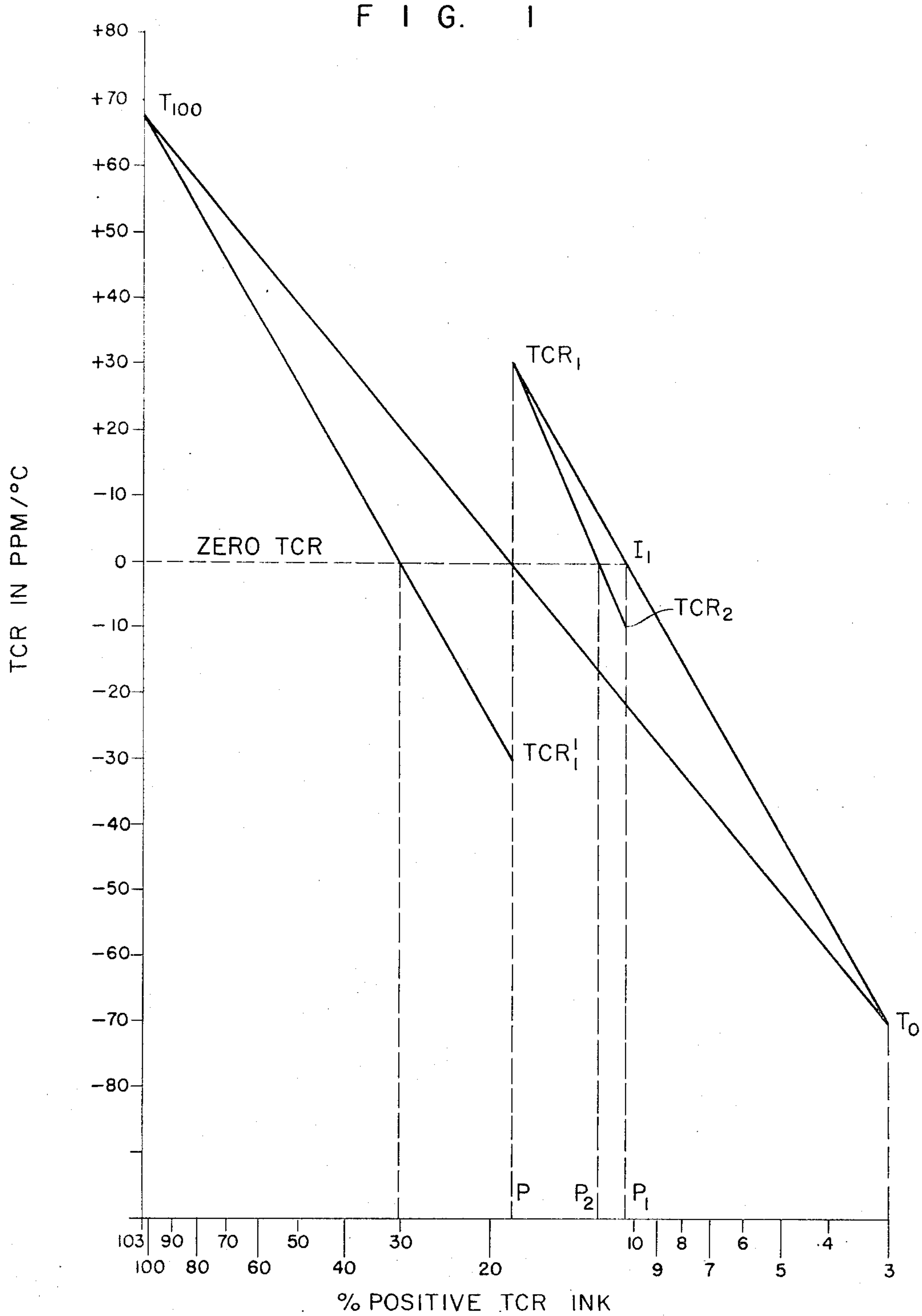
THICK FILM PRECISION RESISTOR FOR USE IN AN ELECTRICAL CIRCUIT AND METHOD OF MAKING SAME

Filed March 2, 1971 5 Sheets-Sheet 1

FIG. 1



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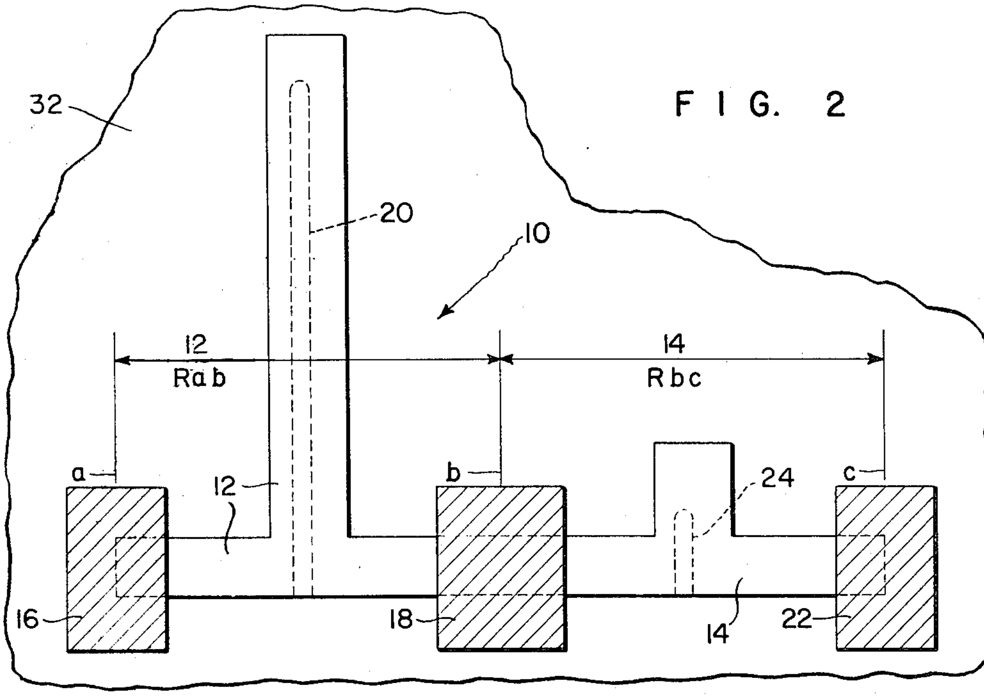

FIG. 2

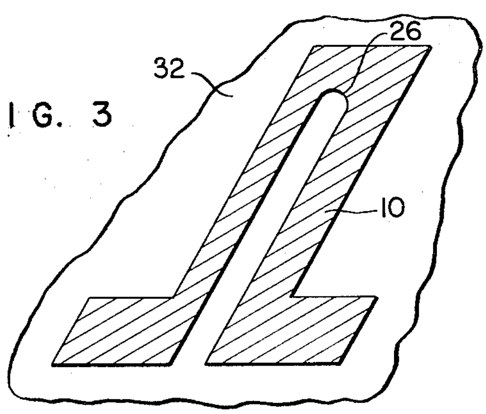

FIG. 3

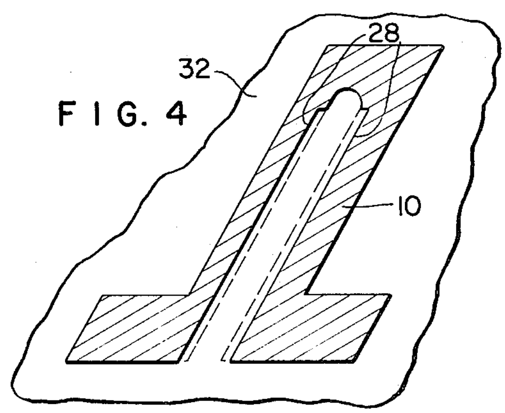

FIG. 4

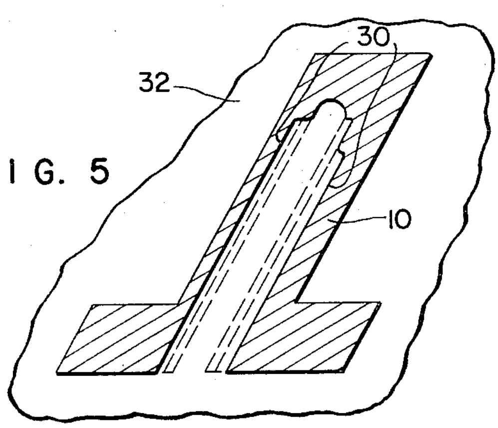

FIG. 5

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FIG. 6

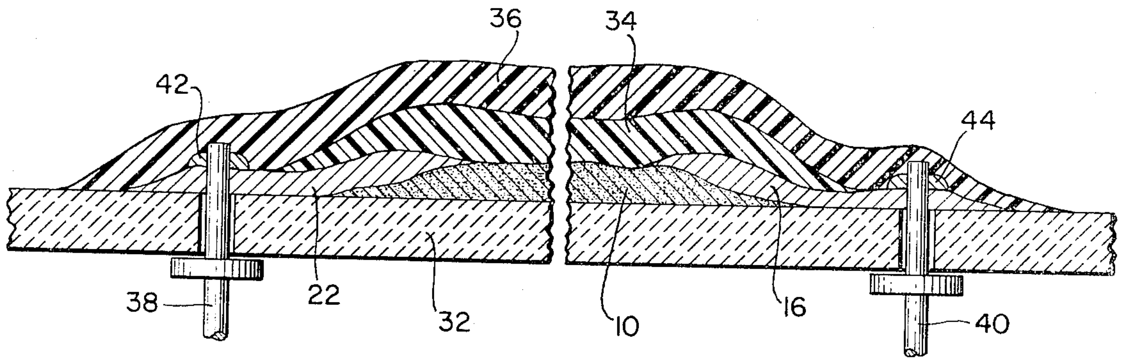

FIG. 7

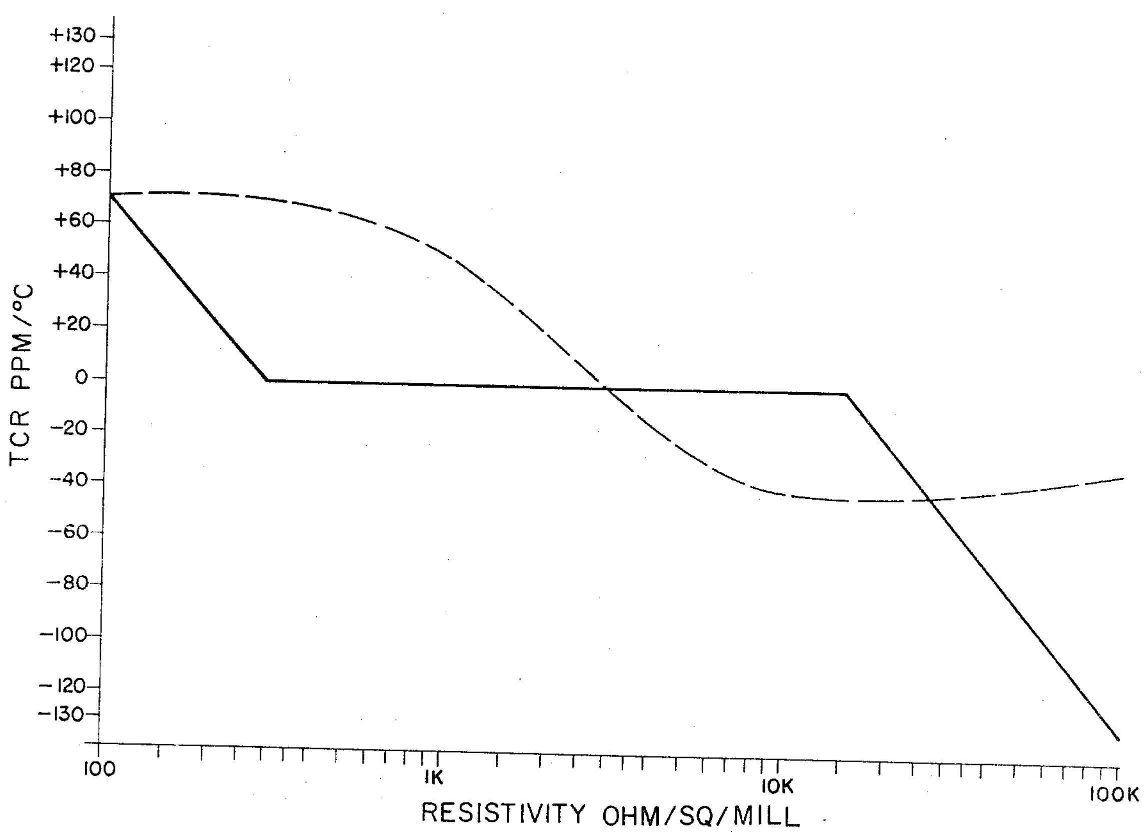

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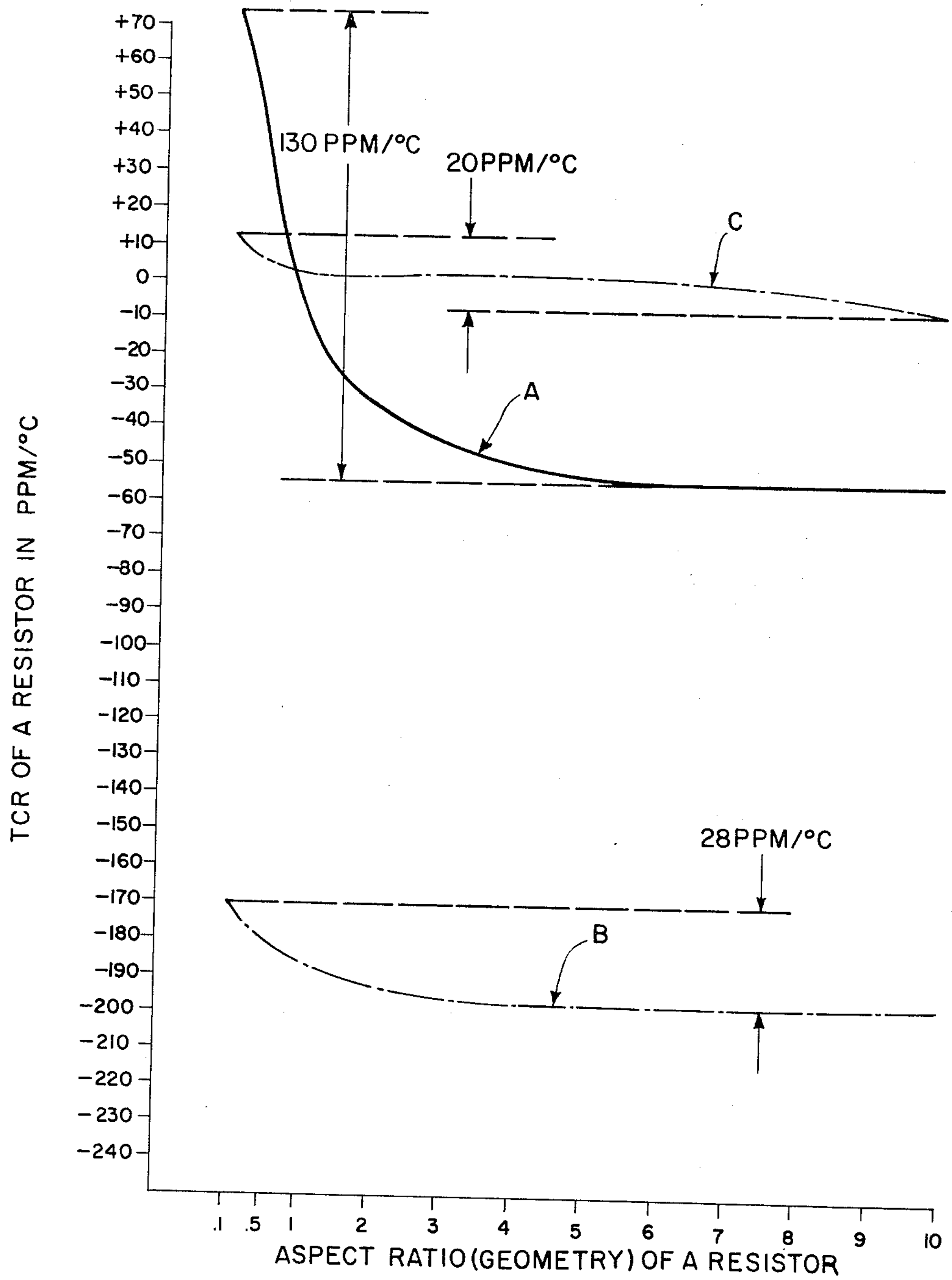
FIG. 8

DEPENDENCE OF TCR ON THE ASPECT RATIO (GEOMETRY) OF A RESISTOR



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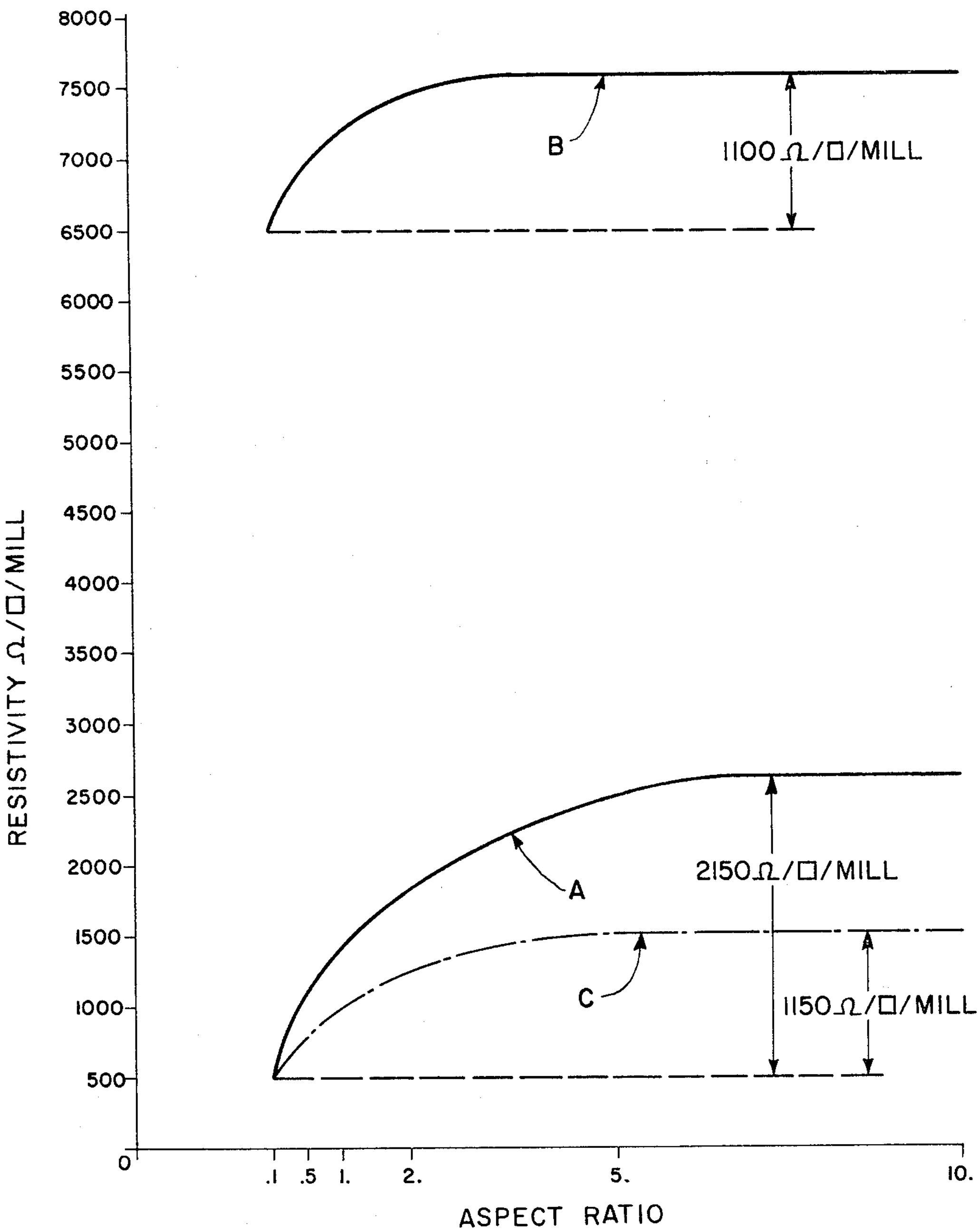
DEPENDENCE OF RESISTIVITY ON ASPECT RATIO (GEOMETRY) OF A RESISTOR



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United States Patent Office

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THICK FILM PRECISION RESISTOR FOR USE IN AN ELECTRICAL CIRCUIT AND METHOD OF MAKING SAME

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Int. Cl. H01c 7/00
U.S. Cl. 117—212 12 Claims

ABSTRACT OF THE DISCLOSURE

A thick film resistor is formed by #1 firing selected mixtures of positive and negative thick film resistor ink materials on a non-electrically conductive substrate at a selected high temperature and #2 subsequently jointly firing the resistor and conductor ink material associated with this resistor, at a temperature that is lower than the first mentioned temperature and which is at a level that will not allow any detrimental diffusion, to occur between the conductor and the resistor materials. This unique process of firing achieves for the first time a successful method of firing a resistor and conductor jointly without allowing any adverse change to occur in the value of the temperature coefficient of resistivity and the resistivity value of the resistor.

It is an object of the present invention to provide a unique precision thick film, cermet, resistor and a unique method that can be employed to manufacture this type of resistor.

It is an other object of the present invention to provide a resistor of the aforementioned type that possesses electrical resistance characteristics, that are precise, and whose performance is unaffected by the time it remains on the shelf, the time period over which it is employed in an electrical circuit and changes in ambient temperature.

More specifically, it is another object of the invention to provide a precision resistor of the aforementioned type whose resistance will remain within an acceptable ±0.1% level over long periods of use that extend beyond a two year period of time.

It is another object of the invention to provide a method of manufacturing a cermet resistor for use in measuring circuits whole accuracy and overall stability is as good and reliable as those possessed by present day commercially available wire wound resistors.

One of the terms that is used to define a critical characteristic of a thick film resistor is its "sheet resistivity." This term sheet resistivity relates to the electrical resistance which a one milli-inch thick square of any size of resistive material offers to a steady current passing between any two opposite faces of this resistive material along which for example a conductive film is attached. This sheet resistivity is known to vary with ambient temperature between e.g., +300 p.p.m./° C. to −300 p.p.m./° C. depending on the sheet resistivity of resistor material being used.

Another term that is used to define the characteristic of a thick film resistor is TCR or temperature coefficient of resistivity which is the change in resistivity expressed in ohms per degree centigrade.

In achieving the aforementioned objectives it has been discovered that an adverse change in resistivity and TCR of a thick film cermet resistor is caused by diffusion of the conductive material in the conductor, which has an extremely low resistivity value, into resistive material of the resistor which has a much greater resistance value when the resistor and conductor are fired on a ceramic substrate. Heretofore it was a common belief that this adverse change was based upon the geometry, or the so-

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called aspect ratio factor which is a ratio of the length to width of the resistor.

It is another object of the invention to recognize for the first time that the aforementioned detrimental effect of diffusion is much greater between the ends of a rectangular strip of resistor and a conductor that extends away from the resistor when the longest opposite sides of the rectangular resistor strip are selected for connection to the conductor for jointly firing onto a substrate rather than the shorter opposite sides of the rectangular resistor strip.

Furthermore, experimentation has shown that firing temperature changes adversely affects TCR and the resulting resistivity of thick film resistors because of the high degree of the aforementioned diffusion that takes place between the resistor and the associated conductors to which it is attached when they are jointly fired.

It is therefore another object of the invention to provide a unique method of firing resistor and conductor inks onto substrates so that no undesired diffusion will take place between the resistive and conductive materials that will adversely effect the TCR and resistivity and therefore the precise resistance offered by the resistor.

To accomplish the aforementioned feat it is another object of the invention to provide a means whereby the dried resistor ink is first fired for a preferred preselected period of time e.g., 15 minutes at a high temperature of e.g., 1000° C. on a substrate to form an amorphic mass and thereafter the conductor extending from either side of the resistor is printed, dried and then fired for a similar period of time at a substantially lower temperature in the neighborhood of 550° C., onto the already fired resistor to eliminate substantially all of the undesired diffusion of the conductive material that would otherwise diffuse into or from the resistor material.

It is another object of the invention to provide a method of the aforementioned type which will allow an ink, such as a resistor ink having a high firing temperature to be fired at a high temperature onto a substrate, and a conductor ink having a lower firing temperature than the resistor ink to be then fired jointly with portions of the already fired resistor ink onto the substrate so that undesired diffusion of the conductor ink material into the fired resistor ink will be negligible and an acceptable cermet resistor having a low TCR to be produced.

Heretofore it was a common practice, after the selecting the size and the aspect ratio of a resistor which would fall within a prescribed resistance range to consult a table or a graph filled with geometry correcting tables that predicts the resistivity and the TCR as a function of the resistors geometry. This procedure is slow, tedious, and has circuit design limitations in that the resistor could only be made of a certain geometric shape and the size. It is well known that these resistors will have different TCR and resistivity values.

It is therefore another object of the invention to eliminate the need for the aforementioned tables.

It is also another object to provide a method of manufacturing a cermet resistor whose shape can be of any one of a number of different forms or configurations, and need not therefore be limited to a restricted shape as has heretofore been required.

It is another object of the invention to provide a construction for a cermet resistor that will present its resistivity and TCR values from being changed by the destructive oxidating or other detrimental effects resulting from the resistors exposure to air, moisture, hydrogen sulfide or other similar ambient atmospheres.

It is another object of the invention to provide a method of blending one or more positive TCR resistor inks with one or more negative TCR resistor inks so that the resulting temperature coefficient of resistivity TCR and the resistivity of the resulting resistor can be precisely predicted by changing the blending proportions of the negative TCR resistor ink and the positive TCR resistor ink before firing in the aforementioned unique manner so that a number of different shaped resistors can be formed which individually possess different precisely fixed resistance values.

