# United States Patent [19]

**Wainer et al.**

[11] **3,805,023**

[45] **Apr. 16, 1974**


[54] **ELECTRICAL HEATING DEVICE HAVING METAL DEPOSITIONS: IN A POROUS ANODIZED METAL LAYER**


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[73] Assignee: **Horizons Incorporated, a division of Horizons Research Incorporated,** Cleveland, Ohio



[22] Filed: **June 28, 1973**

[21] Appl. No.: **374,724**

**Related U.S. Application Data**

[62] Division of Ser. No. 240,019, March 31, 1972, Pat. No. 3,763,004.

[52] **U.S. Cl.** ..... **219/543,** 96/38.4, 96/86 R, 117/215, 204/38 A, 106/1, 219/464, 219/540

[51] **Int. Cl.** ..... **H05b 3/16**

[58] **Field of Search** ..... 219/464, 540, 543; 96/36.2, 38.4, 86 R; 106/1; 161/6; 117/215; 204/38 R, 38 A



[56] **References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,766,119 | 10/1956 | Freedman et al. | 96/86 R |
| 2,995,443 | 8/1961 | Kempe | 204/38 A |
| 3,431,120 | 3/1969 | Weisenberger | 106/1 |
| 3,612,828 | 10/1971 | Siegler | 219/464 |
| 3,615,483 | 10/1971 | Jonker | 96/38.4 |
| 3,615,553 | 10/1971 | Wainer | 96/86 R |
| 3,715,211 | 2/1973 | Quaintance | 96/86 R X |
| 3,763,004 | 10/1973 | Wainer | 204/38 A |
| 3,765,994 | 10/1973 | Quaintance | 161/6 |

FOREIGN PATENTS OR APPLICATIONS

| | | | |
|---|---|---|---|
| 1,064,726 | 9/1962 | Great Britain | 96/38.4 |
| 1,065,354 | 4/1967 | Great Britain | 204/38 A |



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*Attorney, Agent, or Firm*—Lawrence I. Field

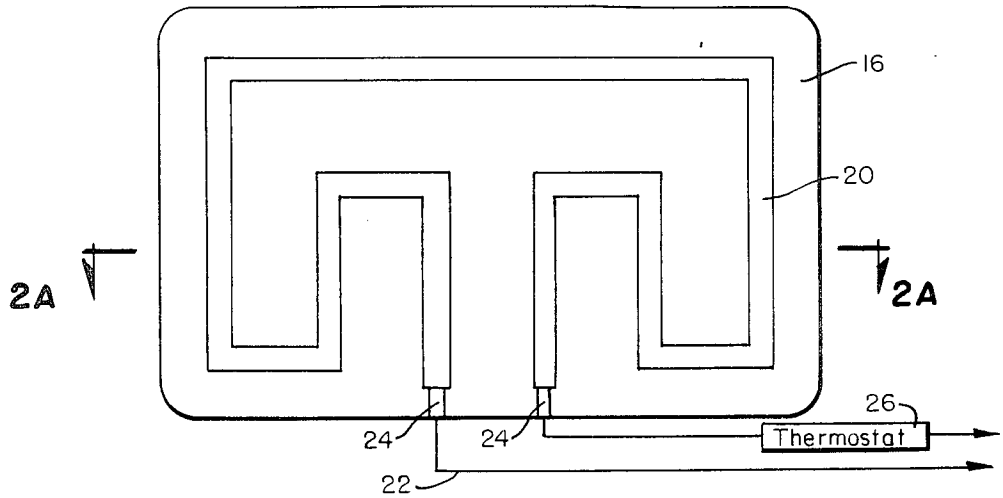


[57] **ABSTRACT**

A novel device exhibiting extensive utility for electric heating purposes is comprised in part of a precious metal image being imbedded in the anodized layer produced by electrolytic oxidation of aluminum in which the aluminum sheet is the anode; and plating thereon in only the precious metal image areas, less noble metals. While silver is the preferred precious metal and nickel is the preferred plating material for many applications, other preferred plating materials are combinations of nickel and chromium, cobalt and chromium, and cobalt, nickel and chromium. For some devices, the aluminum backing which carries the anodized layer with the electrical circuit placed thereon, may be removed for the purpose of increasing the temperature of performance of the electrical heating element thus prepared. In other devices, both the aluminum metal and the anodized layer may be removed.

Through the medium of the combination of the novel materials, processes, designs and other modifications described in this specification, items such as food warmers, simmering temperature devices, food cookers, pot warmers and cookers, room and air warmers and heaters, may be produced. In addition, in one and the same piece, combinations of food warmers, food simmers, and food cookers may be produced simply by choosing a proper design of the heater element produced according to the invention.


**6 Claims, 12 Drawing Figures**



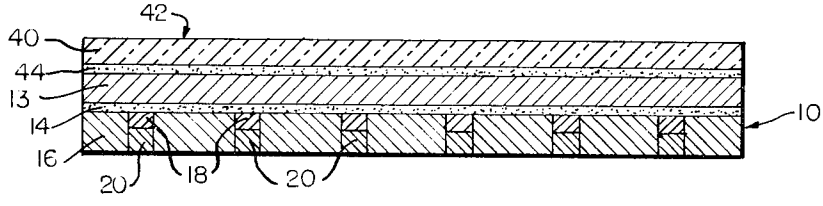



FIG. 1.

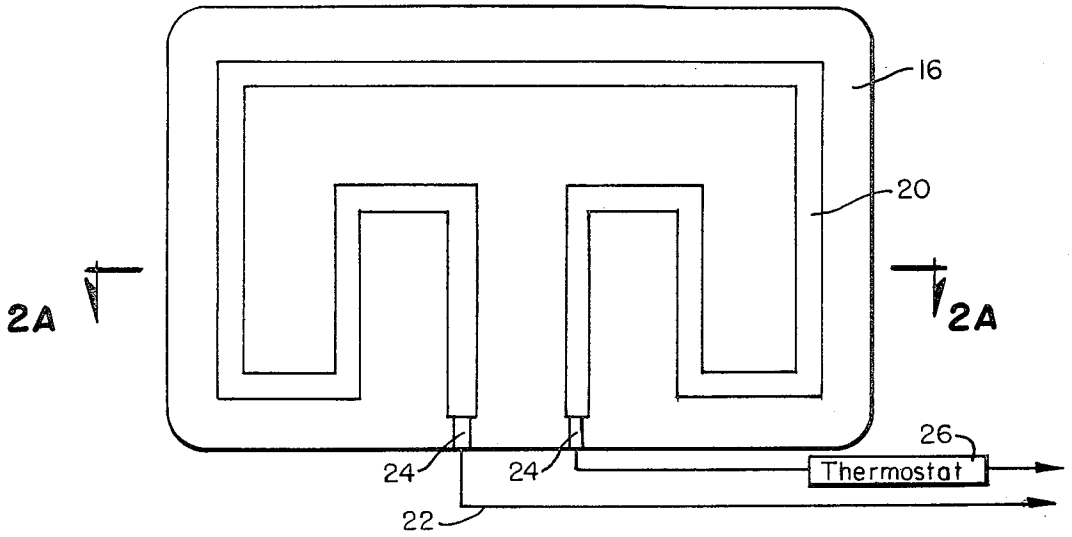



FIG. 2A.

