CERMET RESISTANCE ELEMENT

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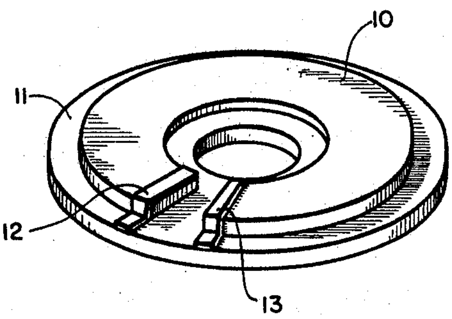

FIG. 1

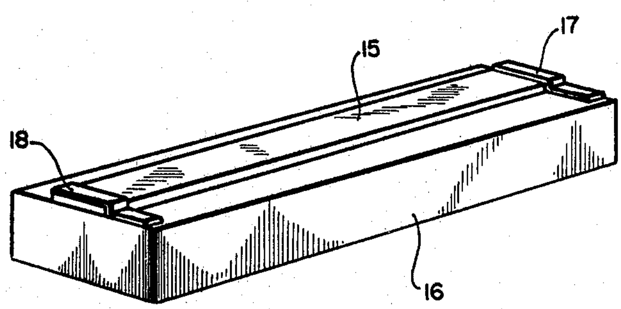

FIG. 2

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CERMET RESISTANCE ELEMENT

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ABSTRACT OF THE DISCLOSURE

A cermet resistance element formed of a non-conductive base member having deposited thereon a single layer of resistance material formed of 50 to 95% by weight of solidified glass and 5 to 50% by weight of a conductive constituent comprising iridium and at least one of the metals selected from the group consisting of platinum, silver, ruthenium, rhodium and palladium, the conductive metal constituent being in finely divided particulate form and uniformly dispersed in electrically conductive relationship throughout the solidified glass.

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

Cermet resistance materials and elements presently known in the art are exemplified by U.S. Patents 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 by a layer of resistance material comprising a heterogeneous mixture of non-conducting material and conducting metals fired to a non-conducting base. The non-conducting material is a ceramic type material such as glass and the layer is formed by heating the metal-glass mixture at least to the melting point of the glass, so as to create a smooth, glassy phase. Additional prior art directed toward resistors formed of a glass-metal composition are U.S. Patent No. 2,837,487 of Daniel E. Huttar, entitled "Resistor Enamel and Resistor Made Therefrom," and U.S. Patent No. 2,924,540 of James B. D'Andrea, entitled "Ceramic Composition and Article."

It is an object of this invention to provide a cermet resistance material for producing resistance elements having increased resistivities in proportion to the relatively large amount of metal contained therein as compared to known types of metal-glass resistance materials.

It is another object of this invention to provide an improved cermet material and an improved resistance element made therefrom having a high power rating, a low noise output, and a low temperature coefficient of resistivity.

A further object of this invention is to provide an improved cermet resistance element which has extremely stable electrical characteristics, e.g., its resistivity and temperature coefficient of resistivity do not vary substantially over long periods of time, either when the element is connected in a circuit or when it is stored in a non-operative state.

Other and further objects, features and advantages of the invention will become apparent as the description proceeds.

In brief, this invention relates to the discovery that a "cermet" mixture formed of glass and an alloy of iridium

and at least one of the other noble metals selected from the group consisting of platinum, silver, ruthenium, rhodium and palladium provides a resistance material having a high resistivity. The amount of resistance obtained is extremely high for the relatively large amounts of iridium alloy metal employed in the mixture thereby producing resistance elements of high metal content capable of performance at high power ratings as compared to known types of glass-metal resistance materials.

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

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

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.

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 **10** for connecting the fired element 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, Forsterite, 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 or under 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 the U.S. Patent 3,134,085 of Kenneth F. Miller et al., entitled "Variable Resistor With Terminal Structure," also assigned to Beckman Instruments, Inc., assignee of the present invention, 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**.

It will be understood that the elements illustrated in FIGS. 1 and 2 are enlarged and that, tn practice, the resistance layers formed on the substrate members are approximately .0005 to .005 inch in thickness. The particular configurations of the resistance layer and the substrate members can vary and are not limited to the arrangements disclosed in FIGS. 1 and 2. The form of the invention illustrated are, however, particularly suitable for use in ltnear variable resistors and potentiometers.

