June 20, 1967 W. E. COUNTS ET AL 3,326,645

CERMET RESISTANCE ELEMENT AND MATERIAL

Filed Sept. 22, 1965

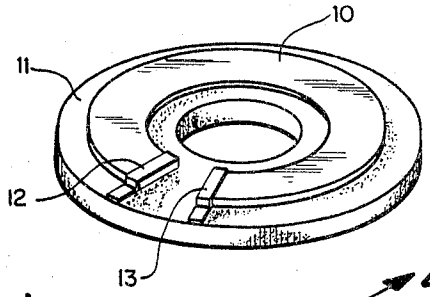


FIG. 1

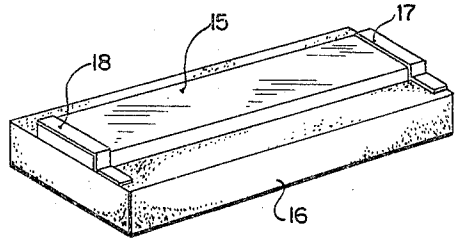


FIG. 2

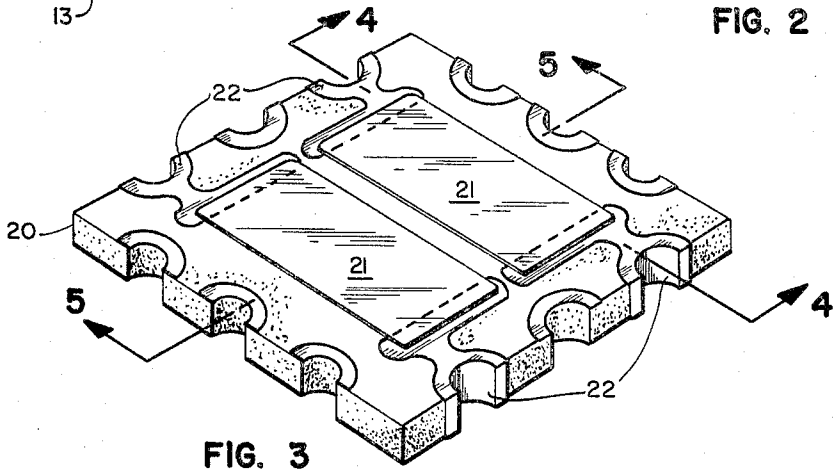


FIG. 3

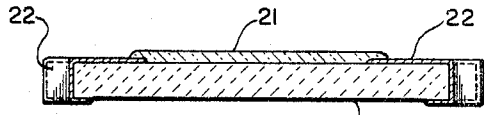


FIG. 4

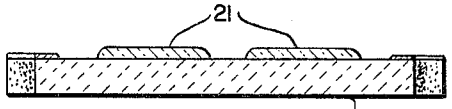


FIG. 5

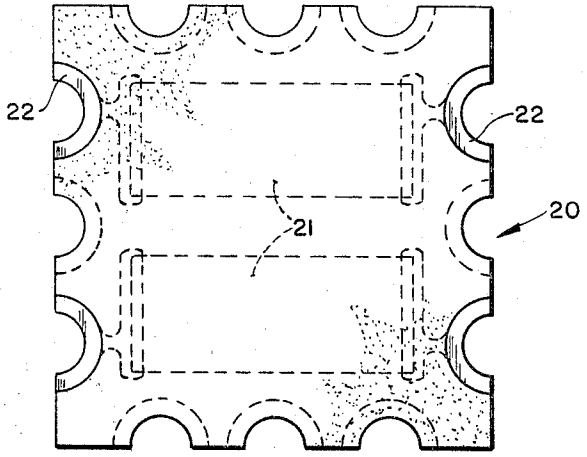


FIG. 6

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CERMET RESISTANCE ELEMENT AND MATERIAL

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4 Claims. (Cl. 29—182.5)

The present invention relates to an improved electrical resistance material formed of a mixture of finely divided particles of glass and metal, of the type commonly called "cermet material," and to resistance elements constructed therefrom.