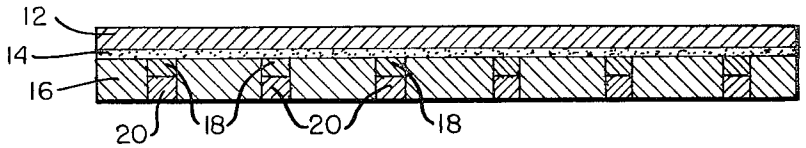



FIG. 2B.

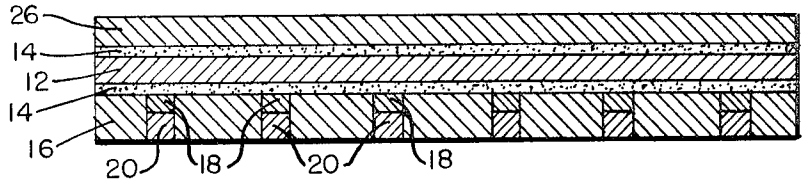



FIG. 2C.

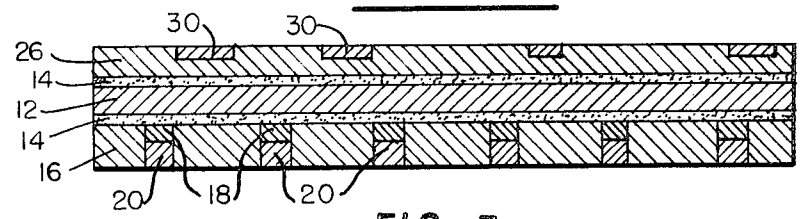



FIG. 3.

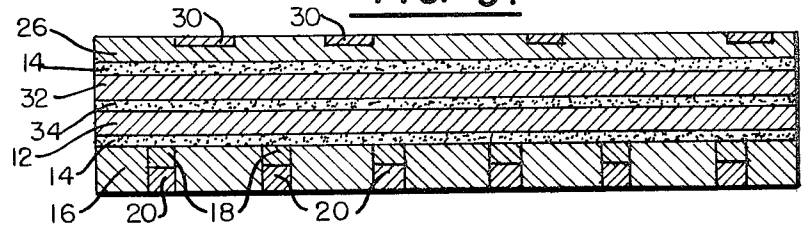


FIG. 4.

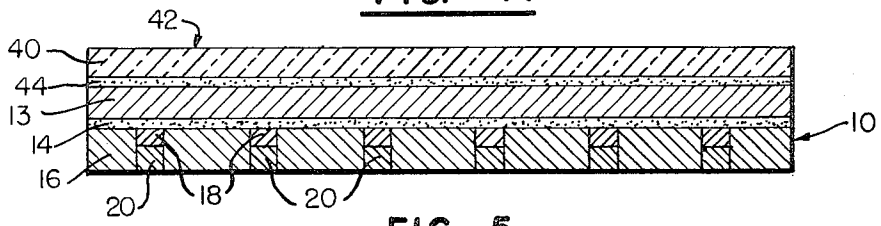



FIG. 5.

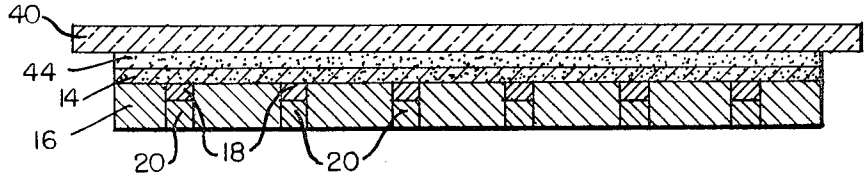



FIG. 6.

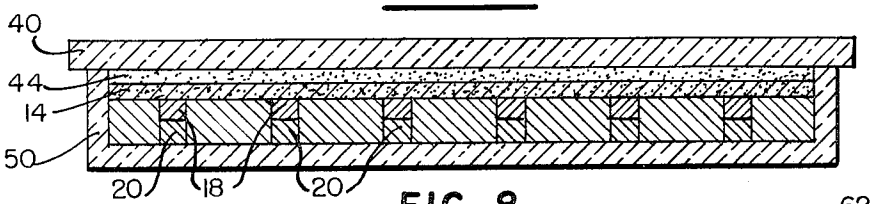



FIG. 8.

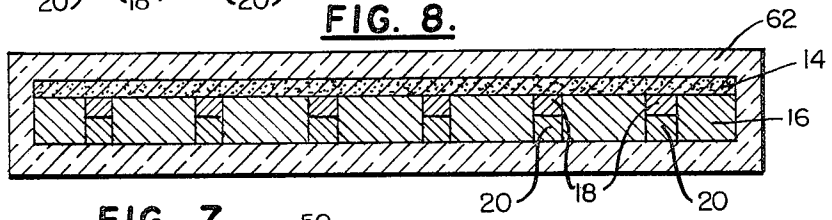



FIG. 7.

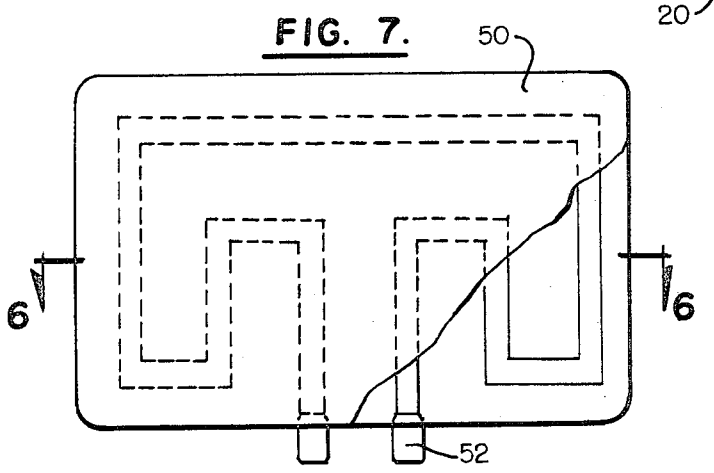
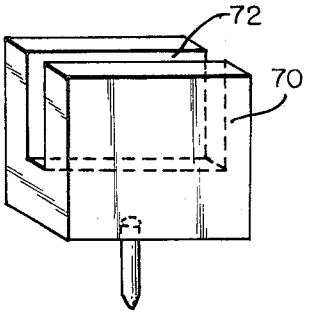



FIG. 10.



