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ELECTROLYTIC METHOD OF ADJUSTING THE RESISTANCE OF PALLADIUM GLAZE RESISTORS
Filed July 29, 1965 2 Sheets-Sheet 1

FIG. 1

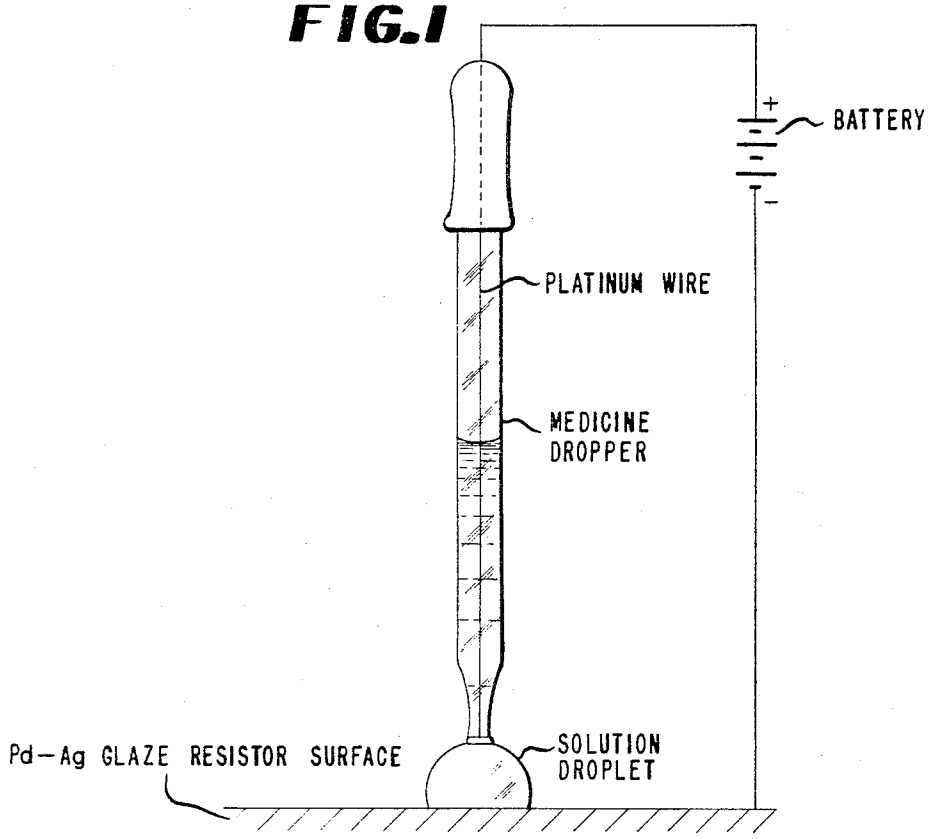
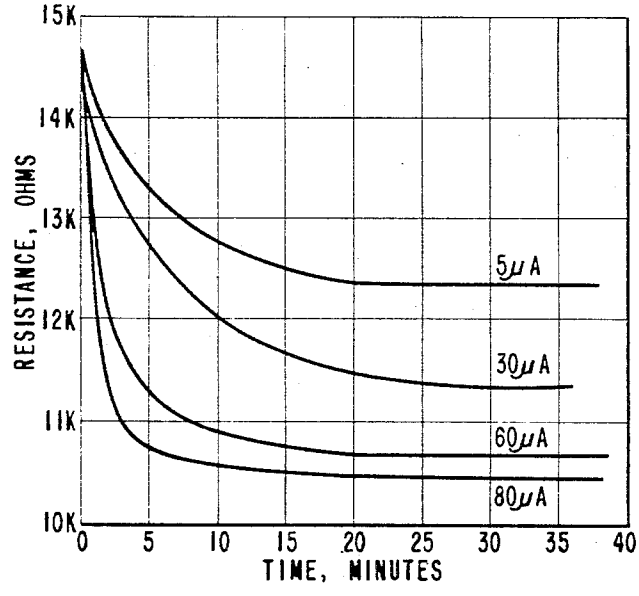


FIG. 2



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FIG. 3

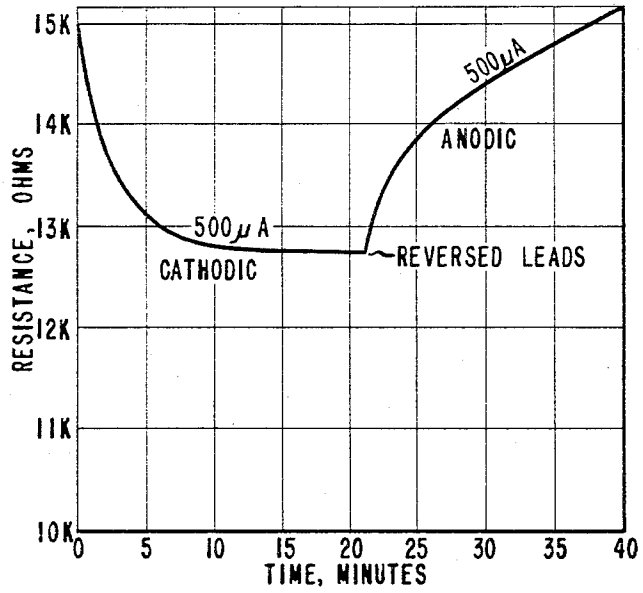
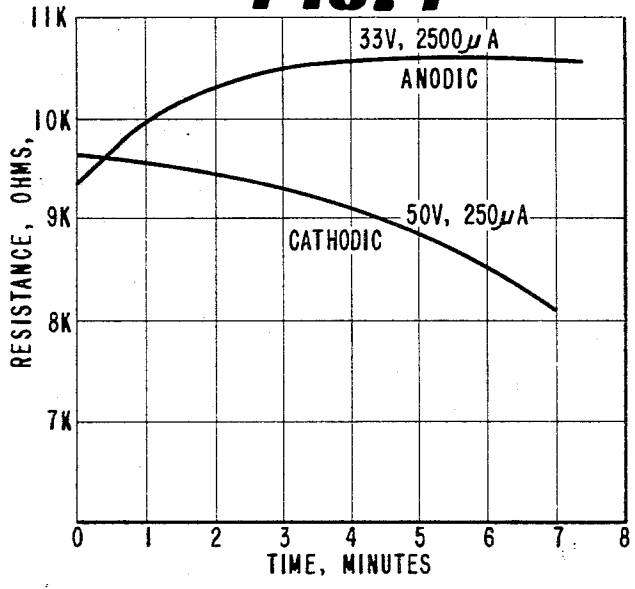


FIG. 4



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ELECTROLYTIC METHOD OF ADJUSTING THE RESISTANCE OF PALLADIUM GLAZE RESISTORS

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15 Claims. (Cl. 204—130)

This invention relates to a method for adjusting the resistances of palladium glaze resistors.

Glaze resistors are formed by applying to a refractory substrate a print in the desired design of a paint or ink comprising a dispersion of finely divided metal powder and a finely divided glass binder in an organic vehicle, and then firing the print upon the substrate. The metal component of such a paint is generally one or more noble metal powders, although noble metal compounds such as noble metal resinates, which decompose to the noble metals during the firing, may be substituted for the noble metal powders. The glass binder component may be of various types of glasses but the metal borate and borosilicate glasses such as the lead, cadmium and alkali metal-cadmium borate and borosilicate glasses, have been most generally used.

It is known that the resistances of such glaze resistors can be varied within rather wide limits by varying the composition of the paint or ink employed. However, when a resistor having a very specific resistance is desired or required, it is generally necessary to "trim" a resistor which initially has a resistance somewhat lower than the desired resistance. Trimming has heretofore been effected by methods employing electric arc erosion or air abrasion techniques. Such methods leave rough edges which react chemically when subsequently exposed to corrosive environments. Furthermore, precise trimming by such methods is difficult to achieve and large, i.e., over 10%, changes in the resistance deleteriously affect certain properties of the resistor such as its load life and stability. This invention relates to an improved method for precisely altering or adjusting the resistances of palladium glaze resistors.

One object of the invention is to provide an improved method for adjusting the resistances of palladium glaze resistors, which method is not subject to the above-mentioned disadvantages which characterize prior trimming methods. A particular object is to provide an electrolytic method for precisely altering or adjusting the resistance of a palladium glaze resistor, whereby its resistance may be either increased or decreased as desired. Still further objects will be apparent from the following description.

The resistance adjusting method of the invention comprises making a palladium glaze resistor, whose resistance is to be adjusted, an electrode in an electrolytic cell provided with an inert electrode of opposite polarity, providing a suitable electrolyte between the electrodes, and passing through the cell a direct electric current at a suitable potential and current density for such a time as well effect the desired adjustment of the resistance of the resistor. When the resistance is to be adjusted upward, the resistor is made the anode of the electrolytic cell and the inert electrode is made the cathode. Conversely, when the resistance is to be adjusted downward, the resistor is made the cathode and the inert electrode is made the

anode. Cell potentials of 1 to 150 volts and current densities of 1 to 200,000 microamperes/cm.^{2} are generally effective to produce changes in resistance at rates of from 0.1 to 20% of the original resistance per minute. The preferred operating voltages and current densities, respectively, are 1.5 to 50 volts and 5 to 10,000 microamperes per square centimeter.

Palladium glaze resistors are glass-attenuated palladium coatings formed by firing onto a refractory substrate a coating, generally in precise pattern form, of a paint or ink which is a dispersion of a metallic palladium powder and a glass binder powder in an organic vehicle. The paint or ink used may contain, in place of part or all of the metallic palladium, a palladium compound, e.g., palladium oxide or an organic palladium compound such as a resinate, which is decomposable to palladium under the firing conditions. The paint or ink may also include one or more other noble metals, or compounds thereof which are decomposable under the firing conditions to their respective noble metals, in which case, the fired glaze resistor will contain both palladium and another noble metal. Thus, a paint which includes both palladium (or PdO or a Pd resinate) and silver, will yield a palladium-silver glaze resistor. Palladium and palladium-silver glaze resistors and their preparation are described in D'Andrea U.S. Patent 2,924,540, Dumesnil U.S. Patent 3,052,573 and Place et al. U.S. Patents 2,950,995, 2,950,996 and 3,149,002.

As indicated, the palladium component of the paints or inks employed in forming palladium glaze resistors may be finely divided metallic palladium, palladium oxide or an organic palladium compound such as a palladium resinate. When the paint is fired on the refractory substrate under the usual firing conditions (in air at 650 to 800° C.) the palladium in the fired glaze resistor will be present partly as metallic palladium and partly as palladium oxide, regardless of whether the palladium was present in the starting paint as metallic palladium, palladium oxide, palladium resinate or mixtures thereof.

I have found that when a palladium glaze resistor is made the anode of an electrolytic cell having an inert electrode (e.g., platinum or graphite) as the cathode and an electrolyte between the electrodes, the resistance of the glaze resistor increases rapidly when a DC current of a density of at least 1 microampere per square centimeter is passed through the cell. On the other hand, when such a resistor is made cathodic to the inert electrode in such a cell, its resistance decreases with the passage of current through the cell. The extent of such changes in resistance can be observed as they occur by simultaneous AC bridge measurements of the resistances during the electrolysis.