It is another object to provide resistors of the aforementioned that extend over a wide range and which will result in each of the resistors having a temperature coefficient of resistivity value, TCR, that is within a few parts per million per degrees centigrade from zero.

Since it is not possible to obtain a precise resistance value for the resistor from the aforementioned unique firing process nor from any other firing process it is therefore another object of the present invention to provide a means of trimming such a resistor after it has been fired so that a more exact value of the resistance can be achieved for these resistors.

A better understanding of the present invention may be had from the following detailed description when read in connection with the accompanying drawings in which:

FIG. 1 shows a nomograph having a uniquely constructed semi-log scale for graphically determining the amount of additional positive or negative ink that should be added to an ink mixture of positive and negative inks to provide a thick film resistor ink of a desired zero TCR;

FIG. 2 shows the steps required in a first method of trimming the aforementioned thick film resistor;

FIG. 3 shows the first step required in a second method of trimming the aforementioned thick film resistor;

FIG. 4 shows the second step required in the second method of trimming a thick film resistor;

FIG. 5 shows the third step required in the second method of trimming the aforementioned thick film resistor;

FIG. 6 shows how the aforementioned trimmed thick film resistor can be encapsulated to prevent the destructive oxidating effect of the ambient atmosphere from effecting its resistivity and TCR value; and

FIG. 7 shows a chart having a solid line thereon to indicate the wide resistivity range of values over which a zero TCR prevails for many different positive and negative cermet resistor ink blends when they are produced by the unique method to be hereinafter described in which no diffusion is allowed to occur between the conductor and the resistor as contrasted by the line shown in dash line thereon which indicates that zero TCR can be achieved for only a single resistivity value of many positive and negative cermet resistor inks when they are produced by the well known profile firing method as a result of undesired diffusion occurring between the conductor and its associated resistor.

FIG. 8 is a graph to vividly illustrate the desirable independent relationship that can be achieved, as shown by curve B, between the temperature coefficient of resistivity and the aspect ratio [geometry] values of thick film resistors by firing them in the previously referred to unique non-diffused maner with their associated conductors onto a substrate. FIG. 8 also shows a curve A which represents the undesired dependent, restricted, temperature coefficient of resistivity versus aspect ratio [geometry] relationship that must be adhered to when thick film resistors and their associated conductors are fired jointly at a high temperature which causes diffusion to occur between the last mentioned conductors and their associated resistors.

FIG. 9 is a graph to vividly illustrate the desirable independent relationship that can be achieved as shown by curve B between the resistivity and the aspect ratio [geometry] values of thick film resistors by firing them in the previously referred to unique non-diffused manner with their associated conductors, in a non-diffused manner, onto a substrate. FIG. 9 also shows a curve A which represents the undesirable dependent restricted resistivity versus aspect ratio [geometry] relationship that must be adhered to when thick film resistors and the associated conductors are fired jointly at a high temperature which causes diffusion to occur between the last mentioned conductors and there associated resistors.

Method of blending cermet inks to fabricate thick film resistors which are not sensitive to temperature changes.

The temperature coefficient of resistivity, TCR, for thick film cermet resistors has heretofore been changed by altering the firing temperature profile and/or by changing the geometry, or in other words the previously referred to aspect ratio of these resistors.

Since the changes in TCR obtained by these methods are several parts per million per degree centigrade, p.p.m./° C., usually in the vicinity of 1 to 10 p.p.m./° C. for one degree C. change in firing temperature, they are therefore not sufficiently exact to obtain the desired TCR value.

A unique method of ink blending to obtain a desired TCR value which does not have to rely on the selection of a desired firing temperature profile will now be described.

The magnitude of change of TCR obtained by this unique method is at least 10 times larger than the previously mentioned method which was based upon a change in firing profile and a change in the geometry of the resistor.

Experimentation has shown that an addition of a metal in powder form such as a gold powder with the particle size of three to twenty microns or a metal powder mixed with lead-boro-silicate glass powder of the same particle size when mixed with a liquid agent such as decanol provide a suspension that will decrease the sheet resistivity of a resistor and cause a change in its TCR in a positive direction. The addition of metal oxide powder, for example ruthenium oxide powder, or a metal oxide powder mixed with boro-lead-silicate glass powder and a liquid agent such as decanol causes a change in TCR in a negative direction. It can therefore be concluded that by adding metal or metal oxide to a cermet ink the TCR is changed in either a desired positive or a negative direction. And, therefore, if two or more resistor inks are available and if one of them has a positive TCR and the other a negative TCR or vice versa, they may be blended to obtain a desired TCR, and the blending proportion can be calculated by the method to be hereinafter described:

Measure the TCR of resistors made from the ink which is to be modified to obtain a zero TCR resistor. This measurement of TCR is accomplished by firing the resistor ink on an electrically non-conductive substrate and then taking measurements of its electrical resistance at room temperature such as 73° F. and at a higher temperature such as 173° F. and calculating the TCR from these values by the following formula

$$\mathrm{TCR} = \frac{\Delta R}{R \Delta t^{\circ}} \times 10^{6} \text{ in p.p.m./}^{\circ}\text{C.}$$

where

ΔR equals the resistance of the resistor at the aforementioned high temperature minus its resistance at the aforementioned room temperature.

R is the resistance value at room temperature and

Δt° equals the difference between the aforementioned high temperature and room temperature.

If the TCR value of the resistor is zero no further modification of the ink is needed. If it is not zero and it is negative, then a metal such as gold is added to the ink. It is then blended and a measurement of its TCR value is again made in a manner similar to that already described.

The amount of metal added to the ink, such as gold must be large enough to provide a positive TCR value of not less than 20 parts per million per degrees centigrade. If the TCR of the ink under modification is found to be positive then metal oxide, e.g. powder 325 mesh, such as ruthenium oxide, is added until the ink provides a negative TCR resistor material of 20 parts per million per degrees centigrade or a higher negative number. The purpose of the above modification of the available commercial inks is to make a pair of inks so that one of the pair will have a negative TCR resistor value and the other of the same pair will have a positive TCR value. These two inks are then blended by mixing them together in a proportion that will provide a blend of zero TCR ink.

The amount of positive TCR ink and the negative TCR ink forming the blended proportion is calculated from the following equation and is done as explained below:

$$P=\mathrm{Exp}\left[A-\frac{T_{100}}{T_{100}-T_0}(A-B)\right]-S$$

Where

P= percent of positive TCR ink in blend for manufacture of zero TCR resistors

Exp=base of natural log

$A=\ln_e(100+s)$

$B=\ln_e S$

S=a constant, based on statistical data derived from experimentation for ruthenium system links which is equal to 3.

T_{100}=TCR of positive TCR ink

T_0=TCR of negative TCR ink

Both T_0 and T_{100} are in p.p.m./° C.

S is dimensionless

The percentage of positive ink in a blend which will provide zero TCR resistors is found through the use of the aforementioned equation. This same percentage can also be found graphically by first plotting the TCR of the positive ink on the semi-log paper chart as shown in FIG. 1. The point T_{100} plotted on the semi-log chart shown in FIG. 1 is the TCR of a positive ink or in other words is the TCR of a blend which consists of 100% positive ink. The abscissa of this point does not correspond with the 100% point on the abscissa axis but instead purposefully corresponds with the 103% point. This offset of 3% is the variable S in the aforementioned equation. In this particular example where ruthenium system ink is used it has been found by experimentation that the value of S=3.

The TCR of a negative TCR ink is then plotted as an ordinate on a linear scale on the semi-log chart of FIG. 1 as the point T_0. This represents the value of a blend which has zero percent of positive ink in it. The abscissa, or log scale value, of this point does not correspond with the zero percent point on the abscissa axis, but rather corresponds with the 3% point selected as a result of statistical data derived from experimentation. This offset of 3% is variable S in the equation. After the positive and negative TCR's of a pair of inks are plotted as described above the percentage of positive ink P which should be in the blend to provide zero TCR resistors is found as follows:

A straight line is drawn between T_{100} and T_0. This line represents a change in TCR of resistors versus percentage of positive TCR ink in the blend and crosses the zero TCR line. Looking at the base of the graph immediately below the point at which the aforementioned line crosses the zero TCR line we find that its value as read on the abscissa is the percentage of positive ink in the blend which will provide desired zero TCR resistor value. It should be noted that the value of this point along the abscissa is the value of the P shown in the previously mentioned equation.