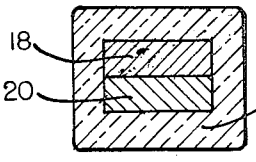




FIG. 9.

# ELECTRICAL HEATING DEVICE HAVING METAL DEPOSITIONS: IN A POROUS ANODIZED METAL LAYER

This application is a division of U.S. Pat. Application Ser. No. 240,019, filed Mar. 31, 1972, which issued as U.S. Pat. No. 3,763,004 on Oct. 2, 1973.

## BACKGROUND OF THE INVENTION

A wide variety of electrically conducting materials are used for food warming and room warming purposes. One of the most important of these is an 80 percent-nickel-20 percent chromium alloy described in Marsh, U.S. Pat. No. 811,859 and commonly known as "Nichrome." The heating circuit usually consists of bare wire placed in a suitable support, or the wire may be encased in a suitable insulator, which is in turn encased in a metal sheath. Other electrically conducting materials used for heating purposes include iron-aluminum alloys, for example as described in Siegla, U.S. Pat. No. 3,612,828; aluminum-silicon alloys; cobalt-aluminum-molybdenum alloys; molybdenum-silicide elements in straight rod form, generally sintered with cobalt, or with cobalt and aluminum; and sintered silicon carbide, also generally available only in rod form.

A more recent development is the emergence of warming trays which, in effect, utilize printed circuits as a means for carrying the current and developing the necessary heat, such as are described in U.S. Pat. Nos. 2,563,265; 2,572,163; 2,976,386; and 3,098,924.

Such previously described and utilized devices exhibit an upper limit of temperature beyond which they become either inoperable or burn out, such limit of temperature generally being around 300°F.

In warming, heating, and cooking of food, there are three levels of temperature which are required to accomodate all of the operations which are imposed by the housewife or chef. The first of these is the warming of food in which the desired temperature utilized in a steady-state condition is in a range between 225°F and 275°F. It is further desirable that these temperatures be reached as soon as possible. The usual food warmer now available in the marketplace will achieve these temperatures satisfactorily, but it requires a time period between 10 and 15 minutes before it reaches full temperature. A second level of temperature is known as the "simmering temperature" which is generally in the range of 500°F to 600°F, and none of the devices utilizing silk-screen printing or the type of printed circuits described in U.S. Pat. No. 2,563,265 are capable of reaching and maintaining this temperature either for suitable periods of time or for withstanding the hundreds of cycles from cold to hot to cold that are normally encountered in service. The third and most important temperature level, also to be reached in a very short period of time (less than 2 minutes), is the full cooking temperature which is normally in the temperature range of dull red heat between 1,200°F and 1,400°F. None of the presently available plated or printed circuits are capable of achieving such temperatures which are usually available only through the use of wire conductors.

Fully sensitized image metal-plated, anodized aluminum represents an ideal base, depending on the nature of its manipulation for achieving the full range of warming, simmering and heating conditions. Certain of



the techniques for the preparation of such metal-plated images for other purposes are described in detail in a copending U.S. Pat. application, Ser. No. 191,635, filed Oct. 22, 1971, entitled "Metal-Plated Images," the disclosure of which is incorporated herein by this reference. The anodized layer on aluminum which represents the carrying base for the purposes of this invention is well known and is described in the literature, e.g., in "The Journal of Electrochemical Society" June 1968, pages 618–620 and the references listed on page 620. Aluminum metal sheet is electrolytically oxidized by making it the anode in a suitable bath under varying conditions of time and temperature. An important part of the layer for the purposes of this invention is the nonporous barrier layer directly against the metal surface on top of which barrier layer there is a porous layer which holds the various salts and materials which are used for the purposes of this invention. The barrier layer thickness is also a function of time, temperature, nature of the electrolyte used and other variables. Combinations of anodizing operations can be utilized to vary the thickness of the barrier layer independently of the time and temperature. For example, the oxidation may be carried out in a boric acid glycol electrolyte, usually an ethylene glycol bath, for extended periods of time, until the desired thickness of the barrier layer is produced and thereafter the electrolytic oxidation is continued with one of the known acid baths, preferably oxalic acid, to yield the highly porous top layer of the desired thickness.

The production of the silver images in the anodized layer on aluminum utilized in this invention are described amply in the copending application entitled "Metal-Plated Images" referred to above. Techniques for the production of images of gold, platinum, or palladium are also described. These four metals, when placed in the proper chemical form, are active catalysts for the electroless deposition of metals suitable for the purposes of this invention and particularly the electroless deposition of nickel, cobalt, chromium, and mixtures thereof. In addition, once these metals are plated down to a suitable level so that they become at least partially electrically conducting, other metallic conductors may be placed on top of such images either by electrolysis or by electrophoresis.

The types of electroless plating baths which may be utilized for the purposes of this invention are described in another copending U.S. Pat. application, Ser. No. 205,493, filed Dec. 7, 1971 and entitled "Indicia Bearing Anodized Articles", which issued as U.S. Pat. No. 3,765,994 on Oct. 16, 1973 the disclosure of which is intended to be incorporated herein, by this reference. The most important for the over-all purpose covering the broad range of temperatures needed for providing full utility are nickel, cobalt, chromium and combinations thereof.

## SUMMARY OF THE INVENTION

Silver halide impregnated and photosensitized anodized aluminum sheets are normally used as the base for producing the metal-plated circuits, of this invention. These silver halide photosensitized anodized aluminum sheets are known in the trade as "Metalphoto," whose manufacture is described in U.S. Pat. Nos. 2,766,119 and 3,615,553. Other photosensitive plates may be used including those based on compounds of gold, platinum, and/or palladium as described in the copending

application Ser. No. 191,635 entitled "Metal-Plated Images," filed Oct. 22, 1971.

