United States Patent [19]

MacLachlan

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[54] **POTENTIOMETER**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 554,653, June 2, 1966, abandoned.

[30] **Foreign Application Priority Data**

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May 3, 1966 Germany........................M 6937821

[52] **U.S. Cl.**....................................**338/160,** 338/308
[51] **Int. Cl.** **H01c 5/02**
[58] **Field of Search**......338/121, 160, 162, 176, 308; 117/212, 215, 227; 29/620, 155.7

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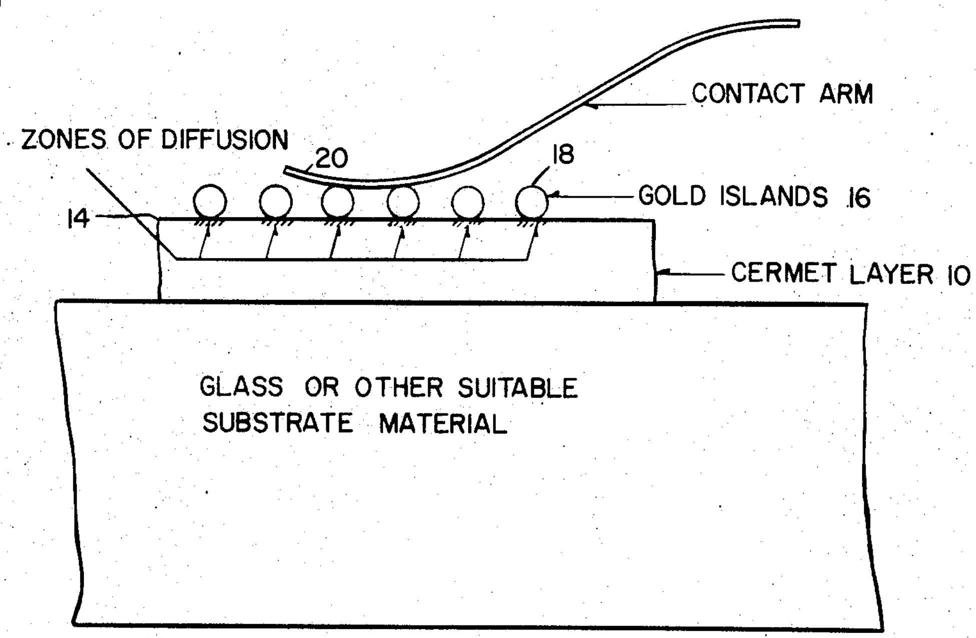
[57] **ABSTRACT**

Cermet resistance element for use in potentiometers having a noble metal infused into the surface which is contacted with the slider, thus reducing the irregularity of its potentiometric resistance behavior, i.e., increasing its resolution, and reducing contact noise.