Knowing the percentage P of the positive ink in the blend the zero TCR blend can then be prepared. However the TCR of the resistors made from this blend will not necessarily be zero it may not even be within the zero plus or minus 20 parts per million per degree centigrade limits. This is so because the previously mentioned equation represents the best fit or linearized condition that can be derived from the TCR versus log percentage of blend that exists for several different blending proportions. The degree of misfit depends on the number of test blends and on the ink composition. If the TCR of resistors prepared from this blend is not zero as calculated from the previously mentioned equation

$$\mathrm{TCR}=\frac{\Delta R}{R\Delta t^\circ}\times 10^6 \text{ in p.p.m./°C.}$$

or is not within the desired limits, the blend must be corrected. It is evident that the process parameters relating to the preparation of resistors must be constant. For example the firing profile, absolute humidity in the furnace, atmosphere in the furnace, and the dried thickness of the resistors must be kept constant.

The following blending proportion correction is preformed in order to bring the TCR of the resistor closer to a zero value.

The actual value of the TCR of the resistor, TCR_1, as derived from the equations

$$\mathrm{TCR}_1=\frac{\Delta R}{R\Delta t^\circ}\times 10^6$$

is determined from representative samples of the blend and is plotted in FIG. 1. If this TCR_1 is positive as indicated by its plotted position in FIG. 1 this point TCR_1 is connected with the already plotted point T_0 or in other words, the point which is the TCR value of the negative TCR ink. This line between the points TCR_1 and T_0 represents a corrected change in TCR of resistors vs percentage of positive TCR ink in the blend or in other words the change in TCR of resistors vs percentage of positive TCR ink in the blend which was previously determined in FIG. 1 was incorrect due to imperfect linearization when parameters were chosen as previously described for the first previously mentioned equation that was used to figure out the value of P.

If this TCR_1 were negative e.g., TCR_1' this TCR_1 point would be connected by a straight line to the point T_{100}. The line connecting point TCR_1 with point T_0 or TCR_1' with point T_{100} must in each instance cross the zero TCR line. In one example the TCR of the resistors made from a blend prepared by the previously mentioned graphical method is positive and plotted at its point TCR_1 in FIG. 1. The abscissa of the point of intersection or point I_1 on FIG. 1 between the TCR_1–T_0 line and the zero TCR line is a corrected percentage of positive ink in the blend which shall provide zero TCR resistors and is marked on FIG. 1 as P_1.

Knowing P_1 which is the corrected and more accurate percentage of positive TCR ink in the blend, the blend can be either corrected by adding corresponding amounts of negative TCR ink to the blend or a new second blend can be prepared based on the information derived in the aforementioned manner.

Even now, the second corrected blend may still not provide zero TCR resistors. If this is the case a second correction is needed and the TCR of the resistors made from #2 blend as determined from the equation

$$\mathrm{TCR}_2=\frac{\Delta R}{R\Delta t^\circ}\times 10^6$$

in FIG. 1 as point TCR_2. In this example TCR_2 turned out to be negative. A line is drawn through this point TCR_2 and the previously obtained point TCR_1. This line represents the second corrected change of TCR vs percentage of positive ink in the blend. The abscissa of the point of intersection between the line TCR_1–TCR_2 and the zero TCR line is a corrected percentage of positive inks in the blend which will provide zero TCR resistors and is marked P_2 in FIG. 1.

Knowing P_2 which is the second corrected percentage of positive TCR ink in the blend, this blend can then be either corrected by adding corresponding amounts of positive TCR ink for example ink with $TCR=T_{100}$ or a new third blend can be prepared based on the aforementioned information.

In the above example the TCR of the second blend TCR_2 was negative. If it were positive then the TCR_2 point would be connected by a straight line with point T_0 and the abscissa of the point of intersection between line TCR_2–T_0 and the zero TCR line would be the percentage of positive TCR ink in the third blend. When addition blend of the correction of the blend is needed, such as in the case where the TCR of the resistors made from the blend are outside of the desired limits, the last obtained and plotted TCR point e.g., TCR_2 is then connected with the nearest TCR point of opposite sign as measured along the abscissa. The abscissa of the intersection point of this last mentioned line which connects the two nearest TCR points of opposite signs with the zero TCR line represents the percentage P_2 of positive TCR ink which should be in the corrected blend.

Experimentation has shown that in the majority of blending operations only two such corrections are sufficient to bring the TCR within the ±20 parts per million per centigrade limits.

It should also be further understood that a method has been described that can be used for obtaining any desired TCR for resistors other than zero by observing where the interconnecting line between T_0 and T_{100} passes a horizontal line on the chart that passes through the desired positive or negative value of the blend that is desired rather than through the other line. This TCR of the blend cannot of course be made more negative or more positive than the TCR value of the two basic inks that were used to make this blend.

The change in TCR resistors causes the change in the sheet resistivity of the resistors and the more negative that the TCR is the higher will be the sheet resistivity. This is so because the addition of metallic oxide to the ink causes the TCR to change in the negative direction and increases the sheets resistivity.

Knowing the sheet resistivity of the two inks which are used for blending and knowing their percentage in the final blend the sheet resistivity of resistors made from this blend can be easily predicted by using kown methods of calculation.

Methods of trimming of high accuracy resistors (cermet) with low accuracy trimming machine

Present day accuracy of cermet resistors after they are printed and fired is about ±20% of the value desired. Therefore, if a better accuracy is desired, they must be corrected. Usually, the correction consists in removing a portion of the resistor until the resistance reaches the desired value. A partial removal of resistor material causes an increase in the resistance. In other words the value on resistance can be corrected only in the direction of increase of the resistance.

Usually the resistance of the resistor under trimming is constantly measured by usually a high precision resistance measuring bridge for example, a Kelvin bridge.

The accuracy of resistance measuring bridges is usually of ±0.05%. However the accuracy of trimmed resistors is seldom better than ±1%. This is caused by unpredictable time lag between the electrical signal from the bidge, indicating that the resistor has reached its desired value and the execution of this signal (i.e., stopping the trimming) by conventional electromechanical and pneumatic links between the bridge and the cutting device. The degree of overtrim or, in other words, over-cuts, depends on the speed of the cutting device which is usually a nozzle which directs the stream of abrasive particles on the resistor and also on the resistivity of the resistors's material. The higher the nozzle speed and the resistivity, the larger will be overtrim or error. Usually the degree of overtrim does not exceed 1% of nominal desired resistance. In other words, even if the trimming machine, which includes resistance measuring bridge and the cutting devices, has a high precision bridge, its total accuracy, i.e., the accuracy of trim, usually is in a low precision range.

Described below are two methods of trimming a high precision resistor **10** with low precision trimming machines, which have high precision resistance measuring bridge. The first method is as follows:

The resistor **10** is laid out so that it consists of two parts **12** and **14** as shown on FIG. 2. Part **12** measured between points *a* and *b* of conductive parts **16, 18** in FIG. 2 must be of sufficient size, length on FIG. 2, to provide at least 98% of the nominal desired total resistance after trimming along trimming path **20**. Part **14** resistor measured between the points *b* and *c* of conductors **18, 22** must have not more than 1% of the nominal total resistance before it is trimmed along the trimming path **24**.

Measuring across the entire resistor i.e., between the points *a* and *c* of conductors **16, 22**, the resistor part **12** is trimmed to 98% of the total nominal resistance because the accuracy of trimming machine is ±1%. The resistance of the entire resistor measured between *a* and *c* will be 98%±1% of the total nominal resistance and the resistance of just trimmed resistor alone measured between *a* and *b* of conductors **16** and **22** can be 98% of nominal ±1% of nominal —R_{bc}, where R_{bc} is the resistance of yet untrimmed part **10** measured between **18** and **22**.

As it was mentioned before, the maximum resistance of untrimmed R_{bc} resistor **10** does not exceed 1% of total nominal resistance, therefore, in the worst case, the minimum resistance of just trimmed R_{ab} resistor is 98%−1%=97% of the total nominal resistance.

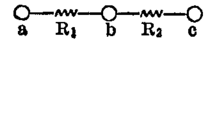
To correct the error after the first trim along trim path **20** the actual value of the trimmed R_{ab} resistor part **12** must be measured. Since the resistance measuring bridge only is involved in this measurement, the measured value of R_{ab} resistor **12** will be within the accuracy of the bridge i.e., usually within ±0.05%. This uncertainty in the trimmed R_{ab} value can obviously not be corrected, and it depends on the accuracy of measuring bridge alone.

Assuming that R_{ab} resistance of resistor part **12** after trim was 97% of total nominal resistance, the yet untrimmed resistor **14** must be trimmed along trimming path **24** until it reaches 100%−97%=3% of the total nominal value.

Because of ±1% accuracy of the tirmming machine, the value of trimmed resistor **14** measured between points *b* and *c* during the trimming, and trimmed along trim path **24** to 3% of total nominal resistance will be 3% of nominal ±1% of 3% of nominal or 3%±.03% of total nominal value vs. desired 3% of nominal. Assuming one of the worst possible cases, the resistance of trimmed resistor part **14** can be 3%−.03%=2.97% of the total nominal value; and the total value will be R_{ab} (part **12**)+R_{bc} (part **14**)=97%+2.97%=99.97% of the total nominal value, i.e. the error after two trims will be —.03%. Adding the uncertainty or the resistance measuring bridge (±.05%) the maximum error after two trims will be (in this example) ±.05—.02=—.08%.