To prepare such plates and place them suitably in condition for electroless nickel plating, for example, the silver halide impregnated and photosensitized anodized aluminum plate is exposed to ultraviolet light for a few seconds through a negative. Generally, an exposure time of 3 to 5 seconds is required sufficient to yield a radiation density at the image plane of 17.5 millijoules per square centimeter. After development and fixing, the plate is rinsed in water for 1 minute and then bleached for 10 seconds in a 5 percent solution of sodium hypochlorite. It is then rinsed in running water for a period of 1 minute. Thereafter, the plate is immersed in an electroless nickel plating those such as the baths described in U.S. Pat. No. 3,431,120. With a time period of immersion in the nickel plating bath at 67°C of less than 2 minutes a dense black image of nonconducting nature is obtained from the original bleached almost colorless silver image. If the time of immersion is extended beyond 2 minutes, a metallic appearing image of good electrical conductivity is obtained and generally the time period for obtaining such conducting coating is about twice that necessary to achieve the dense black image which may be considered, in this dense black, form, as an intensified image, rather than a conducting image.

It has been found that, in general, the greater the exposure level and/or development of the photographic-produced silver image pattern, the greater the rate of deposition of the electroless nickel deposit. Whereas an exposure of 17.5 millijoules per square centimeter with a mercury lamp source is needed to yield the metal-plated image in a time period of 2 minutes or more which is electrically conducting, an exposure of 40 to 50 millijoules, with identical development, fixing, washing and bleaching procedures will permit the deposition of a conducting nickel pattern on the bleached silver image at 67°C to take place in time periods of 10 seconds to 60 seconds.

Within the time periods listed for the two types of conditions, a layer of nickel approximately 0.8 mils thick is deposited on the silver image for an immersion time period of 3 to 4 minutes for a 17.5 millijoule exposure, whereas an immersion time of 1 minute is required to produce a 0.8 mil thickness of nickel when an exposure of 50 millijoules is utilized.

The conductivity and resistivity obtained in such a suitably connected and designed metal-plated image is a function of the thickness of the metal plate, its width, and its resistivity. In the case of nickel, in order to produce an electrical load at 120 volts alternating 60 cycle current, 120 watts are required to produce a temperature of 120°C. Thus, the current demand is 1 ampere and the total circuit resistance is equal to approximately 120 ohms.

The resistivity of a metal-plated image comprised of nickel approximately 0.8 mils thick is in the range of 3 to 5 ohms per square inch. The resistance per linear inch of this 0.8 mil thick nickel plate as a function of its width is given in Table 1.

Table 1

Resistance of Ni Plate Per Linear Inch As A Function of Width of Conductor

| Line Width (Inches) | Resistance (ohms per linear inch) |
|---|---|
| 0.0312 | 150 |
| 0.125 | 50 |
| 0.187 | 25 |
| 0.250 | 20 |
| 0.750 | 7 |
| 1.000 | 3 |

Using the 17.5 millijoules per square centimeter exposure parameter, resistance values were then determined for conducting layer thickness variation for three different line widths as a function of immersion time in the electroless nickel bath operated at 67°C. The results of these three variables are summarized in Table 2.

Table 2

Resistance As A Function of Line Width Versus Immersion Time

| Line Width (inches) | Immersion Time (minutes) | Resistances (ohms per linear inch) |
|---|---|---|
| 0.03 | 1.0 | 1250 |
| | 2.0 | 150 |
| | 3.0 | 75 |
| 0.125 | 1.0 | 100 |
| | 2.0 | 50 |
| | 3.0 | 20 |
| 0.250 | 1.0 | 70 |
| | 2.0 | 20 |
| | 3.0 | 10 |

From these data, it is obvious that almost a complete degree of control is available for rapidly obtaining reproducible electrical resistance values for electrolessly deposited nickel circuits by controlling the immersion time of the bath and exposure time which serves for nucleation and catalysis of the rate factors for the electrolessly deposited nickel.

Through such a determination of the various parameters necessary to produce a given total resistance value, it is now possible to determine the path length and width of the conducting lines necessary to heat a given area to a given temperature. For example, in order to provide 1 ampere of ordinary household current at 120 volts potential to a surface area measuring 6 inches square, a circuit pattern comprised of a continuous series line pattern 30 inches in length and 1 inch in width is made available, which results in an electrical circuit having 120 ohms resistance and which effectively covers about 80 percent of the total surface area to provide extremely uniform heating across the entire plate.

Utilizing the data given in the foregoing paragraphs, an exposure of 90 millijoules is used. After development, fixing, water rinsing, and bleaching, the time required to obtain 120 ohms resistance from the nickel plate deposited on the bleached silver image is 1 minute at 67°C. The resistance from the circuit to the base aluminum is in the range of $5 \times 10^6$ ohms, whereas the resistance of the circuit proper is 120 ohms.

Since aluminum is an extremely good heat conductor, it is not necessary for the nickel electrical conductor circuit to cover the anodized surface as completely as printed circuits on glass, for example. The complete coverage of a printed circuit on glass as a conducting path to produce heat is also necessary to prevent undue strain on the glass supporting layer. Generally, it has been found that if 50 percent of the anodized surface

is symmetrically covered by the nickel conducting surface, less than a 2 degree plus or minus variation at 125°C is found on that part of the surface within a one-fourth inch of the circumference of the outermost edge of the plate. This fact allows for the very thin electroless nickel plated layers to be useful in heating still larger surfaces than the 6 inch square mentioned previously.

For example, an anodized aluminum plate, 6 inches by 12 inches in dimension, containing a photographically produced silver image forming a printed circuit pattern on the same overall dimensions as described above, being characterized by the conduction pattern being spread out such that the total surface area of the conductor effectively covers 50 percent of the anodized surface area in a symmetrical or uniform geometric pattern, it was found that 125 ohms resistance could be obtained on the circuit utilizing the same conditions as described previously which results in a temperature of 125° plus or minus 2°C when the circuit was connected to a thermostatic switch in series with 120 volt, 60 cycle ordinary household current electrical source. By increasing the rectangular plated area to a dimension of 6 inches by 24 inches and incorporating a symmetrical circuit pattern consisting of a conducting path 2 inches wide and 60 inches long of electroless nickel deposited on the photographic-produced silver image embedded within the anodized porous structure, a circuit was produced using the above described conditions having 120 ohms total electrical resistance and encompassing approximately 80 percent of the total anodized aluminum plate surface.

Utilizing a design suitable for carrying the full current load dependent on the nature of the application for which such electrical circuit is to be used for current carrying purposes, an image is first produced in the porous aluminum oxide surface layer of an anodized aluminum plate or sheet member, by decomposition of a suitable compound of silver, gold, platinum, or palladium or mixtures of such compounds. These images are made by photographic or photoresist means or by any other known techniques.