11 Claims, 4 Drawing Figures



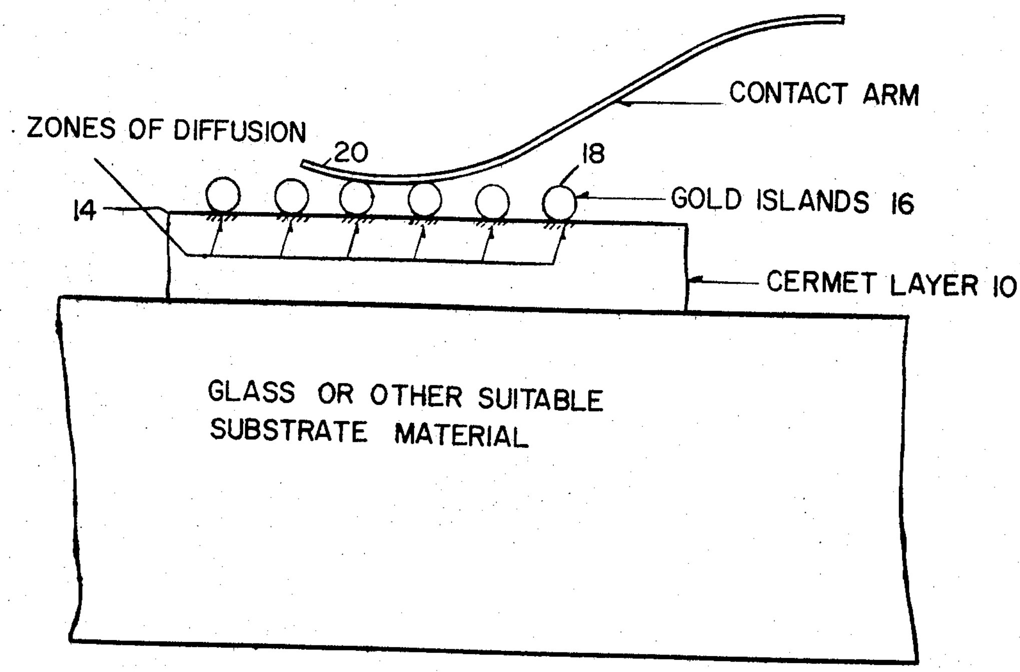

CONTACT ARM
ZONES OF DIFFUSION
20
18
14
GOLD ISLANDS 16
CERMET LAYER 10
GLASS OR OTHER SUITABLE SUBSTRATE MATERIAL

FIG. 1

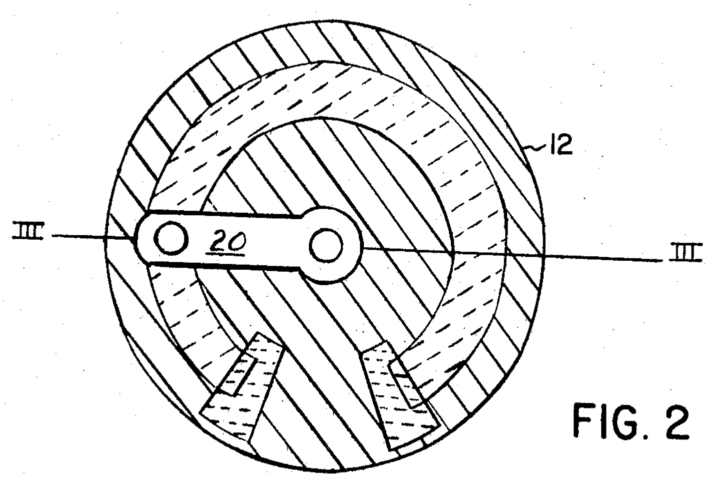

12
III
20
III

FIG. 2

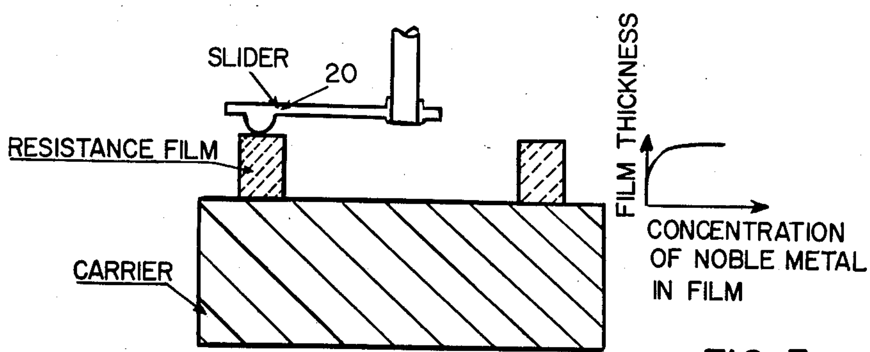

SLIDER
20
RESISTANCE FILM
CARRIER
FILM THICKNESS
CONCENTRATION OF NOBLE METAL IN FILM

FIG. 3

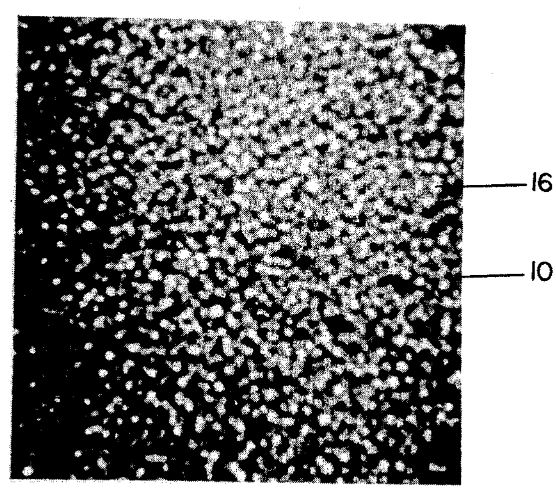

16
10

FIG. 4

POTENTIOMETER

Cross References to a Related Application

This application is a continuation-in-part of U.S. patent application Ser. No. 554,653, filed June 2, 1966 now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to potentiometers having cermet resistance elements, and more particularly to new and improved methods and compositions for improving potentiometer characteristics, i.e., increasing resolution and decreasing noise.

2. Description of the Prior Art

It is well-known in the art of manufacturing potentiometers to use as the material for the electrical resistance elements thereof that class of composite materials known as cermets, i.e., materials comprising a metallic component and a ceramic or ceramic-type component.

Potentiometers having electrical resistance elements fabricated from cermets are described, for instance, in U.S. Pat. No. 3,343,985, issued to Ronald C. Vickery, on Sept. 26, 1967.

Vaporized cermet layers have been found to be particularly suitable for the manufacture of miniaturized potentiometers having relatively high resistance. In such potentiometers, the resistance element is so small that high resistance cannot be realized by the employment of metallic resistance alloys, even when applied in the form of thin layers.

However, when utilized in potentiometers, cermet layers, on account of their hybrid structure, consisting of bodies of relatively high conductivity suspended in a matrix of low-conductivity material, present special problems with respect to the contact between the surface of the resistance element and the sliding wiper. That is to say, the cermet resistance element or layer of many prior art potentiometers is irregular and inconsistent in resistance, thereby providing poor electrical resolution and high noise. More particularly, it may happen that the contact area of the sliding wiper, when in a certain position, comes in contact with a region of the surface