The increase in the resistance occurring when the palladium glaze resistor is made the anode during such electrolysis is believed to be the result of an anodic oxidation reaction

$$Pd^0+\tfrac{1}{2}O_2=Pd^{2+}+O^{2-}$$

by which the metallic palladium content of the resistor is decreased, which decrease raises the resistance. The decrease in resistance occurring when the resistor is made the cathode is believed to be the result of a cathodic reduction reaction

$$Pd^{2+}O^{2-}+2H^+=Pd^0+H_2O$$

by which the metallic palladium content of the resistor is increased, which increase lowers the resistance.

I have further found that the resistance of palladium

glaze resistors can be increased or decreased in the above manner even when silver is present in the resistor. It would be expected that during the electrolysis, silver would be removed from a silver anode as AG^+ ions which would diffuse through the electrolyte and plate out on the cathode as silver. However, the observed changes in resistance which occur when silver anodes are used are much too small to account for the observed changes in resistances when palladium-silver glaze resistors are used as the anodes. Furthermore, whereas a marked decrease in the resistance of a palladium-silver glaze resistor results when such resistor is made the cathode opposite an inert anode in an electrolysis cell, no observable changes in resistance results when a silver cathode is substituted for the palladium-silver resistor cathode in such cell. Therefore, the changes in the resistances of palladium-silver resistors which occur when they are made an electrode of the electrolysis cell in practicing the method of the invention, clearly are not brought about by the presence of silver in such resistors. The energies involved in the electrochemical reactions by which the resistances of palladium glaze resistors are altered when practicing the method of the invention are much lower than those involved in the electrodeposition of silver. Because of the low energies involved, significant changes in resistance can be observed and achieved at current densities as low as a few microamperes/cm.^{2}.

The method of the invention is quite flexible in use in that it may be practiced to adjust or alter the resistances of palladium glaze resistors upwards or downwards as much as about 50% of their original values at rates as high as about 15%/minute or as low as 1%/minute. Naturally, if a large adjustment is required, a high current density will be desirable to obtain a high rate of change of the resistance. By continuously determining the resistance of the resistor during the electrolysis, e.g., by means of AC bridge measurements, the electrolysis can be stopped the instant the desired resistance has been achieved, hence, even large adjustments can be made rapidly with reasonable precision.

Water can be used as the electrolyte, but when large adjustments at rapid rates are desired, it will be desirable to employ as electrolyte a solution of an ionized solute to permit use of high current densities at low potentials. Solutes providing cations such as Li^+, Na^+, K^+, Ca^{2+}, Ba^{2+}, NH_4^+ and H^+, and anions such as OH^-, F^-, Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-} and PO_4^{3-}, have been found to be satisfactory. However, ordinary water such as deionized water contains enough ions to give practical current densities at low voltage. Solutions having pH values of from 1 to 14, obtained by the addition of an alkali or acid to water, have been used successfully. When very precise adjustment of the resistance is required, adjustment under conditions which effect changes in the resistance at a relatively low rate is generally desirable. Such conditions include the use of water at a pH of 6 to 8 and current densities of 5 to 10,000 microamperes/cm.^{2} at a potential of 1.5 to 50 volts. Under such preferred conditions, resistance adjustments to within 0.1% of the desired value can be readily made.

A useful electrolysis arrangement for adjusting resistances in accordance with the invention is shown in FIG. 1. It consists of a platinum wire inserted into a fine-tipped medicine dropper which contains water or a solution which is to serve as the electrolyte. The end of the platinum wire which protrudes from the tip of the medicine dropper is connected to one terminal of a battery (or other suitable source of DC potential) while the other therminal is connected to the resistor whose resistance is to be adjusted. The lower end of the platinum wire should extend into the solution (electrolyte) within the medicine dropper, and preferably will extend to about the bottom of the delivery tip thereof. When a drop of solution at the tip of the medicine dropper is brought into contact with the resistor, the electrolysis cell is complete and electrolysis proceeds. If the connections to the battery are such as to make the resistor the anode and the platinum wire the cathode of the cell, electrolysis increases the resistance of the resistor. The opposite effect is achieved when the connections are reversed. Electrolysis can be stopped at any desired time by raising the medicine dropper so as to break the contact with the resistor surface, or by means of a switch (not shown in FIG. 1) provided at any suitable place in the cell circuit. The changes in resistance can be determined continuously during electrolysis by means of an AC bridge or an AC ohmmeter (not shown in FIG. 1) for measuring resistances. Thus, electrolysis can be stopped the moment the resistance of the resistor has been altered to the desired value.

Another useful arrangement would include an absorbent cellulose fiber pad saturated with the electrolyte solution, which pad is placed in contact with the resistor surface. The inert electrode such as a platinum wire is inserted or embedded in the pad (but maintained separated from the resistor surface), and the other end of the platinum wire and the surface of the resistor are connected to the proper poles of the battery. In such an arrangement, the fiber pad saturated with the electrolyte solution replaces the medicine dropper and the solution droplet shown in FIG. 1.

The electrolysis cell arrangements indicated above can be supplemented in obvious ways so that adjustments in resistances can be carried out on an automated basis, permitting large scale processing of large numbers of resistors.

If only an increase in the resistance of a resistor is desired, the increase can be effected efficiently, simply by placing a drop of water or an electrolyte solution on the resistor surface and connecting a DC potential across the resistor, whereby the resistor surface at one edge of the drop becomes cathodic and the resistor surface at the opposite edge of the drop becomes anodic. Use of this arrangement is illustrated in Example 3. When using such an arrangement, the change in resistance is always an increase because the anodic reaction predominates. In this arrangement, that portion of the surface of the resistor which becomes cathodic at one edge of the drop, is, or may be regarded as the equivalent of, the inert electrode of the cell arrangement of FIG. 1.

The changes in resistance effected by the present method are reversible and can be alternately superimposed. Thus, the resistance of a given resistor can be alternately raised and lowered above and below its original value many times without harmful effect.

Changing the resistance of a resistor in accordance with the invention does not significantly affect the important resistor properties of the resistor, provided the change in resistance does not exceed about 10%; resistance changes in the 10 to 20% range may cause slight changes in resistor properties, while resistance changes in about the 20 to 50% range usually alter the resistor properties moderately. Thus, a number of palladium glaze resistors prepared by firing on a refractory substrate a print of a resistor composition comprising 20% palladium powder, 20% silver powder and 60% by weight of a zinc borosilicate glass powder, were tested to determine their electrical properties, i.e., temperature coefficient of resistance (TCR) and noise and drift ratings. These properties were again determined after various changes in the resistance had been effected in accordance with the invention. The results are reported in Table 1.

The temperature coefficient of resistance (TCR) values reported in Table 1 are the changes in resistance, expressed in parts per million per degree centigrade, for the temperature range of 25–150° C. Noise, which is measured by comparing the output from the resistor under DC load with the output of a signal generator over a decade of frequency, is reported as decibels per decade (db/dec.). Drift is the irreversible change in resistance resulting from

heating the resistor under atmospheric conditions at 150° C. for 500 hrs. It is expressed as the percent of change in resistance, based on the original value.

TABLE 1

Change in resistance, percent	TCR, p.p.m./° C.	Noise, db/dec.	Drift, percent
0 (original)	+200	−15	+0.7
10	+200	−14	+0.6
20	+220	−12	+0.7
30	+240	−10	+0.9
50	+300	−8	+1.1

The above changes in properties are much lower than those resulting when resistances of more than 10% are made by prior air abrading or electric arc eroding methods.

In the following examples, all percentages of components are by weight and all of the electrolyses described were carried out at room temperature.

