESISTANCE COMPOSITION AND METHOD OF MAKING ELECTRICAL RESISTANCE ELEMENTS

The present invention relates to a resistance composition and to a method of making a resistance composition and an electrical resistance element therefrom and, in particular, to an improved resistance composition of the cermet type containing in any form at least one of the noble metals, e.g., an oxide or compound thereof, in a fine particle size preferably 325 mesh or smaller and glass particles or suitable ceramic materials, and to a method of making a cermet resistance element such as a film type resistance element by depositing and firing the composition onto the surface of a base or substrate of a high temperature resistant electrically nonconductive material.

Two of the problem areas in the manufacture of cermet resistance elements over a wide range of resistance values have been: (a) the difficulty in consistently achieving a low temperature coefficient of resistance (TCR) throughout the temperature range of −55°C to +125°C, that is the rate of change in resistance with respect to a change in temperature (dR/Rdt) and (b) the difficulty in obtaining the voltage stability of a cermet resistance element. A suitable test currently employed for determining the voltage stability is the short time overload (STOL) test. The STOL test is specified as the percentage change in resistance of the element with respect to an applied voltage overload or wattage overload. The TCR and STOL tests of a cermet resistance element are extremely important considerations in present day electronics especially for cermet resistors used in high voltage circuits, e.g., bleeder circuits in television sets. If the TCR and STOL resistance values are too high, inevitable changes in the ambient temperature and applied voltages in modern applications could lead to serious consequences. It is particularly important to control these properties over a wide range of resistance values. Cermet resistors having a wide range of resistance values have been known for many years. For example, Daily et al. (U.S. Pat. No. 3,329,526) assigned to the same assignee as the present invention describe a method for producing cermet resistance elements over a wide range of resistance values by mixing together noble metal organometallic compounds in solution, glass frit, and a screening agent. Holmes et al. patent application Ser. No. 169,355 filed on Jan. 29, 1962 discloses the addition of a refractory filler oxide to a cermet resistance composition. Faber et al. (U.S. Pat. No. 3,304,199) assigned to the same assignee as the present invention disclose a cermet resistance element having a TCR of approximately 100 parts per million per degree centigrade (PPM/°C) for ohmic values throughout a resistance range of less than 100 ohms per square to 180,000 ohms per square. Faber et al. discovered that cermet resistance elements could be produced reliably and predictably by using a specified percentage of an oxide of ruthenium and/or an oxide of iridium in making a cermet resistance composition. Holmes (U.S. Pat. No. 3,324,049) also assigned to the same assignee as the present invention discloses means for controlling the TCR of a cermet resistance element at a specific temperature within a temperature range of −55°C to +125°C by adding cupric oxide and/or manganese oxide to the resistance composition and/or to the glass employed in the preparation of the resistance composition. Holmes also was able to achieve a relatively good load life by using such additives even

though the TCR was controlled only at a specific temperature. It therefore would be desirable to produce resistors within the ± 50 PPM/°C TCR range over the resistance range of 50 ohms per square to 100K ohms per square not only at a specified temperature but within the entire temperature range of −55°C to +125°C.

According to current specification requirements of customers, voltage stability preferably is defined as the maximum voltage or wattage that can be applied to the end terminals of a resistor without having an overall resistance change of more than 0.25%.

The short time overload test is conducted by applying to each resistor a voltage potential equal to 2.5 times the rated continuous working voltage of the resistor. The working voltage or voltage rating is the maximum sustained voltage that can be safely applied to a resistor without risk of breakdown or failure during its life expectancy. The voltage potential is applied for a five second duration and the resistance is measured approximately 30 minutes after application of the voltage potential to determine the percent change of resistance. The potential is applied up to a maximum of 3,000 volts per inch of linear resistor. In subjecting resistors having a low sheet resistivity or ohms per square to a voltage stability test, a specified overload voltage cannot be applied to the terminals of the resistor without exceeding the overload wattage rating of a resistor. Therefore, the maximum overload wattage that can be applied to the resistor terminals without exceeding the maximum resistance change of the resistor is specified. Resistors having a high sheet resistivity and a high voltage withstanding capability can be made by following the teachings of Brady U.S. Pat. No. 3,655,440. However, a low TCR, for example, of ± 50 parts per million cannot be achieved throughout the entire temperature range of −55°C to +125°C. It would, therefore, be desirable to make cermet resistors having not only a low STOL resistance but also having a low TCR of ± 50 parts per million throughout the entire temperature range of −55°C and +125°C.