After the image has been converted to the elemental metal the image is chemically treated to place it in the best condition to act as a catalyst for subsequent deposition of metals by electroless plating techniques. In the case of silver, better results are obtained with the silver image if it is first bleached to the oxide form by a brief treatment in a water solution of an alkali hypochlorite, after which the desired metal is plated on such a bleached image by electroless plating from a bath containing salts of nickel, chromium, cobalt, iron, copper, gold, silver, platinum or palladium and mixtures of such salts.

These metals are deposited from an electroless plating bath under specific conditions of time and temperature which are generally mild in nature. The image first produced by photographic techniques, particularly silver, may be sepia toned in color, and by carrying out the electroless plating operation in mild form, a deeply toned black image is invariably obtained which is still not a conductor of electricity, but which is very useful for decorative purposes in the practice of this invention, in view of the high degree of stability of the black image thus produced. If stronger conditions, operating for longer periods of time, of electroless plating are utilized, the image then exhibits a metallic sheen and is electrically conducting.

The invention will be better understood from the description which follows taken in conjunction with the drawings in which:

FIG. 1 is a bottom plan view of a warming device according to the invention;

FIG. 2A is a view, taken along plane 2A—2A of FIG. 1;

FIG. 2B is a similar view of a modification of the device of FIGS. 1 and 2A;

FIG. 2C is a similar view of a further modification;

FIG. 3 is a view similar to FIGS. 2A, 2B and 2C of a modification;

FIGS. 4–6 are views showing a further modification;

FIGS. 7 and 8 are views similar to FIGS. 1 and 2 of a modification thereof;

FIG. 9 is a view in section showing a further free standing heating element; and

FIG. 10 is a view of a connector used with the invention.

## EXAMPLE 1

A first embodiment of this invention is shown schematically in FIGS. 1 and 2A. A sheet **10** of aluminum suitably between 0.030 and 0.25 inch thick, e.g., 0.060 inch thick is uniformly anodized on one side of the sheet by any of the anodizing baths well known in the art, and described, for example, in "Surface Treatment and Finishing of Aluminum and Its Alloys" by S. Wernick and R. Pinner, published in 1956 by Robert Draper, Ltd., Teddington, England, to produce a porous aluminum oxide surface layer **16** and a barrier layer **14** on aluminum base **12.** The porous layer is impregnated with a photosensitive mixture, as described in U.S. Pat. No. 2,766,119 or 3,615,553. Thereafter the photosensitive side is exposed to a pattern of radiation to yield a heating circuit of the intended resistivity. The resulting silver image **18** is exposed, developed and fixed as described in either of the two U.S. patents and then bleached by immersion in a bath of alkali metal hypochlorite after which it is electrolessly plated with nickel **20** the desired thickness according to the procedure and compositions described in U.S. Pat. No. 3,431,120. Then the anodized layer is sealed by immersion in a boiling solution containing 0.5 percent nickel acetate, 0.5 percent cobalt acetate, 2 percent boric acid, balance deionized water. Electrical contents **24** are made to the electrical circuit defined by metal **20** by means of wires **22.** A thermostat **26** is placed in series with the connecting wires.

Referring now to FIG. **1,** this depicts a plan view of the conductor side with the appropriate connections. In this plan view, the electroless plated nickel **20** designated as "the conductive path" is placed in and on the aluminum anodized layer **16.** Electrical connection is made as indicated with a relatively low temperature connecting material such as silver paste or solder since in view of the resistance of this particular specimen the design in FIG. **1** is suited particularly for warming purposes where the temperature will not exceed 300°F. in service. The connectors **24** are attached to the exposed nickel conductor with silver paste or solder as indicated. For practical use a thermostat **26** is placed in series with such connector to prevent the unit from overheating and the unit is now ready for assembly into final form.

FIG. **2B** is a cross sectional view taken through the plane **2A–2A** of FIG. **1,** except that the plate **10** has been anodized on both sides, the aluminum base **12**

then supports a barrier layer **14** and a porous anodized surface layer **16** on both sides of the sheet of aluminum, in which the bottom side contains the conductive path and the top side is a clear anodized layer **26** whose pores have been sealed by the sealing process. The cross section of the conductive path **20** shown in the Figures is schematic and defines the deposition of nickel **20** on a silver image **18** in the areas indicated.

Example 1 is repeated except that an additional non-conductive image **30** is placed in the anodized layer **26** on top of the aluminum heating surface as shown in FIGS. 2C and **3.**

This is accomplished by making the exposure first on one side to produce the conductive circuit and then making a second exposure on the opposite side to produce the ornamental design. The plate is then processed as before and intensifying with nickel until a deep lustrous black is obtained short of the production of a conducting pattern. The plate is then washed and dried for 3 minutes at 90°C after which the upper surface **26** is sprayed with a lacquer based on a solution of polymethylmethacrylate in acetone and allowed to dry, or it can be laminated to a sheet of vinyl film coated with a pressure sensitive polybutylene adhesive. The plate is then re-immersed in the electroless nickel plating bath until the proper thickness of nickel **20** has built up to achieve the 120 ohms resistance (approximately 0.8 mils in thickness). The lacquer or vinyl film is stripped from top **26** by soaking in a suitable solvent for the lacquer or the adhesive.

After sealing the anodized layer by boiling in acetate-boric acid-water solution as described in Example 1, the leads **24** are attached with solder or silver paste and the unit is ready for operation after assembly in a suitable enclosure. The product is shown in FIG. **2C.**

## EXAMPLE 2 (FIG. 3)

FIG. **3** illustrates still another embodiment of the invention in which a conductive circuit is placed on one side of a thin sheet **12** of photosensitized anodized aluminum and the initial exposure is made only on one side as described in Example 1, the sheet being 5 mils thick. This plate is then processed completely to the formation of the desired conductive circuit as in Example 1. Another sheet **32** of sensitized anodized aluminum, 0.03 inches in thickness is then processed in the same manner, including the nickel step up to the point of producing the black non-conductive image **30** and again the image is placed only on one side. This image bearing layer may have the non-image areas dyed with temperature resistance dyes or with inorganic coloring agents in a manner well-known to those skilled in the art to further enhance the merchandising appeal of the heating surface with the nonconductive image thereon so as to have an image comprised of black with a background in another color. These two pieces of aluminum are then cemented back to back with an adhesive cement **34.** Suitable cements for this purpose when the plate is being used for temperatures not exceeding 400°F includes silicones, epoxys, polyimides, polyurethanes, and phenolformaldehyde-polyamide mixtures, two part epoxy resin cements being preferred. FIG. **3** is a cross section view of this embodiment similar to FIGS. 2A, 2B, and 2C.