Example 1

A number of palladium-silver glaze resistors were prepared by firing on a refractory sheet substrate at about 750° C., prints of a resistor composition comprising PdO in an amount equivalent to 17.5% Pd, 14.2% Ag powder and 68.3% powdered lead borosilicate glass frit. Each resistor consisted of a sheet having 30 square prints, each about 2 mm. wide, and each resistor had an initial sheet resistance of about 14,500 (14.5K) ohms. The resistance of each resistor was then altered by making it the cathode in an electrolysis cell arrangement of the kind illustated in FIG. 1. Deionized water of pH 6.8 was used as the electrolyte and the distance from the platinum anode to the surface of the resistor was 0.159 cm. Cell current was furnished by a constant current DC power supply and cell current was measured by means of a precision ammeter. The resistance of the resistor was measured constantly during the electrolysis by means of an impedance bridge at 1,000 cycles/sec. using an oscilloscope as null point detector. The electrolyses were carried out at cell currents of from 5 to 80 microamperes (μa.) and at voltages ranging from 1.5 to 15 volts, the cell current being proportional to the cell voltage. The results are shown by the curves of FIG. 2 wherein, for each cell current the resistance is plotted against time. It can be seen that the rate of decrease in resistance resulting from the cathodic reduction is proportional to the cell current.

Example 2

A glaze resistor consisting of 30 square prints was prepared as described in Example 1 using the resistor composition described in that example. FIG. 3 shows a plot of the resistance against time during electrolysis under a cell current of 500 microamperes. The electrode was initially made cathodic, but after about 22 minutes the leads were reversed so as to make it anodic. When the resistor was cathodic, the voltage was about 85 volts, and when it was anodic, the voltage was about 22 volts. It will be seen from the curve of FIG. 3 that electrolysis reduced the resistance while the resistor was cathodic but increased the resistance when the leads were reversed to make it anodic. Thus, the resistance of a palladium glaze resistor can be either decreased or increased by the method of the invention, depending upon whether the resistor is made cathodic or anodic during the electrolysis.

Example 3

A glaze resistor was prepared as described in Example 1 using the resistor composition described in that example. A drop of water was placed on the resistor surface so as to completely cover the width of the resistor for a distance of 5 mm. A DC current of 350 microamperes was passed through the resistor at 15 volts and AC measurements of the resistance of the resistor were made by means of an impedance bridge as described in Example 1. It was found that the resistance of the resistor increased from 585 ohms to 700 ohms in 30 minutes, the increase being at a rate of about 1%/min. This shows that the anodic reaction (oxidation) is favored over the cathodic reaction (reduction).

Example 4

Two palladium-silver glaze resistors were prepared as indicated in Example 1 by firing on the refractory substrate prints of a resistor composition comprising 16.2% metallic palladium powder, 16.2% silver powder and 66.6% lead borosilicate glass powder. The two resistors had initial resistances of roughly 9,500 ohms. One was made anodic in an electrolysis cell similar to that described in Example 1 and the other was made cathodic in another similar cell. The voltages and cell currents are indicated in FIG. 4, which shows plots of the resistances of the resistors against time.

Example 5

A fired-on glaze resistor prepared using a resistor composition containing 13% metallic palladium powder, 13% silver powder and 74% of a zinc borosilicate glass powder, was anodically oxidized at 75 volts and a cell current of 3,000 microamperes for 6 minutes in a cell of the general arrangement indicated in Example 1. The resistance of the resistor was increased from 1,250 ohms to 1,600 ohms, corresponding to a change of about 4%/min.

Example 6

A fired-on glaze resistor prepared using a resistor composition containing 40% metallic palladium powder, 40% silver powder and 20% of a zinc borosilicate glass powder, was cathodically reduced at 85 volts and a cell current of 10,000 microamperes for 2 minutes in a cell of the general arrangement indicated in Example 1. The resistance of the resistor decreased from 1,630 ohms to 1,250 ohms, corresponding to a change of about 12% per minute.

Example 7

Table 2 summarizes the results of the anodic oxidations of many palladium-silver glaze resistors whose initial resistances varied from about 1 to 10,000 ohms/square.