Accordingly, it is an object of the present invention to provide an improved cermet resistance composition and resistance elements made therefrom. Another object of the present invention is to provide a method for preparing a resistance composition for making resistors having a TCR within ± 100 parts per million per degree centigrade throughout the temperature range of −55°C to +125°C and over the resistance range of 50 ohms per square to 250K ohms per square and which exhibit improved voltage overload characteristics. A further object of the present invention is to produce cermet resistors having a ± 50 PPM/°C throughout the temperature range of −55°C to +125°C and over the resistance range of 50 ohms per square to 100K ohms per square. Further objects and advantages of the present invention will become apparent as the following description proceeds, and the features of novelty characterizing the invention will be pointed out with particularity in the claims annexed to and forming a part of this specification.

Briefly, the present invention comprises mixing together a screening agent, a glass frit and a conductive fraction consisting of ruthenium dioxide or compounds thereof and an organoiridium compound in solution to form a resistance composition. The composition is then applied to a ceramic substrate by conventional methods and fired to produce a cermet resistance element.

Further objects, advantages and features, as well as a more thorough understanding of the invention may be obtained from a consideration of the following detailed description when taken in connection with the accompanying drawings in which:

FIG. 1 is a plot of resistance versus temperature of a resistance element made in accord with the present invention and a prior art resistance element;

FIG. 2 is a plot of TCR versus temperature of the resistance elements referred to in FIG. 1; and

FIG. 3 is an operational diagram of a preferred form of the present invention for producing resistance compositions and elements.

The usual formula for the calculation of the TCR in PPM/°C of a given resistance material is given below:

$$TCR \text{ (in } PPM/°C) = \frac{R_2 - R_1}{R_1 (t_2 - t_1)} \times 10^6$$

where

R_1 = resistance at room temperature (25°C)

R_2 = resistance at test temperature

t_1 = room temperature

t_2 = test temperature in °C.

However, this formula is not an accurate reflection of the TCR of a given resistor at a specific temperature over a temperature range since it only provides an average TCR value between the test point and the room temperature reference point. For example, it is customary to measure the TCR of a given resistor at −55°C and +125°C using room temperature as the reference temperature. The resulting TCR values indicate only the average TCR value between the test temperatures and the reference temperature but give no indication of the actual TCR at any specific temperature.

The correct formula for determining the *TCR* of a resistor at a specific temperature T_1 is:

$$TCR = \frac{dR}{RdT_1}$$

That is, the *TCR* at a specific temperature T_1 is equal to the derivative or rate of change of the resistance with respect to the temperature at T_1 divided by the resistance R at temperature T_1.

To determine the rate of change of the resistance with respect to temperature, it is first necessary to plot resistance (R) versus temperature (T). FIG. 1 shows values of resistance versus temperature of a resistor made from a resistance composition prepared in accord with the teachings of the present invention and a prior art resistor. Prior art resistors also show other types of curves such as linear curves and various convex and concave curves such as U-shaped and S-shaped.

However, the significant distinction of the present invention is that the rate of change of resistance over the range of −55°C to +125°C is significantly less with a resistor made with the resistance composition prepared in accord with the present invention than with a prior art resistor. For the specific curves shown in FIG. 1 over the above temperature range, the spread of resistance for a prior art resistor was about 360 ohms and the spread for a resistor made in accord with the present invention was about 80 ohms or more than 400 percent better.

FIG. 2 shows a plot of TCR versus temperature resulting by plotting the derivative of each point on the curves of FIG. 1 according to the formula $TCR = dR/RdT$.

It should be understood that although the TCR curves of FIG. 2 are approximations based upon the slopes of the curves of FIG. 1, the results are fairly typical of actual calculated values of TCR for prior art resistors and resistors made in accord with the present invention. As illustrated in FIG. 2, the spread of TCR values of the present invention from −55°C to +125°C is relatively small compared to the spread of TCR values of a prior art resistor. In addition, the spread of TCR valves of resistors from 50 ohm to 100K ohms of the present invention is within ± 50 PPM/°C. For the specific curves shown in FIG. 2, the spread of TCR for a prior art resistor was from −10 PPM/°C to +132 PPM/°C and the spread for the resistor made in accord with the present invention was from +15 PPM/°C to +40 PPM/°C. Furthermore, the narrow spread of the TCR values of the present invention exists not only over the temperature range of −55°C to +125°C but also exists over a resistance range of constituents ohms per square to 100K ohms per square.

Referring to FIG. 3, resistance compositions of the present invention are produced by mixing together finely divided glass particles or glass frit, a vehicle and a conductive fraction consisting of ruthenium dioxide and iridium, said iridium being present as an organometallic compound in solution. The ingredients are blended together and applied to the surface of a high temperature resistant electrically nonconductive substrate and then fired.