Cermet resistance elements presently known in the art are exemplified by U.S. Patent 2,950,995 of Thomas M. Place, Sr., et al., entitled "Electrical Resistance Element" and 2,950,996 of Thomas M. Place, Sr., et al., entitled "Electrical Resistance Material and Method of Making Same," both of which are assigned to Beckman Instruments, Inc., assignee of the present invention. These patents describe a resistance element formed of a layer of resistance material comprising a heterogeneous mixture of particles of non-conducting material and conducting metals fixed to a non-conducting base. The non-conducting material is a ceramic-type material such as glass or vitreous enamel and the layer is formed by heating the metal-glass mixture at least to the melting point of the glass or enamel, so as to create a smooth, glassy phase.

In brief, the present invention resides in the discovery that a cermet mixture, formed of finely divided particles of glass and an alloy of about 5 to 50% total weight of ruthenium and rhodium, in which the metal alloy is so correlated to the glass material that the minimum proportions of ruthenium metal is at least 10% by weight of the metal alloy for all proportions of the alloy weight, can be deposited on a non-conductive base member and fired to form a cermet resistance element having a high resistivity and a suitable temperature coefficient of resistance. Such resistance elements have a high resistance for the relatively large amounts of metal material employed and are capable of performance at high power ratings as compared to glass-metal resistance elements employed in the past.

A more thorough understanding of the invention may be obtained by a study of the following detailed description taken in connection with the accompanying drawings in which:

FIG. 1 is an isometric view of an embodiment of the invention which is suitable for use in rotary potentiometers;

FIG. 2 is an isometric view of another embodiment of the invention which is suitable for use in linear potentiometers as well as for fixed resistors;

FIG. 3 is an isometric view of an embodiment of the invention particularly adapted for fixed resistance elements of a micro-miniaturized electrical circuit;

FIGS. 4 and 5 are sectional views taken along lines 4—4 and 5—5 respectively of FIG. 3, and

FIG. 6 is an underside view of the embodiment of FIG. 3.

The cermet material of the present invention is particularly applicable to the manufacture of miniature or micro-miniature resistance elements of all types, representative ones being shown in the figures. Thus, in the structure of FIG. 1, a layer 10 of resistance material is fired to a base 11, the electrodes 12, 13 being provided at each end of the layer for connecting into an electrical circuit. This resistance element may be used as a fixed resistor or may be combined with a rotating contact arm for use as a rotary rheostat or potentiometer. The base 11 may be of any suitable electrically non-conducting

material which will withstand the elevated temperatures normally used to fire the resistance material. Various ceramic materials are suitable for this use, those having a smooth, fine-textured surface and being impervious to moisture and other liquids being preferred. Steatite, fosterite, sintered or fused aluminas and zircon porcelains are examples of preferred materials for forming the base 11.

The electrically conductive electrodes 12, 13 are conventional and may be formed by applying any of the well-known conducting silver or other metal pastes over the layer of resistance material and firing the unit to convert the paste to a layer of metal which is firmly attached to the layer of resistance material. Alternatively, terminal structures such as are shown in Patent No. 3,134,085 of Kenneth F. Miller et al., entitled "Variable Resistor With Terminal Structure" may be employed for making electrical contact with the resistance layer 10.

FIG. 2 illustrates another form of the resistance element of the invention in which a layer 15 of resistance material is applied to a rectangular base 16 and electrodes 17, 18 are then added at the ends of the layer 15. This form of the invention is particularly suitable in fixed resistors and linear potentiometers.

FIGS. 3, 4, 5 and 6 illustrate substantially enlarged views of a micro-miniature circuit element 20 advantageously formed of alumina and supporting a pair of fixed cermet resistance elements 21. The respective ends of these resistance elements engage conductive electrodes 22 as shown.