TABLE 2

Starting Resistance, ohms/square	Cell Potential, Volts	Cell Current, Microamperes	+Δ R/Min., percent of Orig.
1	15	200	3.1
10	30	500	3.0
100	45	3,000	2.8
1,000	60	5,000	1.1
10,000	85	10,000	0.9

When the resistor is made anodic in the electrolysis cell, the rate of increase in its resistance is an inverse function of the resistivity, and the higher the resistance of the resistor, the higher the cell current required to effect changes in the resistance at an observable rate. The rate of change of resistance is greater, the greater the metal content of the resistor.

Example 8

Table 3 summarizes the results of the cathodic reductions of many palladium-silver resistors whose initial resistances varied from about 1 to 10,000 ohms per square.

TABLE 3

Starting Resistance, ohms/square	Cell Potential, Volts	Cell Current, Microamperes	−Δ R/Min., percent of Orig.
1	35	3,500	12.5
10	50	4,000	12.1
100	86	10,000	11.0
1,000	50	2,700	2.4
10,000	50	10,000	2.2

The cathodic reduction requires more current to produce an observable effect, but the rate of change in resistance is more rapid than that obtained in anodic oxida-

tions. Again, the rate of change of resistance is greater, the greater the metal content of the resistor.

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

1. A method for adjusting the resistance of a palladium glaze resistor comprising making said resistor an electrode in an electrolysis cell having an inert second electrode of opposite polarity, said cell having a suitable electrolyte between said electrodes, and passing a direct electric current through said cell, thereby increasing the resistance of said resistor when said resistor is made anodic to said inert electrode, and decreasing the resistance of said resistor when said resistor is made cathodic to said inert electrode.

2. The method of claim 1 wherein the direct current is passed through the cell at a potential of 1 to 150 volts and a current density of 1 to 200,000 microamperes per square centimeter.

3. The method of claim 1 wherein the inert electrode is platinum.

4. The method of claim 1 wherein the electrolyte is water at a pH of 6 to 8 and the current is passed through the cell at a voltage of from 1.5 to 50 volts and a current density of 5 to 10,000 microamperes per square centimeter.

5. The method of claim 1 wherein the resistance of the resistor is measured continuously during the passage of current through the cell, which passage of current is stopped when the desired adjustment in the resistance of the resistor has been effected.

6. A method for increasing the resistance of a palladium glaze resistor, said method comprising making said resistor the anode in an electrolysis cell having an inert second electrode as cathode and a suitable electrolyte between said electrodes, and passing a direct electric current through said cell, thereby increasing the resistance of said resistor.

7. The method of claim 6 wherein the direct current is passed through the cell at a potential of 1 to 150 volts and a current density of 1 to 200,000 microamperes per square centimeter.

8. The method of claim 6 wherein the inert cathode is platinum.

9. The method of claim 6 wherein the electrolyte is water at a pH of 6 to 8 and the current is passed through the cell at a voltage of 1.5 to 50 volts and a current density of 5 to 10,000 microamperes per square centimeter.

10. The method of claim 6 wherein the resistance of the resistor is measured continuously during the passage of current through the cell, which passage of current is stopped when the desired increase in the resistance of the resistor has been effected.

11. A method for decreasing the resistance of a palladium glaze resistor, said method comprising making said resistor, the cathode in an electrolysis cell having an inert second electrode as anode and a suitable electrolyte between said electrodes, and passing a direct electric current through said cell, thereby decreasing the resistance of said resistor.

12. The method of claim 11 wherein the direct current is passed through the cell at a potential of 1 to 150 volts and a current density of 1 to 200,000 microamperes per square centimeter.

13. The method of claim 11 wherein the inert anode is platinum.

14. The method of claim 11 wherein the electrolyte is water at a pH of 6 to 8 and the current is passed through the cell at a voltage of from 1.5 to 50 volts and a current density of 5 to 10,000 microamperes per square centimeter.

15. The method of claim 11 wherein the resistance of the resistor is measured continuously during the passage of the current through the cell, which passage of current is stopped when the desired decrease in the resistance of the resistor has been effected.

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