of the resistance element which is of relatively lowe conductivity, while the contact area of the slider, in some other position, may contact a region of the resistance element having relatively high conductivity. As a consequence, considerably varying contact resistance occurs at the interface between the resistance element and the wiper, thus producing the above-noted undersired irregular deviations from the characteristic resistance curve of the potentiometer, i.e., poor resolution.

These irregularities and inconsistencies in resistance are particularly apparent in miniature potentiometers, which have very small slider contact areas, producing comparatively large deviations fromlinear operation, i.e., poor resolution.

Although this condition can be somewhat improved by increasing the contact pressure of the sliding wiper contact on the resistance element, so doing results in unacceptable wear and decrease in potentiometer life.

SUMMARY OF THE INVENTION

Thus, a principal object of the present invention is to avoid the above-described deficiency of potentiometers having cermet resistance elements, and in particular to remedy these deficiencies in miniature potentiometers having cermet resistance elements, wherein these deficiencies are most aggravated.

Other objects and advantages of the present invention will become apparent from the following detailed description, wherein is disclosed only selected preferred embodiments of the instant invention.

DESCRIPTION OF THE DRAWINGS.

FIG. 1 is a cross-sectional diagrammatic view, greatly enlarged and not to scale of a potentiometer cermet of the present invention;

FIG. 2 is a plan view of a conventional potentiometer having cermet resistance elements;

FIG. 3 is a sectional diagrammatic view greatly enlarged and not to scale, along the lines III—III of FIG. 2, showing the cermet resistance elements of FIG. 1 in assembly with the wiper of the potentiometer, and

FIG. 4 is an enlarged true microphotopicture of the cermet resistance element corresponding to the diagrammatic view of FIG. 1., and

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As shown in the drawings, the cermet resistance element or layer **10** of a potentiometer **12** is infused at least in its surface region **14**, with a noble metal, or a noble metal alloy **16**, and thus the aforementioned problems of the prior art are obviated.

The effect of the infused or doped noble metal molecules or atoms may be explained by postulating that, collectively, they provide a rather large number of additional conductive bridges **18** across the interface between the contact surface of the slider **20** and the resistance element or layer. This is shown in the microphoto view of FIG. **4** exhibiting the noble metal islands **16** as white areas and the grayish to dark areas **10** as the cermet layer. These additional conductive bridges increase the statistical probability that the contact resistance between the slider and the resistance element will be low, and substantially equal, at every position of the slider.

The infused or doped atoms of noble metal, or noble metal alloy, decrease the lateral resistance of the resistance element, but, at the same time, do not appreciably alter its longitudinal resistance.

Thus, as a result of the introduction of these noble metal atoms, the contact resistance across the interface between the slider and the resistance element is maintained substantially constant, in an efficient and economically realizable manner, and is considerably decreased when compared to untreated cermet resistance layers, which also is very desirable.

By contrast, the total resistance of the resistance element or layer, i.e., the resistance of the resistance element or layer, measured from one fixed end contact to the other, is reduced only slightly.

It has also been found that potentiometers **12** constructed in accordance with the instant invention are further characterized by extraordinarily low noise, i.e., undesired momentary variations of resistance which occur during movement of the slider, and which result in undersired, spurious signals, of the kind which are particular undesirable, e.g., in audio equipment, such as hearing aids.

According to a particular feature of the present invention, the noble metal is introduced into the cermet resistance layer, or at least into the surface region thereof, by diffusion.

According to the manufacturing process of the present invention, the cermet resistance layer is first applied to a nonconductive support and thereafter a noble metal is applied to the surface of the cermet layer, preferably in a vacuum chamber, this noble metal layer being thin as compared to the cermet layer, whereafter the noble metal coated cermet is subjected to heat treatment, causing at least substantial portions of the noble metal to diffuse to at least substantial portions of the noble metal to diffuse to at least in island areas of the surface region of the cermet layer.

According to certain preferred embodiments of the instant invention, suitable cermets are those whose base metallic component is chromium and whose ceramic-type component is at least one compound chosen from the group consisting of the siliconoxides. In place of the chromium, or in combination therewith, a material chosen from the group consisting of the chromiumsilicon compounds and alloys can advantageously be employed. The metallic component of the cermet layer might also be silicon, and the ceramic-type component thereof might be chromium oxide. In these representative embodiments of the present invention the surface of the cermet layer is subjected to the additional treatment of doping with atoms of a noble metal.

In accordance with a particular aspect of the present invention, the selected noble metal is one which is nobler than silver. Gold is particularly well-suited for this purpose, because its high corrosion resistance, and its excellent electrical conductivity, for gold is substantially nobler than silver, and, thus, when utilized in the present invention, is not attacked, for example, by sulphur-containing gases.

By a metal nobler than silver is meant a metal whose resistance to corrosion is always better than that of silver, when both metals are subjected to identically corrosive environments.

The present invention is by particular important in miniature potentiometers, wherein the cermet layer serving as the resistance element is present in the form of a thin layer, i.e., a layer having a thickness, at most, of about ten thousand angstrom units.

According to another aspect of the present invention, the cermet layer is applied as shown in FIG. 1 to a glass substrate, or a ceramic substrate, preferably in the form of beryllium oxide or an aluminum oxide sinter mass. These substrates are electrically insulating, and, furthermore, the beryllium oxide sinter mass has the advantage that its heat conductivity is greater than that of aluminum.

In order to improve the adhesion of the resistance layer to the substrate, the substrate is suitably maintained at an elevated temperature while the resistance layer is applied. This elevated temperature may, for instance, be up to 400°C.

The highly conductive noble metal layer applied to the cermet layer would normally short-circuit the resistance element if it formed a coherent layer. However, this short-circuiting effect is eliminated by a special heat treatment to which, according to the present invention, the noble metal coated cermet layer is subjected. This heat treatment causes diffusion of the noble metal into the cermet layer.

The thickness of the applied noble metal layer, as well as the temperature and duration of this heat treatment, are so selected as to eliminate the abovesaid short-circuiting effect.

This heat treatment is preferably carried out in vacuo, and, in the case of gold, is conducted at approximately 400° to 600° C.

After this heat treatment, due to diffusion, the noble metal is distributed in a cermet layer in what is termed a diffusion gradient.

The most suitable amount of noble metal to be incorporated by diffusion can easily be determined by comparative tests. The limit values can be defined, roughly, by considering that the amount of noble metal diffused into the layer must be sufficient to maintain the contact resistance between the path and the slider constant within at least plus or minus 10 percent, and should not exceed an amount which causes the total resistance of the resistance element to be lowered by more than 60 percent.

For example, a chromium-silicon oxide film, subjected to a preliminary aging process, approximately 2000 Angstrom units thick, was provided with a gold layer approximately 100 Angstrom units thick by means of a vacuum vaporization process. The structure was then maintained under vacuum for 1 hour at 550°C.

The good electrical characteristics of the resistance element thus obtained are compared in the table below with the corresponding electrical characteristics of a resistance element which is identical to the resistance element prepared according to the invention, except that it was not diffused with gold.

	without gold treatment	with gold treatment
1. Surface resistance	500 ohms/ square	235 ohms/ square
2. Path resistance between the terminal contacts	6,350 ohms	2,985 ohms
3. Turning noise at 30 r.p.m.		
(a) Slider pressure 5 g.	up to IV/V	0.1mV/V
(b) Slider pressure 15g	0.1 mV/V	0.1mV/V
4. Wear and tear Maximum number of slider rotations at turning noise level of 0.1 mV/V	12,000	above 20,000

According to a further feature of the present invention, it is particularly advantageous to use a cermet layer containing noble metal not only in its surface region, but also in its interior. The noble metal content in such a cermet layer suitably amounts to at least 0.1 percent by weight and at most 10 percent by weight, but preferably should be 1 to 5 percent by weight. The application of the cermet layer containing the noble metal can be made by vaporization in vacuum from a single source to which there is fed a finely powdered mixture of all of the necessary components. Alternatively, two sources are provided, one of which, for example, supplies the metallic component of the cermet composition such as chromium, having an addition of noble metal, and the other supplies the ceramic or ceramic-type component, such as silicon monoxide.

According to yet a further aspect of the invention, the noble metal can be applied simultaneously with the cermet layer in such a manner as to provide the layer with a surface region doped with atoms of the noble metal. To this end, the noble metal can be admixed with the starting material of the cermet layer, or with one of its components, and applied together therewith to the substrate or carrier. Particularly suitable examples as starting materials for the application of the cermet layer are the following compositions whose components, suitably mixed together in finely particulate form, are fed to the device for applying the layer:

a. Silicon, chromium oxide, and gold;

b. Chromium, gold, and at least one compound chosen from the group consisting of the silicon oxides and gold;

c. Silicon, chromium, chromium oxide, and gold;

d. Silicon, chromium, chromium oxide, gold, and at least one compound chosen from the group consisting of the silicon oxides.

In the case of a chromium-silicon oxide cermet, it is assumed that the cermet layer obtained in this manner comprises conductive phases of chromium, silicon, chromium silicide, and chromium oxide (the latter having relatively high specific resistance) in combination with insulating deposits or intermediate layers containing, inter alia, silicon monoxide, silicon dioxide, and chromium silicate.

To prevent conversion of conductive components on the surface of the resistance path, such as chromium and chromium silicide into non-conductive or poorly conductive phases during the later operation of the potentiometer, and the subsequent variation of the path resistance, as well as the contact resistance, between the path and the slider, an artificial aging process can be conducted by subjecting the cermet layer to a heat treatment in order to oxidize conductive surface portions. If the process of the present invention is conducted in such a manner that the noble metal or noble metal alloy is applied to the cermet layer and is incorporated by diffusion at least into the surface region of the cermet layer, it is recommended that the abovesaid aging process be carried out before the noble metal or the noble metal alloy is applied. In this manner, the resistance values become substantially stable over the entire life-time of the potentiometer.

In addition comparative tests were carried out by a reputable research corporation, with the following results:

The Problem

The object of investigation was a small glass plate coated with a layer of cermet of chrome silica oxide film. This cermet layer is by vaporization under vacuum condition coated with a layer of gold in an amount specified hereinafter. An investigation was carried out to ascertain whether or not in this process any gold diffuses into the cermet layer, and if so what extent.

The Method

The presence of gold in a test specimen was detected by the neutron activation analysis, whereby the natural isotope of gold (Au - 197) is transformed under irradiation with thermic neutrons into a radioactive nuclide of gold (Au - 198) whose gamma radiation at 0.41 MeV can be used in the determination of the gold contents.

It is known that a thin layer of gold dissolves completely and within a few seconds in a solution of approximately 5 to 10 percent by volume of bromine in dry methanol, and that such a solution does not traceably attack glass or ceramics within a few seconds. Thus, from a cermet-coated, small glass plate, it is possible to completely dissolve the built-up gold layer with the bromine-methanol solution, while any gold which was diffused into the cermet layer will not be removed, so that its presence can be detected by the neutron activation analysis. Should it nevertheless have happened that the cermet layer was superficially slightly etched by the bromine-methanol solution, it is still possible to detect diffused gold, even though the amount of gold indicated could be somewhat lower.

As reference and comparison specimen are used one each of an uncoated glass plate, a glass plate coated with a cermet layer, and a glass plate coated with a cermet layer and a gold layer; of each one, the gold content is measured.

The Test Performance

Of four glass plates (diameter approximately 2 cm, thickness approximately 0.3 mm) one specimen was preserved for reference purposes, while the three remaining pieces were coated in an identical manner with a cermet layer. Of these three pieces, one was again preserved for reference purposes, while the remaining two were coated in an identical manner with an evaporation layer of gold and subjected to a thermal aging process at a temperature of 430°C in order to interrupt the short circuiting layer. One of the latter two pieces was preserved for comparison purposes, and the other one was dipped for a few seconds into a solution of approximately 10 ccm of bromine in 100 ccm of methanol. On this plate the built-up gold layer disappeared immediately, whereupon the plate was washed in methanol and water and then dried.

For the irradiation with thermic neutrons, the test specimen were placed into a single, suitable container and arranged in such a way that no transfer of gold from one test specimen to any other could occur. For this purpose, the test specimen were separated from one another inside the container by glass plates of identical diameter. Into the container were further placed two samples of gold of 1 microgram and 10 microgram to determine the measurement standard, care being again taken that any contamination is precluded.

Irradiation of the container was performed in the reactor of the Federal Institute for Reactor Research (Eidgenoessisches Institute fuer Reaktorforschung) in Wuerenlingen, using an integrated neutron flux of approximately 5×10^{16} neutrons. This treatment created a number of radioactive gold nuclides Au - 198, in proportion to the amount of natural stable gold isotope Au - 197, the radioactive gold nuclides having a half-time value of 2.7 days and their gamma spectrum having its most intensive line at an energy level of 0.41 MeV.

After 6 days of waiting, the interfering radioactivity of the glass, which was created by the irradiation, had sufficiently faded. All the test specimen and standard specimen were then measured over a period of 4 hours by means of a germanium-lithium detector and a conventional counter apparatus to determine their gamma radiation at 0.41 MeV. Based upon the measurements on the standard specimen, the weight of gold was then determined.