The aforementioned U.S. Patents Nos. 2,950,995 and 2,950,996 teach methods of preparing the cermet resistance layer **10**. A preferred method taught therein comprises mixing the resinates or organic compounds of one or more noble metals. The glass binder, in the form of very small 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 and constantly stirred to remove the volatiles and organic materials from the mixture and to decompose the noble metal compounds. The resulting dry material is ground to a fine powder and calcined for a short period to assure removal of all organic materials. The resulting calcine is ground to a fine powder, producing a dry material consisting of very small glass particles mixed with extremely small particles of metal.

The mixtures formed by the method described above may be stored indefinitely and may be used in small portions to produce unlimited numbers of resistance elements. When it is desired to make resistance elements using the material, the dry powder is mixed with a suitable liquid carrier to form a fluid composition which can be applied to the base material. The base with the layer applied thereto is then fired to drive off the volatiles and fuse the mixture into a continuous phase of solidified glass.

It has been discovered that high resistance values can be obtained in cermet resistance elements formed of mixtures of finely divided particles of glass and alloy of iridium combined with one or more of the noble metals perferably selected from the group consisting of palladium, platinum, silver rhodium, and ruthenium. In this material, the metal content in the form of an iridium alloy comprises from about 5 to 50% by weight of the mixture and glass or ceramic material comprises about 50% to 95% by weight of the mixture. The following are examples of iridium alloys in cermet mixtures formed with iridium and metals taken from the group consisting of silver, palladium, platinum, ruthenium and rhodium.

EXAMPLE A

Iridium-silver, 5% metals by weight

	Percent
Glass	95
Iridium	2.5
Silver	2.5

The resistivity of a resistance layer of approximately .001 inch thickness formed from this material was 140,000 ohms/square and its temperature coeffcient of resistivity was +195 p.p.m./° C.

EXAMPLE B

Iridium-silver, 10% metals by weight

	Percent
Glass	90
Iridium	5.0
Silver	5.0

The resistivity of a resistance layer of approximately .001 inch in thickness formed from this material was 50,000 ohms/square and its temperature coefficient of resistivity was +86 p.p.m./° C.

EXAMPLE C

Iridium-silver, 20% metals by weight

Glass	percent	80
Iridium	do	18
Silver	do	2
Resistance	ohms/square	3920
Tempco	p.p.m./° C.	160

EXAMPLE D

Iridium-silver, 30% metals by weight

Glass	percent	70
Iridium	do	15
Silver	do	15
Resistance	ohms./square	3000
Tempco	p.p.m./° C.	+58.7

EXAMPLE E

Iridium-silver, 40% metals by weight

Glass	percent	60
Iridium	do	20
Silver	do	20
Resistance	ohms./square	1500
Tempco	p.p.m./° C.	+147

EXAMPLE F

Iridium-silver, 50% metals by weight

Glass	percent	50
Iridium	do	25
Silver	do	25
Resistance	ohms./square	600
Tempco	p.p.m./° C.	+227

EXAMPLE G

Iridium-palladium, 5% metals by weight

Glass	percent	95
Iridium	do	4.17
Palladium	do	.83
Resistance	ohms./square	300,000
Tempco	p.p.m./° C.	−382

EXAMPLE H

Iridium-palladium, 10% metals by weight

Glass	percent	90
Iridium	do	2.5
Palladium	do	7.5
Resistance	ohms./square	168,600
Tempco	p.p.m./° C.	−426

EXAMPLE I

Iridium-palladium, 20% metals by weight

Glass	percent	80
Iridium	do	5
Palladium	do	15
Resistance	ohms./square	25,400
Tempco	p.p.m./° C.	−42.3

EXAMPLE J

Iridium-palladium, 50% metals by weight

Glass	percent	50
Iridium	do	46.15
Palladium	do	3.85
Resistance	ohms/square	130
Tempco	p.p.m./°C.	+330

EXAMPLE K

Iridium-platinum, 10% metals by weight

Glass	percent	90
Iridium	do	6.67
Platinum	do	3.33
Resistance	ohms/square	77,300
Tempco	p.p.m./°C.	−386

EXAMPLE L

Iridium-platinum, 20% metals by weight

Glass	percent	80
Iridium	do	16
Platinum	do	4
Resistance	ohms/square	1,590
Tempco	p.p.m./°C.	+102

EXAMPLE M

Iridium-platinum, 50% metals by weight

Glass	percent	50
Iridium	do	46.15
Platinum	do	3.85
Resistance	ohms/square	200
Tempco	p.p.m./°C.	+303

EXAMPLE N

Iridium-ruthenium, 5% metals by weight

Glass	percent	95
Iridium	do	4.5
Ruthenium	do	.5
Resistance	ohms/square	17,000
Tempco	p.p.m./°C.	−256

EXAMPLE O

Iridium-ruthenium, 30% metals by weight

Glass	percent	70
Iridium	do	10
Ruthenium	do	20
Resistance	ohms/square	38.4
Tempco	p.p.m./°C	+286

EXAMPLE P

Iridium-ruthenium, 40% metals by weight

Glass	percent	60
Iridium	do	10
Ruthenium	do	30
Resistance	ohms/square	12.5
Tempco	p.p.m./°C	+464

EXAMPLE Q

Iridium-ruthenium, 50% metals by weight

Glass	percent	50
Iridium	do	46.15
Ruthenium	do	3.85
Resistance	ohms/square	100
Tempco	p.p.m./°C	+229

EXAMPLE R

Iridium-rhodium, 5% metals by weight

Glass	percent	95
Iridium	do	4.5
Rhodium	do	0.5
Resistance	ohms/square	160,000
Tempco	p.p.m./°C	—400

EXAMPLE S

Iridium-rhodium, 25% metals by weight

Glass	percent	75
Iridium	do	9.51
Rhodium	do	15.59
Resistance	ohms/square	400
Tempco	p.p.m./°C	+77

EXAMPLE T

Iridium-rhodium, 50% metals by weight

Glass	percent	50
Iridium	do	16.30
Rhodium	do	33.70
Resistance	ohms/square	102
Tempco	p.p.m./°C	—105

The particular composition of the glass utilized is not critical to the practice of the invention except that it must have a melting temperature below that of the metal constituents of the mixture. Four illustrative examples are as follows:

GLASS NO. 1

Fused composition (percent)

Lead oxide (PbO)	68.00
Zinc oxide	4.97
Boric oxide	14.71
Silicon dioxide	12.32

GLASS NO. 2

Fused composition (percent)

Lead oxide (PbO)	65.68
Zinc oxide	5.41
Boric oxide	10.00
Silicon dioxide	16.51
Zirconium dioxide	2.4

GLASS NO. 3

Fused composition (percent)

Lead oxide (PbO)	67.6
Calcium oxide	5.6
Silicon dioxide	26.8

GLASS NO. 4

Fused composition (percent)

Lead oxide (PbO)	31.0
Sodium oxide	3.6
Calcium oxide	4.5
Aluminum oxide	3.4
Boric oxide	13.0
Silicon dioxide	43.5
Zirconium dioxide	1.0

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

Combinations of these glasses and other resistance materials using an alloy of iridium with more than one of the other specified metals have been employed. Examples of these are:

EXAMPLE U

Iridium-ruthenium-rhodium, 5% metals by weight

Glass No. 1	percent	47.5
Glass No. 2	do	47.5
Iridium	do	1
Ruthenium	do	3
Rhodium	do	1
Resistance	ohms/square	14,000
Tempco	p.p.m./°C	—400

EXAMPLE V

Iridium-ruthenium-rhodium, 30% metals by weight

Glass No. 1	percent	35
Glass No. 2	do	35
Iridium	do	2
Ruthenium	do	16
Rhodium	do	12
Resistance	ohms/square	80
Tempco	p.p.m./°C	+43.7

EXAMPLE W

Iridium-ruthenium-rhodium, 50% metals by weight

Glass No. 1	percent	25
Glass No. 2	do	25
Iridium	do	10
Ruthenium	do	30
Rhodium	do	10
Resistance	ohms/square	10

Tempco, approximately 300 p.p.m./° C.

Although it is not completely understood why the presence of iridium, in an alloy with the metals silver, platinum, palladium, ruthenium and rhodium, inhibits the tendency for such materials to agglomerate or form globules in the fused glass binder, it appears that iridium contributes to the interaction between the respective surfaces of the finely divided metal and glass particles and prevents agglomeration of the metal particles even though they are present in relatively large quantities. This apparently causes the mixture to retain its homogeneity during firing and results in a more stable resistance element having substantially larger quantities of metal. It is known, for example, that an alloy of gold, palladium and silver, when utilized in a glass-metal (cermet) resistance mixture, in which the gold, palladium, silver content is about 11.5% of the mixture, produces a resistance element having a resistance of approximately 55 ohms per square for a layer approximately .001 inch in thickness. Compare this with an iridium-silver alloy using 20% metal content. Such a cermet material produces a resistance element (of like thickness) having a resistance of 3920 ohms per square, which is over 71 times more resistance using almost twice as much metal in the resistance element. A cermet using iridium-silver alloy at 40% metal content produces a resistance of 1500 ohms per square and at 50% metal content the iridium-silver alloy still produces a resistance of over 600 ohms per square. It will be noted that a cermet mixture using the alloy iridium-ruthenium-rhodium at 50% metal content produces a resistance of 10 ohms per square, and at 30% metal content (which is approximately three times that of the above-mentioned cermet using an alloy of gold, palladium and silver) still produces a resistance of 80 ohms per square which are extremely high resistances for the large quantities of metal utilized in the cermet element.

The significance of the above becomes more apparent when it is understood that the ability of a resistor to dissipate heat and thereby to withstand higher power levels depends to a large extent upon the metal content of the device. The greater the metal content of the resistor, the more heat it can dissipate, permitting application of much greater power to the device. The metal content of cermet mixtures containing alloys of iridium and the above-mentioned metals is in the order of 5 to 20 times that of glass-metal resistors heretofore employed in the art for comparable resistances, thereby permitting an extremely broad range of power applications.

The high metal content of cermet resistance elements using these iridium alloys is extremely important in another respect. One of the major problems encountered when using cermet resistors as variable resistors or potentiometers is the high "electrical noise" characteristics of 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 vast increase in the metal content of cermet elements containing iridium alloys for high resistance elements, it will be understood that there are a substantially greater number of metal particles available for contact with the wiper. This greatly reduces the "electrical noise" of such elements and makes their application to variable resistance devices and potentiometers extremely advantageous.

Another extremely advantageous improvement attained with cermet resistance materials containing these iridium alloys is in the manner in which they can be fired to a nonconductive base member. With cermet materials formed of the above specified iridium metal alloys in the ranges 5% to 50% metal content, it is possible to deposit the material on a base member, place it in a furnace which is at the fusion temperature of the glass, and, after a short firing period, remove the elements and cool them at room temperature. This "quick fire" method makes it possible to produce resistance elements in a period of a few minutes, which contrasts with the much longer cycles of previous films.

In most instances the iridium alloy cermet resistance elements have a very smooth surface, which is important when such elements are used in variable resistance devices and potentiometers. The iridium alloy materials do not agglomerate or produce blisters on the surface of the resistance elements during the firing operation. These materials produce extremely stable resistance elements that can be produced on a batch to batch basis with uniform resistance values and with temperature coefficients of resistance that are well within the range ±500 p.p.m./° C. that is considered essential for application of such resistance elements to potentiometers and variable resistance devices.

These high metal content elements have been found to have a substantially increased stability. That is, elements so constructed may be stored or used for very long periods of time, either in or out of a circuit, without substantially changing their resistivity, temperature coefficient of resistivity, noise and resolution characteristics. These resistance materials have also been found to have very improved thermal stability, i.e., they may be heated and subsequently cooled without effecting a permanent change in their electrical characteristics.

What is claimed is:

1. A cermet resistance element characterized by a resistivity in the range of 10 to 700,000 ohms/square and a temperature coefficient of resistivity of less than ±500 p.p.m./° C. comprising a high-temperature resistant, electrically non-conductive base having fired thereto a single layer of cermet resistance material having a thickness of .0005 to .005 inch comprising
about 50 to 95% by weight of solidified glass and
over 5 to 50% by weight of an alloy formed of iridium and one or more of the metals selected from the group consisting of silver, ruthenium, rhodium, platinum and palladium, said alloy being in finely divided form and uniformly dispersed in electrically conductive relationship throughout said solidified glass.

2. A cermet resistance element comprising
a high temperature resistant, electrically non-conductive base having fired thereto a single layer of glass-metal mixture having a thickness of .0005 to .005 inch characterized by a resistivity of greater than 2000 ohms/square when the ratio of glass to metal content by weight is 20 to 1 and a resistivity of greater than 10 ohms/square when the ratio of glass to metal content by weight is 1 to 1 comprising
about 50 to 95% by weight of solidified glass and
over 5 to 50% by weight of an alloy formed of iridium and one or more of the metals selected from the group consisting of silver, ruthenium, rhodium, platinum and palladium, said alloy being in finely divided form and uniformly dispersed in electrically conductive relationship throughout said solidified glass.

3. A cermet resistance element comprising
a high temperature resistant, electrically non-conductive base having fired thereto a single layer of glass-metal mixture having a thickness of .0005 to .005 inch characterized by a resistivity of greater than 2000 ohms/square when the ratio of glass to metal content by weight is 20 to 1 and a resistivity of greater than 10 ohms/square when the ratio of glass to metal content by weight is 1 to 1 and a temperature coefficient of resistivity of less than ±500 p.p.m./° C. comprising
about 50 to 95% by weight of solidified glass and
over 5 to 50% by weight of an alloy consisting essentially of iridium and silver, said alloy being in finely divided form and uniformly dispersed in electrically conductive relationship throughout said solidified glass.

4. A cermet resistance element comprising
a high temperature resistant, electrically non-conductive base having fired thereto a single layer of glass-metal mixture having a thickness of .0005 to .005 inch and characterized by a resistivity of greater than 2000 ohms/square when the ratio of glass to metal content by weight is 20 to 1 and a resistivity of greater than 10 ohms/square when the ratio of glass to metal content by weight is 1 to 1 and a temperature coefficient of resistivity of less than ±500 p.p.m./° C. comprising
about 50 to 95% by weight of solidified glass and
over 5 to 50% by weight of an alloy consisting essen-

tially of iridium and ruthenium, said alloy being in finely divided form and uniformly dispersed in electrically conductive relationship throughout said solidified glass.

5. A cermet resistance element comprising

a high temperature resistant, electrically non-conductive base having fired thereto a single layer of glass-metal mixture having a thickness of .0005 to .005 inch and characterized by a resistivity of greater than 2000 ohms/square when the ratio of glass to metal content by weight is 20 to 1 and a resistivity of greater than 10 ohms/square when the ratio of glass to metal content by weight is 1 to 1 and a temperature coefficient of resistivity of less than ±500 p.p.m./° C. comprising

about 50 to 95% by weight of solidified glass and

over 5 to 50% by weight of an alloy consisting essentially of iridium and palladium, said alloy being in finely divided form and uniformly dispersed in electrically conductive relationship throughout said solidified glass.

6. A cermet resistance element comprising

a high temperature resistant, electrically non-conductive base having fired thereto a single layer of glass-metal mixture having a thickness of .0005 to .005 inch characterized by a resistivity of greater than 2000 ohms/square when the ratio of glass to metal content by weight is 20 to 1 and a resistivity of greater than 10 ohms/square when the ratio of glass to metal content by weight is 1 to 1 and a temperature coefficient of resistivity of less than ±500 p.p.m./° C. comprising

about 50 to 95% by weight of solidified glass and

over 5 to 50% by weight of an alloy consisting essentially of iridium, ruthenium and rhodium, said alloy being in finely divided form and uniformly dispersed in electrically conductive relationship throughout said solidified glass.

7. A cermet resistance element characterized by a resistivity in the range of 10 to 700,000 ohms/square and a temperature coefficient of resistivity of less than ±500 p.p.m.° C. comprising a high-temperature resistant, electrically non-conductive base having fired thereto a single layer of cermet resistance material having a thickness of .0005 to .005 inch and comprising

about 50 to 95% by weight of solidified glass and

over 5 to 50% by weight of an alloy consisting essentially of iridium and platinum, said alloy being in finely divided form and uniformly dispersed in electrically conductive relationship throughout said solidified glass.

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WILLIAM L. JARVIS, Primary Examiner

U.S. Cl. X.R.

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