The constitutuents of common glasses or vitreous binders that are used in the practice of the present invention are as follows:

GLASS I

B_2O_3	12.6%
Bi_2O_3	10.6%
PbO	66.7%
SiO_3	10.1%
	100.0%

GLASS II

B_2O_3	12.6%
Bi_2O_3	10.8%
PbO	66.2%
SiO_3	10.4%
	100.0%

GLASS III

SiO_2	6.9%
B_2O_3	51.2%
BaO_2	41.9%
	100.0%

GLASS IV

SiO_2	5.0%
B_2O_3	60.0%
SrO	35.0%
	100.0%

Any conventional vehicle or screening agent capable of being completely volatilized or decomposed by heat can be used. Preferably, the vehicle should contain a viscosifying agent to keep the glass frit in suspension after the mixture has been screened on the substrate. Ethylcellulose dissolved in a pine oil solution is an example of a screening agent also serving as a viscosifying material. The organometallic compound in solution can be, e.g., a metal resinate, glycinate, etherate, esterate or napthanate.

The following formulations are exemplary of the basic resistance compositions that can be produced in accordance with the present invention using iridium resinate and ruthenium dioxide as the principle conductive fraction. Some of the improved properties of fired resistance elements formed from such compositions are also stated for each example. Each of the resistance elements was produced by screening the resistance composition onto a high temperature substrate, it being understood that the vehicle and other organic materials are decomposed and volatilized upon firing.

EXAMPLE A

	Percent by Weight
Screening Agent	35.6%
Glass I	40.0%
RuO_2	17.2%
Ir Resinate	7.2%
	100.0%
Sheet Resistance	50.0 ohms per square
Short Time Overload	−0.035 at 3,100 volts per inch
TCR (PPM/°C)	−45 at −55°C
	+45.8 at +125°C

EXAMPLE B

	Percent by Weight
Screening Agent	28.4%
Glass II	38.1%
RuO_2	9.2%
Ir Resinate	24.3%
	100.0%
Sheet Resistance	400 ohms per square
Short Time Overload	−0.017 at 3,100 volts per inch
TCR (PPM/°C)	−22.9 at −55°C
	+39.4 at +125°C

EXAMPLE C

	Percent by Weight
Screening Agent	36.0%
Glass III	25.5%
RuO_2	10.5%
Ir Resinate	28.0%
	100.0%
Sheet Resistance	3K ohms per square
Short Time Overload	+0.018 at 3,100 volts per inch
TCR (PPM/°C)	+70.0 at −55°C
	+60.0 at +125°C

EXAMPLE D

	Percent By Weight
Screening Agent	45.3%
Glass III	41.9%
RuO_2	3.5%
Ir Resinate	9.3%
	100.0%
Sheet Resistance	100K ohms per square
Short Time Overload	−0.064 at 3,100 volts per inch
TCR (PPM/°C)	−50 at −55°C
	+2.4 at +125°C

EXAMPLE E

	Percent By Weight
Screening Agent	23.7%
Glass IV	44.9%
RuO_2	1.2%
Pd	.7%
Ir Resinate	8.3%
Cu Resinate	21.2%
	100.0%
Sheet Resistance	250K ohms per square
Short Time Overload	−0.060 at 3,100 volts per inch
TCR (PPM/°C)	−95.5 at −55°C
	+28.0 at +125°C

Small amounts of other noble metals or compounds thereof can be added to the RuO_2 and Iridium resinate conductive fraction. As seen in Example E, palladium powder and Cu resinate have been added in amounts of 0.7 percent and 21.2 percent.

The five primary formulations set forth above comprise a resistive system covering the range from 50 ohms per square to 250K ohms per square. Intermediate resistance values are obtained by blending adjacent primary formulations. That is, to obtain resistance values between 50 ohms and 400 ohms, Example A and Example B are blended. To obtain resistance values between 400 ohms and 3,000 ohms, Example B and Example C are blended. By limiting the blending to adjacent formulations, TCR's of ± 100 PPM/°C can be obtained for the blends without additional TCR adjustment and often TCR's of ± 50 PPM/°C are achieved without any additional adjustment. Example F below shows a blend of 50% Example C with 50% Example D to obtain a sheet resistance of 11.5K ohms per square and a TCR within ± 50 PPM/°C.

EXAMPLE F

	Percent by Weight
Example C	50%
Example D	50%
	100%
Sheet Resistance	11.5K ohms per square
Short Time Overload	−0.140 at 3,100 volts per inch
TCR (PPM/°C)	+35.9 at −55°C
	+37.2 at +125°C

The foregoing Examples A through F are produced in the following manner. A conventional screening agent or vehicle, ruthenium dioxide particles, glass frit, and iridium resinate are weighed into a suitable container and mixed well with a spatula by hand stirring to produce a resistance composition. It is understood that the conductive fraction employed in the examples is a ruthenium dioxide powder obtainable either by dehydating ruthenium oxide hydrate or by heating ruthenium to ruthenium dioxide and ball milling the ruthenium dioxide to obtain the desired particle size. If the glass frit has not been ground to suitable particle size, the mixed ingredients of the composition are ground on

a roll mill. The composition is then screened on a ceramic substrate and fired in a kiln at about 850°C.