Results

The weight of gold contained in the four test specimen, as well as the associated measurement errors, are listed in the table below:

Designation of test Specimen	Weight of Gold (microgram)	Measurement Error (microgram)
Glass plate, uncoated	less than 0.1	
Glass plate, coated with cermet only	less than 0.1	
Glass plate, coated with cermet and gold	136	3
Glass plated, coated with cermet and gold, subsequently dissolved	6	0.5

A comparison of the above results shows that no gold can be detected on the glass plates and in the cermet layer before gold plating, and that at least 6 mg gold was diffused into the test specimen after dissolution of the gold layer. The results also prove that no gold-contamination took place between the test specimen.

Tests conducted using smaller amounts of gold under conditions, same as above, in particular under the same temperature and length of heat treatment following the vaporization of the gold layer, disclosed that the amount of the gold diffused within the cermet layer remains constant. In one of these tests instead of the 136 mg of gold stated in the above example, only 30 mg of gold were applied, whereby again only about 6 mg gold were found in the cermet layer.

The detection limit of gold for the analysis described lay at approximately 0.1 microgram. A comparison of the gamma spectra of the various test specimen showed that the evaluation of the gamma line selected for the gold analysis at 0.41 MeV was not interfered with by the gamma rays of other nuclides present in the glass or in the cermet layer, and that it was therefore usable for the calculation of the amount of gold.

The measurement error indicated refers exclusively to the measurement of the gamma ray intensity and is computed for a probability of 95 percent. In addition to this measurement error, the following other errors are possible:

a. weighing errors during the preparation of the standard specimen, for practical purposes, however, the latter can be disregarded; and

b. errors caused by non-homogeneity of the neutron flux during the irradiation in the reactor. The latter errors are unknown to us, but, under certain circumstances, they may attain values which are not negligible. Still, the latter are not large enough that they could adversely affect the conclusion which can be drawn from the analysis on the bass of the values in the above table.

The thickness of the layer, the type and mutual relationship of the cermet components, the conditions under which the layer is applied, such as the temperature of the support, and the conditions of the heat treatment, influence the magnitude of the total resistance of the resistance element, which is thus controllable.

Although the invention has been disclosed hereinabove by way of embodiments in which the noble metal infused into the resistance element was gold, it is to be understood that the present invention may be carried out by the use of alternative noble metals, e.g. rhodium, platinum, or palladium.

Actual tests have been carried out in order to establish that rhodium, platinum, or palladium may be used as the infused noble metal, instead of gold, in the practice of the present invention. Five specimen potentiometers were constructed. The cermet composition used in each of these specimens consisted of 86 parts by weight of silicon and 14 parts by weight of chromium oxide. These materials, originally in the form of a fine powder, were admixed for 24 hours. Water was then added to the mixture and the resulting paste was pressed into tables. These were then broken into pellets suitable for flash evaporation. The pellets were fed to a flash evaporation source in vacuum atmosphere, and a cermet track was formed by depositing the evaporated mixture onto glass substrates through suitable masks. Evaporation was carried on for a period of time which had been previously empirically determined to produce tracks of the desired resistance value. One specimen, designated as Specimen A, was not subjected to any further treatment, i.e., no noble metal was deposited or infused. The second specimen, designated Specimen B, was then provided with a gold layer of about 70 angstrom units thickness by vacuum evaporation. The third specimen, designated Specimen C, was provided with a layer of rhodium in a similar manner. The fourth specimen, designated Speciman D, was provided with a layer of platinum in a similar manner. The fifth specimen, designated Specimen E, was provided with a layer of palladium in a similar manner. These specimens were then maintained under vacuum for about three-quarters of an hour at about 400° C. (It will be realized, of course, that the cermet track of the specimen which was not provided with a noble metal layer had to be thicker, and therefore required a longer evaporation time, than the specimens which were provided with noble metal layers, in order to produce the same desired resistance value.) The thus prepared specimen tracks were then mounted in potentiometers, and plots of contact resistance versus rotation were made. The contact resistance of Specimen A, which did not embody the present invention, had a maximum value of about 45 percent of the total resistance of the potentiometer, and a deviation between the maximum and minimum of about 38 percent of the total resistance of the potentiometer. Further, repeated tests showed the contact resistance of Specimen A to be nonrepeatable, i.e., to vary from one test to the next in an unpredictable manner. In addition, a contact resistance plot of Specimen A was not smooth, but rather characterized by a large number of spike-like discontinuities. By contrast, the maximum value of contact resistance found Specimen B through E, embodying the present invention, was about 2.5 percent of the total resistance of the potentiometer, and the greatest deviation between maximum and minimum contact resistance (Specimen E. palladium) was about 1 percent of the total resistance of the potentiometer. The contact resistance of all of the specimen embodying the invention was not only very small, but was also highly repeatable. As is well-known to those having ordinary skill in the art, small, high repeatable values of contact resistance, such as these tests show to be produced by the present invention, are negligible for practical purposes.