The invention contemplates a cermet composition for use in the above-described resistor elements comprising about 50% to about 95% glass and the balance an alloy of the metals ruthenium and rhodium. The particular amounts of ruthenium and rhodium necessary in the metal alloy to produce a resistance layer having a commercially applicable temperature coefficient of resistivity depends on the total metal content employed in the cermet composition. For relatively high resistance elements, in the order of 10,000 ohms/square, the range of proportions of ruthenium content may be about 95% by weight of the total metal content of the cermet compositions. In general, the maximum preferred allowable proportion of ruthenium decreases as the total metal content of the metal-glass cermet is increased. Preferably, the ruthenium-rhodium containing alloy is so related to the ceramic material that when the total content of metal alloy in the cermet composition is 5–10% the maximum proportion of ruthenium metal is about 95% by weight of the alloy and the maximum proportion of rhodium is about 40% by weight of the alloy; when the total content of the metal alloy in the cermet composition is between 10–20% of the composition, the maximum proportion of ruthenium metal is about 90% by weight of the alloy and the maximum proportion of rhodium is about 55% by weight of the alloy; when the total metal content of the cermet composition is between 20–35% of the composition, the maximum proportion of ruthenium metal is about 70% by weight of the alloy and the maximum proportion of rhodium is about 60% by weight of the alloy; when the total metal content is between 35–50%, the maximum proportion of ruthenium metal is about 65% by weight of the alloy and the maximum proportion of rhodium is about 75% by weight of the alloy.

In a preferred embodiment of the invention, the cermet compositions of this invention may be prepared by mixing the resinates of ruthenium together with the resinates of rhodium. The glass binder, in the form of finely divided glass particles, is mixed or milled with the resinate solution so that each glass particle is thoroughly wetted with the metal solution. This mixture is gradually heated

to approximately 700° F. and constantly stirred to remove the volatiles and organic materials from the mixture and to decompose the metal compounds. The resulting dry material is ground to a fine powder and calcined at about 850° F. The resulting calcine is ground to a fine powder, producing a dry material consisting of very small glass particles coated with or mixed with extremely small particles of the metal alloy.

The particular range of proportions of glass to metal by weight in the final resistance material may be varied in the procedure just described by varying the amount of glass added to a given resinate solution. Each of the individual resinate solutions contains a predetermined quantity by weight of ruthenium-rhodium alloy. After heating the glass and metal resinate solution, only the glass and metal remain, the total weight or amount of metal particles coating the glass particles being that amount of metal which was originally in the resinate solutions.

The mixtures formed by the method described above may be stored indefinitely and may be used to produce stable resistance elements. When it is desired to make resistance elements using the material, the dry powder is mixed with a suitable liquid carrier, e.g., 7% ethyl hydroxyethyl cellulose-93% octyl alcohol to form a fluid composition which can be applied to the base member by any suitable process such as silk screening, spraying or stenciling. The base with the layer or layers applied thereto is then fired to drive off the volatiles and fuse the glass material into a continuous phase of solidified glass with the metal alloy particles uniformly distributed therein. One firing procedure comprises inserting the base with applied resistance layer or layers into a cold furnace. The furnace is slowly heated, e.g., over a period of four hours to a temperature of the order of 1450 to 1550° F. This temperature is maintained a short time period, e.g., 20 to 30 minutes, after which the furnace is slowly cooled, e.g., over a period of four hours before withdrawal of the cermet elements. This procedure is referred to below as the "slow firing" technique. Another firing procedure which may be used (denoted hereinafter as the "fast firing" method) involves inserting the base of the fired resistance layer or layers into a furnace which has been pre-heated to a temperature in the range of 1400–2000° F. The fired element is then removed after a relatively short time period, e.g., 5 to 30 minutes.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative examples are given for various cermet resistance elements using ruthenium-rhodium alloys fired onto a steatite base member to form a thin resistance layer approximately .001 inch in thickness. In these examples, it will be understood that the time and temperature of firing and the type of substrate material employed may cause some minor variations in the resistivity and temperature coefficient of the resulting resistance elements.

Example A (5% metals by weight):	Percent
Glass	95
Ruthenium	3.33
Rhodium	1.67

The resistivity of a resistance layer of approximately .001 inch thickness formed of the material was approximately 10,000 ohms/square and its temperature coefficient of resistivity (TEMPCO) was −338 p.p.m./° C.

Example B (10% metals by weight):	Percent
Glass	90
Ruthenium	6.67
Rhodium	3.33

The resistivity of a resistance layer of approximately .001 inch thickness formed of this material was approximately 1900 ohms/square and its TEMPCO was −160 p.p.m./° C.