In the preceding examples, the iridium resinate used contained approximately 6% iridium metal. If an iridium resinate is used that contains more or less than 6% iridium metal, then adjustments should be made to the amount of iridium resinate added to the mixture to obtain the desired properties. The desired properties are generally obtainable with between 2% to 20% of iridium metal and ruthenium metal by weight in the mixture before firing, the iridium metal present as an organometallic compound in solution and the ruthenium present as RuO_2, the RuO_2 to iridium ratio usually being greater than 2:1.

The present invention has been described in conjunction with certain specific embodiments; it will be appreciated that these were described for illustrative purposes and that many modifications will readily suggest themselves to those skilled in the art.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A method of forming an electrical resistance element having a TCR in the range of ± 100 PPM/°C over the temperature range of −55°C to +125°C comprising the steps of:

a. mixing together powder-like particles of glass, a conductive phase comprising ruthenium dioxide and iridium, said iridium being present as an organometallic compound in solution and a volatile liquid carrier to form a paste and provide a resistance composition, the ruthenium dioxide and iridium comprising 1 to 70% by weight of the composition,

b. applying the resistance composition onto a surface of a high temperature resistant, electrically nonconductive base, and

c. firing the nonconductive base with the resistance composition deposited thereon to reduce said organometallic compound in solution and remove the volatiles and organic material therefrom and to produce a continuous glassy phase having a smooth surface with the ruthenium dioxide and reduced organometallic compound dispersed therein.

2. The method of claim **1** wherein the organometallic compound in solution is iridium resinate and contains less than 3% iridium metal by weight of said resistance composition.

3. The method of claim **2** wherein said layer of said resistance composition contains less than 3% by weight of iridium metal and said organometallic compound in solution is iridium resinate.

4. The method of claim **3** wherein the step of firing the resistance element includes the step of heating the electrically nonconductive base and layer of resistance composition applied thereon to a temperature sufficient to melt the powder-like particles of glass, reduce the iridium resinate, and volatilize the organic screening agent and burn off the carbonaceous residue, but below the temperature necessary to soften the base, to produce film of glass on the base containing ruthenium dioxide and iridium in some form dispersed therein.

5. In a method of manufacturing an electrical resistance element having a TCR in the range of ± 100 PPM/°C over the temperature range of −55°C to +125°C, the steps of:

a. forming a viscous mixture of a screening agent solvent, a glass binder and a conductive fraction consisting of ruthenium dioxide and iridium resinate, said resinate containing iridium of less than 3% by weight of the mixture,

b. applying a uniform layer of the viscous mixture to a high temperature resistant electrically nonconductive base, and

c. heating the base and layer to a predetermined temperature at least as high as the melting point of the glass but less than the melting point of the ruthenium dioxide and iridium to form a continuous glassy phase with ruthenium dioxide and iridium dispersed therein.

6. A resistance composition for making cermet resistance elements having a TCR in the range of ± 100 PPM/°C over the temperature range of −55°C to +125°C comprising at least 30% by weight of a finely divided nonconductive vitreous binder and 1 to 70% by weight of a conductive fraction comprising particles of ruthenium dioxide and iridium, said iridium being present in an organometallic compound in solution.

7. The resistance composition of claim **6** wherein said particles of ruthenium dioxide comprise 0.9 to 60% by weight of said resistance composition and said iridium comprises 0.1 to 10% by weight of said resistance composition.

8. The resistance composition of claim **6** wherein said particles of ruthenium dioxide comprise 0.9 to 67% by weight of said resistance composition and said iridium comprises 0.1 to 3% by weight of said resistance composition.

9. The composition of claim **6,** wherein said organometallic compound in solution is iridium resinate and wherein the ratio of the ruthenium dioxide to the iridium in the resistance composition is greater than 2:1.

10. The composition of claim **6** wherein the size of the ruthenium dioxide particles is greater than the size of the iridium in solution.

11. A resistance composition for application onto a high temperature resistant electrically nonconductive substrate and for firing to form an electrical resistance element having a TCR in the range of ± 100 PPM/°C over the temperature range of −55°C to +125°C and consisting essentially of at least 30% by weight of a finely divided nonconductive vitreous binder and 1 to 70% by weight of a conductive fraction comprising ruthenium dioxide and iridum resinate, said resinate containing iridium of less than 3% by weight of said composition.

12. The resistance composition of claim **11** wherein the resistance element has a TCR in the range of ± 100 PPM/°C over the resistance range of 50 ohms to 250K ohms.

13. The resistance composition of claim **11** wherein the resistance element has a TCR in the range of ± 50 PPM/°C over the temperature range of −55°C to +125°C.

14. The resistance composition of claim **13** wherein the resistance element has a TCR in the range of ± 50 PPM/°C over the resistance range of 50 ohms to 100K ohms.

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