The deposition of the layer of gold on the cermet layer referred above in par. 1 of the report was made in accordance with the present invention.

It should be understood, of course, that the foregoing disclosure relates only to certain preferred embodiments of the present invention, and the numerous modification or alternations thereof may be made without departing from the spirit and scope of the invention. It is desired, therefore, that only such limitations be placed on the invention as are imposed by the prior art and set forth in the appended claims.

What I claim is:

1. A potentiometer with a resistance element, comprising:

a movable slider,

a cermet layer with a surface for contact with said slider,

a carrier, said cermet layer adhering to said carrier,

said cermet layer comprising a metallic component and a ceramic-type component;

said cermet layer comprising in the region of said surface a noble metal distributed in a diffusion gradient in a concentration which is substantially higher than the concentration of noble metal in said metallic component in the remainder of said cermet layer.

2. A potentiometer according to claim **1**, said cermet layer containing said noble metal in its surface region and said metallic component in its interior, in a uniform distribution.

3. A potentiometer according to claim **1**, the content of said noble metal in said surface region in the cermet layer amounting to at least 0.1 percent by weight of said cerment layer to at most 10 percent by weight.

4. A potentiometer according to claim **1**, said cermet layer containing as the metallic component a component selected from the group consisting of chromium and chromium-silicon alloys, and as the ceramic-type component at least one compound selected from the group consisting of the silicon oxides.

5. A potentiometer according to claim **1**, said cermet layer containing as the metallic component, a component selected from the group consisting of silicon and chromium-silicon compounds and, as the ceramic-type component, chromium oxide.

6. A potentiometer according to claim **1**, said cermet layer having the shape of a thin film.

7. A potentiometer according to claim **1**, said carrier being a beryllium oxide sintered mass.

8. A potentiometer according to claim **1**, the carrier being an aluminum oxide sintered mass.

9. A potentiometer according to claim **1**, the content of said noble metal in said surface region amounting to at least 1 percent by weight and at most 5 percent by weight of the total weight of said cermet layer.

10. A potentiometer with a resistive element comprising:

a carrier,

a cermet layer adhering to said carrier, said cermet layer having a metallic component and a ceramic-type component, said metallic component being selected from the group consisting of chromium and chromium silicon alloys and said ceramic-type component being at least one compound selected from the group of silicon oxides,

said cermet layer further comprising in its contact surface region a noble metal in diffusion in an amount of **0.1%** to **10%** by weight, which concentration of noble metal is substantially higher than the concentration of noble metal in the remainder of said cermet layer.

11. A potentiometer with a resistive element comprising:

a carrier,

a cermet layer adhering to said carrier, said cermet layer a metallic component and a ceramic-type component, said metallic component being selected from a group consisting of silicon and chromium silicon compounds and said ceramic-type component being chromium oxide,

said cermet layer further comprising in its contact surface region a noble metal in diffusion in an amount of 0.1 to 10 percent by weight which concentration of noble metal is substantially higher than the concentration of noble metal in the remainder of said cermet layer.

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