Example C (10% metals by weight):	
Glass, percent	90
Ruthenium, percent	5
Rhodium, percent	5
Resistance, ohms/square	8000
TEMPCO, p.p.m./° C.	−738

This composition produced a resistance layer having a TEMPCO outside the more desired commercially applicable range of ±500 p.p.m./° C. In order to produce a resistance element and within the more commercially applicable TEMPCO range, it is desirable to limit the maximum proportions of rhodium in those resistance materials having a metal content of between 5–10% to about 40% of the total metal content.

Example D (15% metals by weight):	
Glass, percent	85
Ruthenium, percent	10
Rhodium, percent	5
Resistance, ohms/square	870
TEMPCO, p.p.m./° C.	−43.6

Example E (15% metals by weight):	
Glass, percent	85
Ruthenium, percent	7.5
Rhodium, percent	7.5
Resistance, ohms/square	900
TEMPCO, p.p.m./° C.	−420

Example F (20% metals by weight):	
Glass, percent	80
Ruthenium, percent	12
Rhodium, percent	8
Resistance, ohms/square	166
TEMPCO, p.p.m./° C.	−88.5

Example G (20% metals by weight):	
Glass, percent	80
Ruthenium, percent	10
Rhodium, percent	10
Resistance, ohms/square	272
TEMPCO, p.p.m./° C.	−458

Example H (20% metals by weight):	
Glass, percent	80
Ruthenium, percent	6.67
Rhodium, percent	13.33
Resistance, ohms/square	1055
TEMPCO, p.p.m./° C.	−681

This composition produced a resistance element having a TEMPCO outside the more desired commercially applicable range of ±500 p.p.m./° C. In order to produce a resistance element within the more commercially aplicable TEMPCO range, it is desirable to limit the maximum proportions of rhodium in those resistance materials having a metal content of between 20–35% by weight to about 60% of the total metal content.

Example I (20% metals by weight):	
Glass, percent	80
Ruthenium, percent	17.14
Rhodium, percent	2.86
Resistance, ohms/square	85
TEMPCO, p.p.m./° C.	+245

Example J (25% metals by weight):	
Glass, percent	75
Ruthenium, percent	12.50
Rhodium, percent	12.50
Resistance, ohms/square	95
TEMCO, p.p.m./° C.	−98

Example K (25% metals by weight):	
Glass, percent	75
Ruthenium, percent	11.18
Rhodium, percent	13.82
Resistance, ohms/square	190
TEMPCO, p.p.m./° C.	−428

Example L (30% metals by weight):

Glass, percent	70
Ruthenium, percent	15
Rhodium, percent	15
Resistance, ohms/square	68
TEMPCO, p.p.m./° C.	−208

Example M (35% metals by weight):

Glass, percent	65
Ruthenium, percent	20
Rhodium, percent	15
Resistance, ohms/square	35
TEMPCO, p.p.m./° C.	+101

Example N (35% metals by weight):

Glass, percent	65
Ruthenium, percent	15.55
Rhodium, percent	19.45
Resistance, ohms/square	83
TEMPCO, p.p.m./° C.	−295

Example O (40% metals by weight):

Glass, percent	60
Ruthenium, percent	20
Rhodium, percent	20
Resistance, ohms/square	32
TEMPCO, p.p.m./° C.	−42.8

Example P (50% metals by weight):

Glass, percent	50
Ruthenium, percent	25
Rhodium, percent	25
Resistance, ohms/square	32
TEMPCO, p.p.m./° C.	+124

Variations in the glass composition utilized may change the resistance and TEMPCO values achieved to a minor extent. It is believed that almost any glass composition may be employed so long as the glass constituents do not react with the metal constituents at the firing temperatures employed and so long as the glass has a melting temperature below that of the metal constituents of the mixture. The particular compositions of the glass were employed in various quantities in the above examples.