## EXAMPLE 3 (FIG. 4)

FIG. 4 is a cross sectional view of an assembled heater capable of operating at temperatures between 400°F and 1,000°F. In this case, a 5 mil sheet **12** of anodized aluminum is prepared with conductive circuit as in Example 1 except that the nickel deposit is modified to provide the desired resistance in accordance with Tables 1 and 2 to enable the conducting circuit to achieve the desired temperature.

Only one side of the 5 mil aluminum sheet **12** is exposed and provided with a conducting circuit **20** and the back side of sheet **12** is neither anodized nor photosensitized. This back side is then laminated to a suitable layer **40** depending on the nature of the intended application. Covering layer **40** may be made of a heat and shock resistant ceramic, tempered glass, heat and shock resistant glasses of the "Pyroceram" type, or a vitreous enameled metal sheet.

For the intended service temperature range of 400°F to 1,000°F, the adhesive is preferably a sodium silicate bonded cement filled with refractory particulate material, e.g., a sodium silicate with a silica to sodium oxide ratio of 3.5 per 1 to which is added finely divided aluminum oxide electrically fused refractory grain in sufficient quantities fo form a relatively thick paste. A range of mixtures is between 20 percent by volume of the sodium silicate and 40 percent by volume of the sodium silicate liquor to 80 percent by weight of the refractory grain to 60 percent by weight of the refractory grain. Advantageously, the refractory grain is comprised of 65 parts by weight of −100 mesh +200 aluminum oxide and 35 percent by weight of −325 mesh aluminum oxide. In assembly, the top surface **13** of the aluminum metal plate **12** is smeared with a layer **44** of cement and smoothed down with a doctor blade. The cover layer **40** is attached to the adhesive inorganic cement **44** with pressure in the range of 1 to 5 lbs. per square inch to squeeze out any excess adhesive cement since very thin layers are sufficient to provide the degree of adhesion and refractoriness needed. The assembly is then allowed to stand at room temperature while pressure is still being applied for at least 24-hours after which the entire assembly is heated in a furnace to 1,000°F for 30 minutes to completely dehydrate the cement and to produce the desired degree of refractory adhesiveness as made available by the layer **44,** after which step the assembly is ready for use in the temperature range indicated.

## EXAMPLE 4 (FIGURES 5, 6 AND 7)

A further embodiment is shown in FIGS. **5, 6** and **7** for service temperatures of operation above 1,000°F. This is accomplished by removing the aluminum backing layer **12** from the original sheet after the desired conducting path **20** has been laid down on the opposite side of such aluminum sheet. This aluminum backing layer **12** may be removed easily by dissolving the metallic aluminum away with a solution of 18° to 22° Beaume hydrochloric acid containing 50 to 10 percent by volume of 30 volume percent hydrogen peroxide, after first suitably protecting the circuit surface, e.g., with an acid resistant strippable film described earlier in Example 1. Such solution is normally complete for a 5 mil thickness of aluminum in a space of a few minutes. As shown in FIG. **5,** the barrier layer **14** thus exposed is then laminated to a desired heating surface with a refractory air-setting or heat-setting cement of the types previously described. Again, the heating surface **40**

may be made of ceramic, high temperature glass, metal and/or vitreous enameled metal.

A further modification is depicted in FIGS. **6** and **7** in the cross section view. The base construction is identical with that of FIG. **5**, except that the conducting heating element and the various attachments thereto are covered with a vitreous high temperature insulation **50** after the heating surface **40** has been laminated to the barrier layer **14**, this vitreous high temperature covering insulation being shown as **50** in FIG. **6**.

FIG. **7** is a plan view of the back side or conducting side similar to the view in FIG. **1** and showing the added ceramic or vitreous high temperature insulation layer **50** and a recommended schematic and relative design of the connector pads **52** needed for high temperature purposes. It is noted that the width of the connector pad **52** shown in FIG. **7** is substantially greater than the width of the conducting path **20** also shown in this figure.

## EXAMPLE 5 (FIG. 8)

FIG. **8** is a view taken on plane **8—8** of FIG. **7** and is similar to FIG. **2** and depicts the cross section of an embodiment in which the conductive path is in a free-standing element **60**. The conducting circuit **20** is made as in Example 1 and the aluminum backing **12** dissolved off in the hydrochloric acid-hydrogen peroxide mixture of Example 4. This yields a conductive element **20** imbedded in the anodized (hydrated aluminum oxide) layer **16**. A high temperature vitreous insulation **50** which encloses the element except for the connecting pads **52** (see FIG. **7**), is then applied by brushing, spraying, or dipping. Preferably the conducting path is a nickel chromium alloy electrolessly deposited by a modification of the teachings of U.S. Pat. No. 3,431,120.

One of the more useful electroless plating baths for the purpose of this invention is defined in U.S. Pat. No. 3,431,120 covering the deposition of nickel, cobalt, and copper. The metal can be employed in the bath as a salt thereof, such as the sulfate, sulfamate, chloride, acetate, formate, citrate, or tartrate or other metal salt of a mono or dicarboxylic acid. For the purposes of this invention, the acetates plus a small amount of the sulfate are preferred. Conveniently, the metal salt is present in the bath in an amount sufficient to provide a concentration of metal in amounts ranging from 0.5 to 60 grams per liter, and the preferred range is 4 to 10 grams per liter of the bath solution.

The amino-borane employed as the reducing agent in the plating bath can be a primary, secondary, or tertiary amino-borane. Concentration of the amino-borane in the plating bath can range between 0.5 and 20 grams per liter, with the preferred range being between 1 and 10 grams per liter of the bath solution.

Heptagluconates are added to the plating bath as heptagluconic acid or the water soluble salt such as the ammonium, alkali, or alkaline earth metal salt. The sodium and potassium heptagluconates are preferred. The principal function of the heptagluconate ion is to confer stability to the bath. The concentration of the heptagluconate can range between 1 to 160 grams per liter, with the preferred range being between 10 and 100.

In deposition, the pH of the bath is maintained between 3.5 and 7 and the plating may be carried out at temperatures ranging between 15°C and 85°C.

A typical bath is comprised of 45 grams of hydrated nickel sulfate ($NiSO_4 \cdot 6H_2O$); 10 grams of methyl amino-borane; 25 grams of sodium heptagluconate; all dissolved in 1 liter of distilled water, the ingredients being added to the solution in the order given. The pH of the solution is then brought to a value between 6.5 and 7 by adding a 50 percent solution of glacial acetic acid in water dropwise with stirring until the desired pH is achieved. Normally, this will require between 10 and 15 cc's of the 50 percent acetic solution.

Similar baths are capable of depositing nickel, cobalt, and/or copper, and mixtures thereof, in which the mixtures probably deposit in alloy form. We have found that if the bath contains, in addition to the foregoing ingredients, 35 grams of nonhydrated chromous acetate, the metal which deposits will contain between 2 and 5 percent chromium, possibly as an alloy of nickel and chromium. We have found further that if the composition of the bath is modified so that it contains not more than about 4 grams of sulfate ion per liter, generally the amount of chromium deposited in such a bath along with the nickel is usually in the range of 5 to 7 percent, and, finally, that if a 50 percent solution of hydrazine hydrate is added at the rate of approximately 1 drop per second during the deposition process to such a sulfate modified bath, that the amount of chromium which is deposited along with the nickel is in the range of 10 to 15 percent.

The specific composition of the bath which yields the simultaneous deposition of nickel and chromium is given in Table 3, which follows:

Table 3

Composition of Electroless Plating Bath For Deposition of Nickel-Chromium Alloy

Composition A - Primer Bath

| |
|---|
| 11 g of $NiSO_4 \cdot 6H_2O$ |
| 28 g of $Ni(OOCCH_3)_2 \cdot 4H_2O$ |
| 35 g of $Cx(OOCCH_3)_2$ |
| 10 g of methyl aminoborane |
| 25 g of sodium heptagluconate |

Above dissolved in 1 liter of water. Acidify to pH 6.5 by addition of 50 percent acetic acid.

Composition B - Replenisher

| |
|---|
| 100 g of $Ni(OOCCH_3)_2 \cdot 4H_2O$ |
| 10 g of $Cr(OOCCH_3)_2$ |
| 25 g of methyl aminoborane |
| 20 cc's of glacial acetic acid |

Above dissolved in 1 liter of water.

Whether or not the bath is designed to deposit nickel, cobalt, and/or nickel-chromium alloys, the bath is normally operated at 65°C to 70°C. If desired, composition A can normally be operated until substantially all the nickel content is exhausted. However, in practice, it is advisable to replenish the bath at fairly frequent intervals which is determined specifically by chemical analysis and subjectively by the speed at which the nickel normally deposits. A deposit thick enough to carry the desired wattage or electrical current required usually will deposit on a suitably prepared silver image in about 30 seconds to 2 minutes. When the deposition is about 3 minutes, this is equivalent to an exhaustion of 60 to 65 percent of the nickel content of the bath. When the deposition time required is around 4 minutes, this is

equivalent to an exhaustion of about 90 percent of the nickel content available from the bath. In practice, it is then normal to replenish the bath at about 60 percent exhaustion by adding thereto approximately 200 cc's of composition B which is designated as the replenisher, after which time the bath operates as effectively as previously. Another precedure for determining whether the bath needs replenishment is by measurement and control of the pH. Once the pH drops to a value of 3.5, the bath must then be replenished by adding measured portions of composition B in order to permit it to continue to operate in the manner desired for the purposes of this invention.

The chromium content in the electroless plate can be increased by using a combination of electroless plating and the application of an electromotive force. In this particular case, the catalyzed surface is exposed to the bath given in Table 3 in an electrolytic cell comprised of an inert container made of glass, or polyvinylchloride or other material not attacked by the electrolyte. A lead anode is provided, whose size is equivalent to the over-all size of the circuit to be prepared. A nickel image is first produced by immersion in the bath indicated as composition A in Table 3 for a period of about 30 seconds to 1 minute. Thereafter, electrical connections are made to the continuous nickel circuit by clamping, the circuit is then made the cathode in the electrolytic cell. An electrolysis is performed in a bath indicated as composition A in Table 3 at a current density of approximately 40 amperes per square decimeter at room temperature with a potential of approximately 10 volts. Under these conditions, and after about 5 to 10 minutes of electrolysis, a metal deposit of about 1 mil thickness is obtained which exhibits a chromium content of 20 to 25 percent, the balance being nickel.

This technique for preparing metal-plated images comprising a mixture of nickel and chromium, or an alloy thereof, may be further modified first by depositing electroless plating, followed by electrolytic chrome plating, which may or may not be followed by a flashing of electroless nickel plating on top the electrolytic chrome plating, and the sequence may be repeated as often as desired.

In this modification, electroless nickel is first deposited on the bleached silver image, using an aminoborane type of electroless plating bath which does not contain chromium. Using such a bath at 67°C, it is found that a layer of nickel approximately 0.8 mils thick is deposited in completely uniform fashion in approximately 1 to 2 minutes. The plated specimen is removed from the bath, washed with distilled water and dried. Using a lead anode and the metal image object as the cathode, metallic chromium is then deposited on the clean nickel at a current density of 45 amperes per square decimeter utilizing a bath containing 250 grams per liter of chromic acid and 2½ grams of sulfate ion per liter in the form of sodium sulfate. With such a bath, 1 mil of chromium can be deposited in 18 minutes. In order to achieve the desired alloy, the electrolysis is continued for a period of 6 minutes at room temperature, leaving a deposit of bright chromium firmly adhered to the nickel which is approximately 0.3 mils in thickness. After removal of the cathode from the bath containing the image circuit, the plate is again immersed in the electroless bath for a period of 30 seconds which leaves a 0.1 to 0.2 mil thickness of nickel overcoating the chromium. By use of the high temperature annealing treatments the nickel and chromium are diffused into each other so as to produce an alloy.

By this technique, substantially any ratio of nickel to chromium may be produced and it has found that for high temperature use a chromium content in the range of 20 to 40 percent is preferred.

The coatings which eventually become conductors of electricity in the devices manufactured in accordance with this invention have been based on nickel and alloys of nickel with chromium. However it is to be noted that cobalt may be substituted in whole or in part for the nickel and in many cases the presence of cobalt represents an advantage, particularly if overcoating with nonmetallic materials, such as high melting point glasses is utilized.

Once the conducting path of suitable thickness is produced, topcoatings of both an insulator and/or a conductor may be applied on top this conducting path by electrophoretic techniques. Mixtures of conductors and nonconductors may be also utilized.

After such electrophoretic coating is applied to the surface of the conductive coating, a post-treatment comprising heating or annealing the assembly in a controlled atmosphere at temperatures of the order of 1,200°C is often advantageous.

Examples of electrophoretic coatings which may be applied on nickel, cobalt, chromium or alloys thereof and which are useful for the purposes of this invention are described in examples which follow.