The above example shows that, dividing the resistor **10** into two parts **12, 14** and performing two trims **20, 24,** the final accuracy obtained is more than 10 times better than the accuracy of conventional trimming machine and that it approached the accuracy of a precision resistance measuring bridge.

The accuracy obtainable by this two trim method is determined as follows:



R=Nominal (desired) value of R_T (Ohms)
C=Accuracy of resistance measuring bridge (percent)
A=Accuracy of trimming machine (including percent bridge accuracy)
B=Value of R_2 untrimmed (in percent of nominal)
R_1=part 1 of total resistor R_T (or R_{ab} resistor (Ω)
R_2=part 2 of total resistor R_T (or R_{bc} resistor (Ω)
R_T=Total resistance ($R_T=R_1+R_2$) (Ω)

$$E=\pm(2A^2+AB+A^3+C)$$

E=Total maximum error in R_T after trimming (in percent of nominal)

After 1st trim described above:

$$R_T=(1-A)R\pm(1-)RA$$

Note: The resistor is trimmed to (1–A) percent of nominal value. A is expressed in decimals.

$$R_{1\ \text{trimmed}}=R_T-R_{2\ \text{Untrimmed}}=(1-A)R\pm(1-A)RA-BR=R[1-(A+B)\pm A(1-A)]$$

Note: B is expressed in decimals

$$\text{Error in } R_{1\ \text{trimmed}}-R=R-(A+B)\pm A(1-A)=-R(A+B)\pm A(1-A\pm CR)$$

Note: C is expressed in decimals the error in R_1 trimmed is measured with res. bridge of ±C percent accuracy.

After the second trim i.e., after R_2 is trimmed to

$|[R_{1\ \text{trimmed}}-R]|$value:

$$R_{2\ \text{trimmed}}=R[(A+B)\mp A(1-A)]\pm CR\pm AR[(A+B)\mp A(1-A)]=R(A+B)\mp A(1-A)\pm CR\pm A[(A+B)\mp A(1-A)]=\{(A+B)\mp A(1-A)\pm C\pm[A^2+AB\pm A^2(1-A)]\}$$

$$R_T=R_{1\ \text{trimmed}}+R_{2\ \text{trimmed}}=R\{[1-(A+B)\pm A(1-A)]+[(A+B)\mp A(1-A)]\pm C\pm[A^2+AB\pm A^2(1-A)]\}=R\{1-(A+B)\pm A(1-A)+(A+B)\mp A(1-A)\pm C\pm[A^2+AB+A^2(1-A)]\}$$

$$\text{Error in } R_T=R_T-R=R\}-(A+B)\pm A(1-A)+(A+B)\mp A(1-A)\pm C\pm[A^2+AB\pm A^2(1-A)]\}=R\{\pm C\pm[A^2+AB\pm A^2(1-A)]\}=\pm R\{A^2+AB\pm A^2\mp A^3\mp C\}$$

$$\text{Max error in } R_T=\pm R\{2A^2+AB+A^3+C\}$$

$$\text{Percent max error in } R_T=\frac{\text{max error in } R_T}{R}=\pm(2A^2+AB=A^3+C)$$

Note: A, B, C, expressed in percent
A numerical example where

A=±1%
B=1%
C=.05%

as it was described before will yield the following accuracy in the resistor trimmed by described method:

$$\text{Max. error}=\pm(2(.01\%)+.01\%+.0001\%+.05\%=\pm.0801\%$$

A second method of trimming high precision resistors with low precision trimming machine (with high precision bridge) is described below, and shown on FIGS. 2, 3, and 4.

The resistor **10** is trimmed along a trimming path as shown at 26 to 98% of its desired value. The maximum error after this trim is usually ±1%.

Without changing the resistor position in the trimming machine, the resistor **10** is trimmed again to 99.5% of the desired value along trimming path **28**. That is the cutting device (which usually is a nozzle which provides a jet of abrasive particles suspended in air) repeats the same cutting pattern. Exeriments have shown that the amount of resistor's material removed by this second trimming is about 0.5% of that removed in the first trimming. This is equivalent to slowing down the trimming speed by the factor of 1/200.

The same trimming pattern is repeated for a third time along trimming path **30** and the resistor is trimmed to its desired value. The amount of resistor material removed by this third trim is about .05% of that removed by the first trim, which is equivalent to slowing down the trimming speed by the factor of 1/2000 as compared with the first trimming speed.

The accuracy of the trimmed resistors (assuming the accuracy of resistance measuring bridge as ±.05%) is usually in the order of 0.08–0.09%, which is comparable with the first described method.

The accuracy of trimmed resistors can be improved further if four trims are used instead of three, approaching the accuracy of the resistance measuring bridge.

Both of the methods described herein allow a single thick film resistor to be trimmed to any one of a number of desired values.

The aforementioned precise trimming method enables a reduction to be made in the cost of manufacturing resistors having different resistor values because the same common blend of positive and negative resistor ink having a 0 TCR can be fired onto each one of a number of substrates before different individual selective trimming of each of these resistors occurs.

It should be noted that trimming of the cermet resistor by either of the aforementioned methods is done after the previously described selected zero TCR blend of positive and negative cermet resistor ink that was used to form resistor **10** has been fired onto the aluminum oxide substrate **32**.

When a thick film cermet resistor **10** of the aforementioned type is left exposed to its surrounding atmosphere its precisely manufactured resistance and TCR value will be altered with time because of the destructive oxidation and other similar detrimental effects which air, moisture, hydrogen sulfide or other similar destructive delequescent materials have on the resistor **10**.

More particularly the stability of cermet resistors that are not protected from the ambient atmosphere, whether under a load or no load condition, is usually in the order of 0.3–0.5% per year. In other words, the resistance of these resistors have heretofore changed by 0.3%–0.5% a year after they are manufactured.

Such a poor stability precludes the possibility of the manufacture of high precision resistors which have a tolerance of ±0.1% or better.

Manufacturing a thick film resistor in the manner to be hereinafter described provides a resistor which will retain a stability of 0.1% for at least two years.

In other words the resistance of these resistors will change no more than 0.1% of their nominal value after two years of active use in a circuit or during the period in which they are stored on the shelf for this length of time.

Experimental tests showed that the main reason for the instability of thick film resistors, or in other words, drift in resistivity with time was caused by oxidation of the metals in the resistor and by absorbtion of water, contained in the atmosphere.

Therefore, the resistors must be insulated from the ambient atmosphere.

To solve this problem an insulator layer must be provided which has the same temperature coefficient of expansion as the ceramic substrate **32** and the resistor **10** and conductor **16** and **22**. Otherwise thermal stresses will develop with an accompanying change in resistance. Another way is to make the insulating layer flexible enough to prevent stresses from occurring in the resistor which would change its resistance by more than ±.05% for the desired specified temperature range e.g., a 100° change in ambient temperature. Also the layer which physically contacts the resistor must be chemically inert with respect to resistor material, for example, it should not cause oxidation or reduction of the resistor material to occur and at the same time it must be able to adhere to the resistor **10**. Another factor that had to be considered was that since the flexible insulation layer must possess a soft flexible characteristic it needs additional protection from mechanical damage such as scratches etc. The encapsulating structure on the substrate as described below provides a system of layers to protect the cermet resistor from ambient air, water vapors, water, and hydrogen sulfide (H_2S). Furthermore the layers to be described have been found satisfactory in protecting the resistor from being effected when continuous changes in ambient temperature that may vary from the standard reference level of 25° C.±50° C. so that no more than ±.1% change in value of the resistor can at least occur.

The ceramic substrate **32** which is preferably a 96% pure aluminum oxide material is exposed to 1000° C. for 15 to 20 minutes. It is assumed that the substrate **32** is clean prior to this operation if it is not it is cleaned ultrasonically in ethyl or methyl alcohol for three minutes. Next the previously mentioned resistor **10** and conductor inks **16, 22** are printed, dried and fired in the manner previously described as shown in FIG. 6 of the drawing.

A silicon polymer filled with magnesium oxide **34** such as dimethylpolyxylene which is commercially available from the EMCA Company as plastic coat 1139B is then printed or brushed over the resistor **10** and conductor areas **16, 22** except for the conductor areas that are reserved for the terminals **38** and **40**. The substrate **32** is then heat cured at 108° C. for 24 hours to provide polymerization and the resistor **10** is trimmed through the plastic coat **34** to 99%±1% of its desired value as previously described and the terminals **38, 40** are then soldered with suitable soldering material **42, 44** as shown in FIG. 6.

Next, the substrate **32** is heat cycled twice between 25° C. to 125° C. at the temperature-time slope of 20° C. per minute and kept for 2 hours at 125° C. then cooled down on the same rate to 25° C. The same heat cycle is repeated for a second time, and then for a third time a period of fifteen hours instead of two hours and at the same temperatures.

The resistor is then finally trimmed as previously described under the description of FIGS. 2–5 to minus .03% of the desired value. The resistor is then cleaned with a jet spray of nitrogen. A mixture of iron oxide with magnesium silicate suspended in xylene **36** such as glyptal 1201B paint that is commercially available is aprayed over the entire substrate including the resistor conductors and portions which form the solder joint and terminals. The substrate is then exposed to 100° C. for four hours.

The thickness of the flexible silicone polymer layer **34** that is selected is never less than twelve microns and the thickness of the hard glyptal layer **36** is not less than fifty microns. A cross sectional view of the projected resistor **10** is as shown in FIG. 6.

Experimentation has also shown that cermet resistors that are prepared in the above-described manner will remain stable within ±.1% for at least two years or more.

The plotted dotted line shown in FIG. 7 indicates that it is possible through the use of a conventional diffusion introducing profile firing method to obtain only a single resistor blend of ink that has a zero TCR value from a series of different blends of inks which possess different sheet resistivity values.

FIG. 7 also shows a second plotted solid line to indicate that a series of resistors having different resistivity values over a wide resistivity range can be obtained which each has a 0 TCR value when the resistor is first fired by the unique non diffusing method previously described in which the resistor is first fired to the substrate at one temperature and the conductor and resistor are thereafter jointly fired at a second temperature that is approximately 500 C. lower than the first mentioned temperature.

The unique steps employed in the preparation of a zero-TCR thick film resistor are:

(1) Ultrasonically clean substrate **32** in methanol for thirty seconds.
(2) Prefire substrate **32** at 1,000° C.
(3) Clean substrate **32** with N_2, print resistor.
(4) Dry resistor at 107° C. for 45 minutes.
(5) Ascertain the correct firing temperature of the furnace.
(6) Fire resistor at a plateau temperature of 1,000° C. on a two inch per minute moving belt.
(7) Clean substrate **32** with N_2 and print conductors **16, 22**.
(8) Dry conductors at 107° C. for 45 minutes.
(9) Ascertain the correct firing temperature of the furnace.
(10) Fire the conductors at a plateau temperature of 550° C. on a 2" per minute moving belt.
(11) Anneal by heat cycling at 177° C. for 15 hours.
(12) Clean resistor **10** and conductors **16, 22** with N_2 and screen on flexible layer **34**.
(13) Dry flexible layer **34** at 126° C. for 12 hours.
(14) Stake pins **38** and **40** and solder at **42, 44**.
(15) Trim resistor **10** to ninty eight percent of its normal resistance value and clean with N_2.
(16) Heat cycle at 121° C. two times for two hours and then overnight to eliminate stresses induced by trimming.
(17) Trim to desired value and clean with N_2.
(18) Spray on hard layer **36**.
(19) Dry hard layer **36** at 93° C. for 4 hours.

The significance of eliminating the harmful effects the diffusion has on TCR and resistivity which has heretofore been brought about by firing the resistor and conductor at substantially the same high temperature is clearly illustrated in FIGS. 8 and 9.

FIGS. 8 and 9 show for example how TCR and the resistivity of thick film resistors are dependent on the previously referred to geometry, or aspect ratio of the resistor when they are fired with associated conductors at the same high temperature and how this dependence was practically eliminated when the unique process heretofore described was employed.

Curve A in FIG. 8 shows the dependence of TCR on the aspect ratio when a thick film precision resistor is manufactured by using conventional methods in which the resistor and conductor is fired at the same high temperature. It can be seen in this conventional method that the TCR value changed from +74 p.p.m./degree C. at the aspect ratio of .1 to −56 p.p.m./degree C., at the aspect ratio of 10. In other words curve A shows that a total change in TCR of 130 p.p.m./degree C. occurred when the previously mentioned ruthenium system ink is used as the resistor material, platinum gold ink is used as the conductor material and after the resistor ink and conductor were fired at the high temperature of 1000° C.

FIG. 8 curve B shows how the dependence of TCR on the aspect ratio is for all practical purposes eliminated when the thick film resistor is manufactured by the previously described unique method of manufacturing.

The dependence of TCR on the aspect ratio decreases from 130 p.p.m. per degree C. for conventional methods that have heretofore been used as shown in FIG. 8 curve A to 28 p.p.m. per degree C. for the unique method of manufacturing that has for the first time been disclosed herein.

Furthermore, in addition to the decrease in the TCR dependence on the aspect ratio it can be seen that the TCR versus aspect ratio curve shifts in a negative direction after the unique manufacturing method was used.

More specifically both curves A and B represented the relationship between the TCR and the aspect ratio for the same ruthenium system ink resistor material. The only difference in the manufacturing process depicted in the curve A and B shown in FIG. 8 is that in curve A the resistors and their associated conductors were fired at approximately the same temperature such as about 1000° C. and for curve B the resistors were first fired at 1000° C. and thereafter the resistors and their associated conductors were jointly fired at about 550° C.

It should also be noted that the conductor connected the resistor represented by curve B contains silver combined with glass instead of the conventional platinum-gold (PdAu) combined with glass type conductor as represented by curve A. The only reason for the change in conductor material from Pd Au to silver was that it was not possible to fire a Pd Au type conductor at 550° C. whereas a silver type conductor can be fired at this temperature.

A shift of curve B in a negative direction shows that the degree of diffusion of conductor material into the resistor material has decreased and that the true TCR of the resistor ink is in reality that shown on curve B rather than the generally heretofore assumed value that is shown on curve A.

Curve C, FIG. 8 depicts the dependence of TCR on the aspect ratio after the resistive ink was blended with ink having positive TCR such as Pt Au type conductor ink or pure gold powder. After blending the resulting ink lies approximately between +13 p.p.m./degree C. and −8 p.p.m. degree C. TCR and its dependence on the geometry (aspect ratio) for all practical purposes is nil.

FIG. 9, curve A shows the dependence of resistivity on the aspect ratio when the thick film resistors are manufactured by conventional methods.

2150 ohm per square per mil was the change in resistivity that occurred when a change in aspect ratio went from .1 to 10.

Curve B of FIG. 9 provides a way of showing the independence of resistivity on the aspect ratio when the resistor is manufactured by the unique method previously described for FIG. 8, curve B.

The dependence of resistivity on the aspect ratio [geometry] decreases from 2150 ohm per square per mil on curve A to 1100 ohm per square per mil on curve B.

FIG. 9 curve C shows the resistivity versus aspect ratio after blending as previously described under FIG. 8C.

It has been determined by experimentation that substantially 20% by weight of RuO_2, 40% by weight of Ru and 40% by weight of glass frit is one type of positive temperature coefficient of resistivity resistor ink that can be employed to advantage in the aforementioned described ink mixtures that are formed from positive and negative temperature coefficient of resistors ink. It has also been determined by experiment that substantially 40% by weight of RuO_2, 20% by weight of Ru and 40% by weight of glass frit is one type of negative temperature coefficient resistivity resistor ink that can be advantageously used in the aforementioned ink mixture to make the resistor **10**.

It can therefore be seen that the unique apparatus and method of first firing the resistor **10** onto a substrate **32** at 1000° C. and the later joint firing of the resistor **10** and its associated conductors **16**, **22** onto the substrate **32** at a lower temperature, namely 550° C., will substantially eliminate diffusion that has heretofore occurred between the conductor material and the resistor material.

By procuring a resistor and its associated conductors after firing in the substantially same undiffused state that they were in before firing it is for the first time possible to eliminate the TCR and resistivity dependency on the geometry of the resistor commonly referred to as aspect ratio that has heretofore existed when other firing means have been employed for this purpose.

Because of the aforementioned advantages derived from the unique firing technique it is now possible for the time to manufacture precision thick film resistors with-

out concerning oneself with the heretofore existing problem of:

(1) Selecting the right aspect ratio or in other words the length-wide ratio, or the geometry, of the resistor that is to be fired onto a substrate.

(2) Spending time in consulting geometry correcting tables to predict resistivity and the TCR of the resistor as a function of the resistors geometry and

(3) Requiring the creative ability of the designer who is designing an electrical thick film circuit from being able to present the most desired economical compact circuit because the resistors that have heretofore been used were required to be of a prescribed geometric shape in size.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for firing a precision thick film resistor and an associated partially overlapping conductive material on an electrically nonconductive substrate in such a manner that substantially none of the conductive material is diffused into the resistor whereby the temperature coefficient of resistivity of the resistor will have a value that is within a few parts per million per degrees centigrade from zero, said resistor further being characterized that the said temperature coefficient of resistivity and sheet resistivity thereof is free from dependence upon the geometric shape thereof, said process comprising the steps of applying a resistor ink to the substrate, drying the resistor ink, firing the resistor ink in amorphous form to the substrate at the sintering temperature of the resistor ink, applying the conductive material to the substrate in partially overlapping relationship with said fired resistor, drying the conductive material, firing the conductive material at a sintering temperature which is substantially lower than the first mentioned firing temperature whereby the tendency for diffusion of said conductive material into said fired resistor is substantially prohibited.

2. The process as defined in claim **1** wherein the resistor contains different combinations of positive and negative resistor ink mixes and the conductor film is constructed of substantially seventy percent by weight of silver powder, substantially ten percent by weight of lead boro silicate glass and the remainder decanol alcohol.

3. The process as defined in claim **1** wherein the resistor is a ruthenium system ink, the conductor film is a mixture of seventy percent by weight pure silver powder with at least ten percent by weight of lead boro silicate glass and the remaining percent by weight of the mixture is comprised of a decanol alcohol in which said powder and glass are suspended and the substrate is comprised of ninety-six percent pure aluminum oxide.

4. The process as defined in claim **1** wherein said first temperature is 1000° C. and the lower temperature is substantially 550° C.

5. A thick film resistor for use in an electrically conductive circuit, comprising a selected one of a series of composites made of different combinations of positive and negative resistor ink mixes fired in amorphoric form at 1000° C. onto an electrically nonconductive substrate and into a sintered state, the selected composite of the fired resistor and a conductive ink forming a part of said conductive circuit being held in overlapping relationship with said resistor on the substrate by firing said conductor at a temperature that is at its sintering temperature and substantially below the temperature level at which said resistor is changed into its said sintered state to thereby substantially prohibit diffusion of the conductive material into the resistor and wherein the resulting temperature coefficient of resistivity value of the resistor is within a few parts per million degrees centigrade from zero.

6. The cermet resistor as defined in claim **5** wherein the selected composite of resistor ink and ink forming said conductive circuit are jointly fired onto the substrate at a temperature that is 550° C.

7. The process as defined in claim 1 wherein the resistor contains different combinations of positive and negative resistor ink mixes, the conductor film is constructed of a cermet conductor mixture which is sintered and adhered to the substrate at said lower temperature and the percent of positive temperature coefficient of resistivity ink required in the blend to provide a resistor ink blend having a zero temperature coefficient of resistivity is determined by first plotting the respective positive and negative temperature coefficient of resistivity values of the inks that are to form the blend above and below a zero temperature coefficient of resistivity line formed on a semi log graph at separate points located at opposite ends of a characterized log scale of the graph, reading a line between said plotted points, and reading the value on said long scale where the intersection of said two lines occur to obtain the percent of positive temperature coefficient of resistivity ink in the blend that is required to obtain a zero temperature coefficient of resistivity mix.

8. The thick film resistor defined in claim 5 wherein the positive temperature coefficient of resistivity resistor ink is comprised of substantially 20% by weight of RuO_2 40% by weight Ru and 40% by weight of glass frit and the negative temperature coefficient of resistivity resistor ink is comprised of substantially 20% by weight of RuO_2, 20% by weight of R_u and 40% by weight of glass frit.

9. The thick film resistor defined in claim 5 wherein the positive temperature coefficient of resistivity resistor ink is comprised of substantially 2% by weight of RuO_2, 40% by weight of R_u and 40% by weight of glass frit and the negative temperature coefficient of resistivity resistor ink is comprised of substantially 40% by weight of RuO_2, 20% by weight of Ru and 40% by weight of glass frit, and wherein the addition of pure gold powder is employed to make the zero temperature coefficient of resistivity more positive and an oxide of group VIII of the metals is employed to make the ink more negative.

10. A method for firing a plurality of precision thick film resistors and associated conductor materials on a common electrically non-conductive substrate, which resistors may be of the same or different geometric shape, comprising the steps of applying thick film resistor material to the substrate, drying the thick film resistor material and firing said resistor material at its sintering temperature in amorphous form on the substrate and the subsequent steps of applying said associated conductor on said substrate and in overlapping relationship to a portion of said resistor and firing at a temperature that is substantially lower than the first mentioned temperature at which said resistor material is fired on said substrate whereby the tendency for diffusion of said conductor material into said resistor is substantially prohibited and the temperature coefficient of resistivity and the sheet resistivity of said resistor is independent of the size and geometric shape thereof.

11. A method for firing a plurality of different thick film resistors which have different geometric shapes and associated conductor materials onto a common electrically non conductive substrate so that the temperature coefficient of resistivity and the resistivity of any selected one of the resistors can be made independent of its aspect ratio, comprising the steps of applying the thick film resistor to the substrate, drying the thick film resistor and firing the resistor onto the substrate at 1000° C. and the sintering temperature of the resistor and the subsequent steps of applying said associated conductor to said substrate and overlapping relationship to a portion of said resistor and firing the said selected one of said conductors onto the substrate at 550° C. which temperature is substantially lower than the first mentioned temperature at which said resistor is sintered to thereby produce a resistor in which diffusion is substantially prohibted during said last mentioned firing.

12. A process for firing a thick film resistor and an associated conductor film onto an electrically non conductive substrate which process inhibits diffusion of material from said conductor film into said resistor film whereby the temperature coefficient of resistivity of said resistor film is substantially unaffected by said process, said process comprising the steps of first applying the thick reistor film to the substrate, drying the thick film resistor firing the resistor film to the substrate at a first temperature that is at the sintering temperature of the resistor and thereafter applying the conductor film to the substrate and in overlapping relationship with said resistor, drying the conductor and firing said conductor film at its sintering temperature onto said substrate while said resistor film remains substantially below its sintering temperature.

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RALPH S. KENDALL, Primary Examiner

U.S. Cl. X.R.

117—217; 338—309

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,788,891 Dated January 29, 1974

Inventor(s) Sergei Schebalin

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the drawing, Figure 1, change "-10" to read -- +10 --.

Column 1, line 13, cancel "#1"; line 16, cancel "#2"; line 37, "and" should read -- or --; line 54, insert a comma --, -- after "which" and after "example"; line 68, "resistance value" should read -- resistivity --. Column 2, line 22, after "therefore" insert a comma -- , --; line 64, "present" should read -- prevent --. Column 3, line 10, before "that" insert -- type --; line 75, cancel ", in a non-diffused man-". Column 4, line 1, cancel "ner," ; line 15, after "words" insert a comma --, --. Column 5, lines 3 and 4, cancel "such as". Column 6, line 42, "TCR", second occurrence, should read -- TCR' --; line 67, before the period "." insert -- is then determined --; line 68, cancel "A" and insert -- This is accomplished by drawing a --; cancel "is drawn". Column 7, lines 12 and 13, "addition blend of the" should read -- an additional --; line 33, "other" should read -- zero TCR --; line 42, "sheets" should read -- sheet --; line 57, "on" should read -- of --; line 65, after "by" insert -- the --; line 66, "bidge" should read -- bridge --. Column 8, line 9, after "have" insert -- a --; lines 13 and 14, cancel "in Figure 2"; line 14, cancel the comma ",", first occurrence, and insert -- and --; cancel "on Fig. 2"; lines 29 and 32, "10", each occurrence, to -- 14 --; line 29, "yet" should read -- the --; line 45, cancel "yet"; line 50, before "value" insert -- resulting --; after "14" insert a comma -- , --; line 52, cancel "to" and insert -- , will be --; lines 52 and 53, cancel "will be 3% of nominal"; line 65, "10" should read -- ten --. column 9, line 62, cancel "(with" and insert -- which employs a --; line 63, cancel ")"; line 70, cancel "That is" and insert -- In other words --; line 73, "Exeriments" should read -- Experiments --. Column 11, line 15, cancel "at least"; line 16, before "96" insert -- at least --;

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,788,891 Dated January 29, 1974

Inventor(s) Sergei Schebalin Page - 2

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

line 16, cancel "a" and insert -- at least --; line 41, after "time" insert -- for --; line 49, "aprayed" should read -- sprayed --. Column 12, lines 16 and 19, after "conductors" insert -- 16, 22 --. Column 13, line 9, after "conductor" insert -- which is --; after "connected" insert -- to --; line 26, after "blending" insert a comma -- , --; line 44, "8C" should read -- 8 --; line 75, before "time" insert -- first --. Column 14, line 14, "in" should read -- and --. Column 15, line 25, after "R_uO_2" insert a comma -- , --; line 32, "2%" should read -- 20% --. Claim 7, line 15, "reading" should read -- drawing --. Claim 8, line 6, "20%" should read -- 40% --. Claim 11, line 12, after "and" insert -- in --.

Signed and sealed this 24th day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
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C. MARSHALL DANN
Commissioner of Patents