Glass formulae	Glass #1	Glass #2	Glass #3
	Percent	*Percent*	*Percent*
PbO	65.68	58.10	59.20
ZnO	5.41	5.41	
MgO		.39	
B_2O_3	10.00	11.30	14.40
SiO_2	16.51	24.50	20.00
ZrO_2	2.40	1.20	
Na_2O			6.40

The above formulae are the fritted percentages. The glass may be produced by any conventional process. It is preferred, however, that it be as homogeneous as possible. One method of making glass includes thoroughly mixing a batch of the raw materials together while dry, melting the batch in ceramic crucibles to produce a clear fluid glass, quenching the molten glass by pouring it into cold water, drying the resulting shattered glass and then grinding it to a very fine powder.

As will be noted from the examples, relatively large quantities of ruthenium-rhodium alloys can be utilized in these cermet compositions to form resistance elements having relatively high resistance values as compared to cermet resistance elements produced in the past. It is known, for example, that an alloy of gold, palladium and silver, when utilized in a glass-metal (cermet) resistance mixture of finely divided particles in which the gold, palladium, silver content is about 11.5% of the total mixture, produces a resistance element having approximately 55 ohms per square for a layer approximately .001 inch in thickness. As will be seen in Example B hereinabove, a cermet composition using 10% ruthenium-rhodium alloy produces a resistance element (of like thickness) having a resistance of 1900 ohms per square and having a

TEMPCO within the commercially applicable desired range of ±500 p.p.m./° C. This is over 34 times more resistance using approximately the same quantity of metal in the cermet composition. The resistance of the cermet composition utilizing 50% ruthenium-rhodium alloy is still approximately 30 ohms per square which is extremely high when one considers that the total metal content is approximately five times that of the above-described gold, palladium, silver cermet composition.

While it is not completely understood why the ruthenium-rhodium metal alloy can be employed in such large quantities to form a resistance material, it is believed that the presence of ruthenium inhibits the tendency for the metal to agglomerate and form strings or globules in the fused glass binder. It appears that ruthenium contributes to the interaction between the respective surfaces of the finely divided metal alloy and glass particles and prevents the agglomeration thereof even when they are present in relatively large quantities. This apparently causes the mixture to retain its homogeneity during firing and results in a much more stable resistance element having relatively large quantities of metal for the resistance values obtained.

The homogeneity of resistance elements formed of cermet composition using ruthenium-rhodium alloys is believed to be one reason why these elements are capable of withstanding higher power levels. Because the materials do not agglomerate when the glass material is fused and, therefore, do not produce strings or globules of metal alloy, the current flow through the resistance element is believed to be more uniformly applied across the entire volume of the resistance element. That is, the metal particles are uniformly distributed throughout the element and there are no areas or regions through which electrical current flow is confined to a single or narrow path through any portion of the element. This, in addition to the greater metal content of the resistance element, creates a more even distribution and dissipation of the heat produced.

The relatively high metal content of cermet elements formed of ruthenium-rhodium cermet material and the extremely uniform distribution of the metal alloy throughout the element is extremely important in another respect. One of the major problems encountered when using cermet resistors as variable resistance devices, such as precision potentiometers and circuit trimmers, is the high electrical noise characteristics associated with such devices due to the contact made between the movable wiper of such devices and the resistance element. It is believed that this "electrical noise" is at least in part due to the somewhat sporadic contact made by the wiper and the metal particles on the surface of the element. Due to the high metal content of cermet elements employing ruthenium-rhodium alloys for relatively high resistance elements, and because the metal particles do not agglomerate but are evenly distributed throughout, it can be understood that there are substantially greater numbers of metal particles available for contact with the wiper. This greatly reduces the "electrical noise" associated with such elements.

Resistance elements formed of cermet compositions using ruthenium-rhodium cermet material also have an extremely smooth surface. This is considered extremely important when such elements are employed in variable resistance devices, such as potentiometers. These ruthenium-rhodium cermet materials do not produce blisters or other irregularities on the surface of the element when the minimum percentage of ruthenium in the composition is at least 10% of the total metal alloy content in the composition. For example, in order to produce smooth surfaced resistance elements, the ruthenium content should not be less than .5% of the total composition when the total metal content is 5% of the composition and should not be less than 5% of the composition when the total metal alloy content is 50% of the composition. Of course, it will be understood that the above minimum percentage

of ruthenium does not necessarily produce a resistance element having a temperature coefficient of resistivity falling within the desired commercially applicable range of ±500 p.p.m./° C. and, for the more desired range, greater percentages of ruthenium must be employed.