## EXAMPLE 6

A suspension is first prepared comprising a mixture of 2.5 grams of −325 mesh electrically fused aluminum oxide, 7.5 grams of nickel oxide (NiO) and 10 grams of the boron-aluminium-silicate glass known by the trade name "Pyrex" and 600 grams of isopropyl alcohol. The solids are first placed in an amount of isopropyl alcohol to yield a thick paste. Generally, a ratio of 25 grams of solids to 100 cc's of isopropyl alcohol is sufficient for this purpose. This is then ball milled utilizing one-fourth inch stainless steel balls and the milling is continued for 24 hours. The batch is then removed from the jar and diluted with the remaining isopropyl alcohol to yield the formulation given above.

Utilizing the metal-plated circuit as the cathode with a suitable connection supplied by clamping, a graphite anode in the form of a plate equivalent in size to the metal-plated circuit, an electrode spacing of 3 centimeters, a coating of 0.4 mils in thickness is obtained when the metal-plated circuit is made the cathode in about 10 seconds with an applied direct current of about 100 volts.

After the coated article is removed from the bath and dried, it is then annealed in hydrogen at 1,200°C for 30 minutes.

## EXAMPLE 7

The same as in Example 6, except that the electrophoretic mixture used to supply the coating is comprised of 2.5 grams of −325 mesh electrically fused aluminum oxide, and 7.5 grams of a powdered high vitrifiable glass.

## EXAMPLE 8

A variety of metal alloys are available in powdered form and when suitably sintered yield thermal and oxi-

dation resistant films on devices. These are usually alloys of nickel, chromium, iron, and cobalt and mixtures thereof with aluminum. An example of electrophoretic coating of a nickel-chromium composition which may be placed on top the nickel plated image as described previously will be used for definition of this technique of overcoating for beneficial modification of the metal-plated image.

While the example to be given relates the deposition of an alloy containing approximately 80 percent nickel and 20 percent chromium, it is understood that any ratio of nickel and chromium is available in powdered form and may be deposited in accordance with the description given hereinafter.

An electrophoretic bath is prepared in accordance with the composition given in Table 4.

Table 4

| Electrophoretic Coating To Produce An Alloy Of 80% Ni and 20% Cr | |
|---|---|
| Nickel Oxide (NiO.) (passing 325 mesh) | 8.6 gms |
| 80/20 Ni–Cr Powder (passing 325 mesh) | 43.4 gms |
| Nitromethane | 245 gms |
| Isopropyl alcohol | 111 gms |
| Zein | 0.8 gms |

The zein is in the form of a solution prepared in the following manner: 13 grams of Eastman Kodak technical grade zein is shaken for several hours with 1 liter of a mixture of isopropyl alcohol and nitromethane (60/40 percent by weight). The clear supernatant zein containing solution which results from this operation is decanted and checked for solids concentration. Sufficient stock solution is then added to a suspension vehicle to provide the necessary weight of zein.

Using a graphite anode, coatings of 2 to 3 mils in thickness are deposited on the metal image cathode in 30 to 60 seconds at 200 volts.

The electrophoretic coating is deposited on the nickel base and densified by heating in hydrogen or in vacuum at 1,200°C for 1 hour.

## EXAMPLE 9

The metallic circuit of either nickel of a nickel-chromium alloy made by either electroless plating or a combination of electroless plating and electrolytic plating may be freed completely from its metallic aluminum and aluminum oxide substrate, if desired. In these cases, this completely freed circuit may then be utilized as a base for electrophoretic depositon of the vitrifiable insulators defined in Example 6. The entire assembly is then fired under controlled conditions to yield an insulated encased conductor which may be free-standing for purposes of heating up to temperatures of about 1,400°F.

## EXAMPLE 10

FIG. **9** depicts in cross section a free-standing conductor resembling that in FIG. **8** except that the both aluminum metal layer **12** which remains in the sheet **10** after proper preparation of the conductor **20** and the aluminum oxide layer **14** are both dissolved completely away from the conductor **20** by the use of a 10 percent sodium hydroxide solution in water. This vigorous reagent does not affect the conductor **20.**

## EXAMPLE 11 (FIG. 10)

FIG. **10** depicts one type of connector which is preferred for preventing the connecting ends **24** or **52** of the conducting circuit from burning out in view of its thinness relative to its width. The connector comprises a block of copper **70** serving as a heat sink and connector to the connecting tabs **52** or **24.** One side of block **70** is provided with a thin slot **72** adapted to receive ends **52,** and the opposite side has an electrical lead **74** attached thereto by any suitable technique. The block **70** is substantially larger in lateral dimension than the width of tab **52.** In order to secure a good attachment of block **9** to tab **52,** a metal shim, e.g., a piece of 1 mil copper, is folded over tab **52** prior to insertion in the block. Connecting tabs **52** may be permanently bonded to the connector, heat sink block **70** in any suitable way.

We claim:

**1.** An electrical heating device in which the heat is produced by the resistance of an electrically conductive path at least a portion of which has been formed by deposition in the pores of an anodized layer comprising:

a metal substrate having a porous anodized layer on at least one surface thereof;

and an electrically conductive path consisting of metal deposited in the pores of said layer, said path consisting of precious metal selected from the group consisting of platinum, palladium, gold and silver, and an additional metal deposited on the precious metal of said path, said additionally deposited metal having a thickness adequate to provide a desired electrical resistance and said additional metal being selected from the group consisting of nickel, cobalt, chromium and mixtures thereof;

and a terminal at each end of said path.

**2.** The electrical heating device of claim **1** including in addition a connector for connection to each of said terminals comprising a heat sink block of metal having a slot in one face thereof adapted to receive said terminals and a metal conductor bonded to and extending from another face of said block.

**3.** The electrical heating device of claim **1** wherein the metal from which the porous anodized layer is formed is aluminum.

**4.** The electrical heating device of claim **3** including a non-porous layer of aluminum oxide underlying the porous anodized layer.

**5.** The electrical heating device of claim **3** including in addition a cover layer of ceramic, metal or high temperature glass.

**6.** An electrical heating device comprising:

a metal substrate consisting of an aluminum base, a barrier layer of aluminum oxide on said base and a porous surface oxide layer on said barrier layer;

a silver image of an electrically conductive path deposited in some of the pores in said surface layer;

a deposit of at least one metal selected from the group consisting of nickel, chromium and cobalt and mixtures, constituting an electrically conductive path on said image;

a protective coating enclosing said electrically conductive metal deposit.

* * * * *