Although exemplary embodiments of the invention have been disclosed and discussed, it will be understood that other applications of the invention are possible and that the embodiments disclosed may be subjected to various changes, modifications and substitutions without necessarily departing from the spirit of the invention.

What is claimed is:

1. A cermet composition adapted to be fired onto a non-conducting base member to form a thin resistance layer consisting essentially of:

about 50 to 95% by weight of glass material; and

5 to 50% by weight of an alloy of ruthenium and rhodium in which the metal alloy is so correlated to the glass material that the minimum proportion of ruthenium metal is at least 10% by weight of the metal alloy for all proportions of the alloy content, said glass material having a melting point lower than that of said alloy of ruthenium and rhodium.

2. A cermet composition adapted to be fired onto a non-conducting base member to form a thin resistance layer consisting essentially of:

about 50 to 95% by weight glass material; and

about 5 to 50% by weight of an alloy of ruthenium and rhodium, said glass material having a melting point lower than that of said alloy of ruthenium and rhodium, said alloy constituents being so co-related to said glass material that when the total metal content of said composition is between 5–10%, the maximum proportion of ruthenium is about 95% by weight of the alloy and the maximum proportion of rhodium is about 40% by weight of the alloy; when the total metal content is between 10–20% of the composition, the maximum proportion of ruthenium is about 90% by weight of the alloy and the maximum proportion of rhodium is about 55% by weight of the alloy; when the total metal content is between 20–35% of the composition, the maximum proportion of ruthenium is about 70% by weight of the alloy and the maximum proportion of rhodium is about 60% by weight of the alloy; and when the total metal content is between 35–50% of the composition, the maximum proportion of ruthenium is about 65% by weight of the alloy and the maximum proportion of rhodium is about 75% by weight of the alloy.

3. A cermet composition adapted to be fired onto a non-conducting base member to form a thin resistance layer consisting essentially of:

about 50 to 95% by weight glass material; and

about 5 to 50% by weight of an alloy of the metals ruthenium and rhodium in which the maximum proportions of ruthenium metal to total metal content

is inversely proportional to the total metal content and the maximum proportion of ruthenium is about 95% by weight of the alloy when the metal content is 5% and the maximum proportion of ruthenium in the alloy is about 65% when the total content is 50% by weight of the cermet composition, said glass material having a melting point lower than that of said alloy of ruthenium and rhodium.

4. A cermet resistance element comprising

a high temperature resistant, electrically non-conducting base;

a thin layer of fused glass-metal mixture fired to said base, said layer consisting essentially of 50 to 95% by weight of solidified glass and 5 to 50% by weight of an alloy of the metals ruthenium and rhodium in finely divided form homogeneously mixed throughout said fused glass, said glass having a melting point lower than that of said alloy of ruthenium and rhodium, said metal alloy being so co-related to said glass constituents that when the total metal content of said composition is between 5–10%, the maximum proportion of ruthenium is about 95% by weight of the alloy and the maximum proportion of rhodium is about 40% of the alloy; when the total metal content is between 10–20% of the composition, the maximum proportion of ruthenium is about 90% by weight of the alloy and the maximum proportion of rhodium is about 55% by weight of the alloy; when the total metal content is between 20–35% of the composition, the maximum proportion of ruthenium is about 70% by weight of the alloy and the maximum proportion of rhodium is about 60% by weight of the alloy; and when the total metal content is between 35–50% of the composition, the maximum proportion of ruthenium is about 65% by weight of the alloy and the maximum proportion of rhodium is about 75% by weight of the alloy thereby providing a resistance element having a resistivity of 30 to 10,000 ohms per square when said layer is approximately .001 inch in thickness and a temperature coefficient of resistivity of less than ±500 p.p.m./° C.

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A. J. STEINER, *Assistant Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,326,645 June 20, 1967

William Edward Counts et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 5, after "total" insert -- alloy --.

Signed and sealed this 2nd day of July 1968.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents