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[54] **HEATING ELEMENT & METHOD OF MAKING**

[72] Inventors: **John K. Blatchford,** St. Joseph; **Edward C. Peterson,** Benton Harbor; **Jan C. Burda,** Eau CLaire, all of Mich.

[73] Assignee: **Whirlpool Corporation**

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[52] **U.S. Cl.**.....**219/543,** 117/70 A, 117/212, 117/217

[51] **Int. Cl.** **H05b 3/10,** B44d 1/18

[58] **Field of Search**.....117/217, 212, 70 A; 219/543, 219/549; 338/308, 309

[56] **References Cited**

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Primary Examiner—Alfred L. Leavitt
Assistant Examiner—Cameron K. Weiffenbach
Attorney—James S. Nettleton, Thomas F. Turcotte, Burton H. Baker, Gene A. Heth, Franklin C. Harter, Anthony Niewyk, Robert L. Judd and Hofgren, Wegner, Allen, Stellman & McCord

[57] **ABSTRACT**

A method of making a heating element such as a heating panel for an oven or other heating device comprising applying to a heat resistant base such as a metal panel a fired vitreous ceramic first coating, then applying over this first coating a fired vitreous ceramic second coating containing dispersed metal particles and then applying over this second coating a plating of metal chemically bonded to metal particles contained in the second coating and then applying over the metal plating a fired vitreous ceramic protective coating with the result that there is provided an electrically conducting resistant heating layer that is protected by the ceramic protective coating. The disclosure also includes the heating element so produced.

9 Claims, 4 Drawing Figures

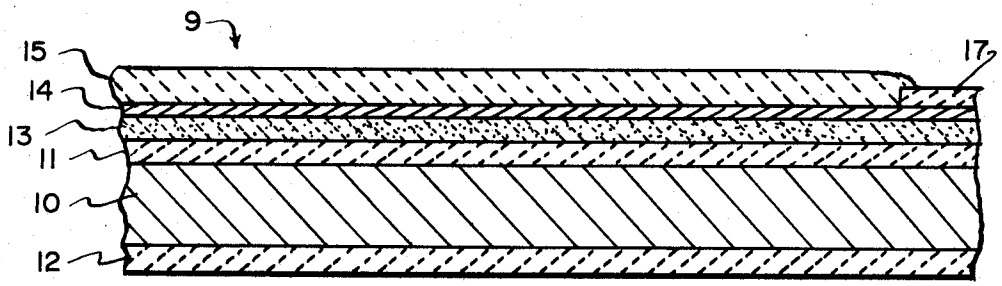


FIG.1

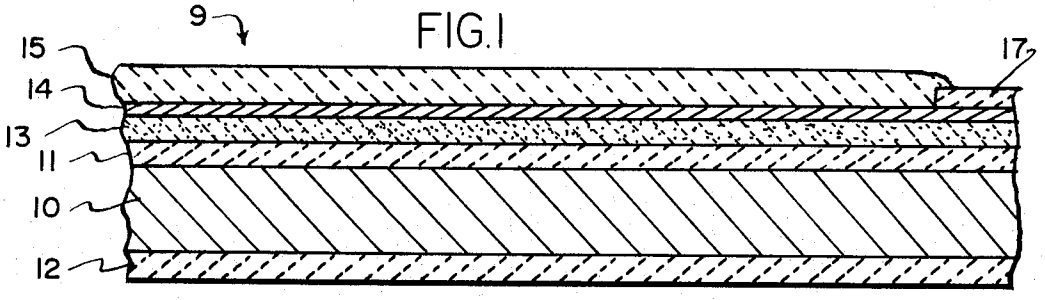


FIG.2

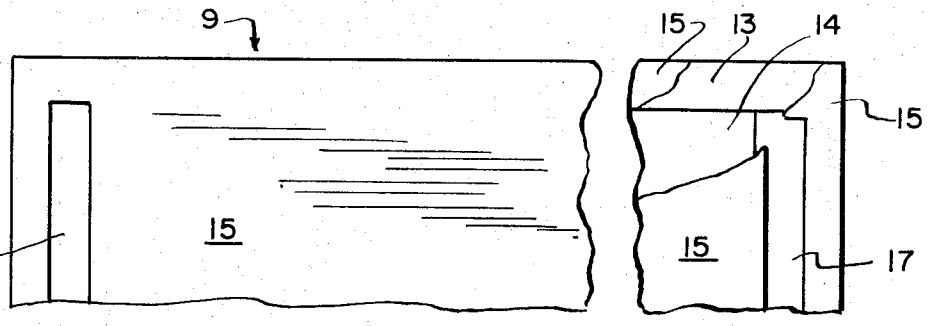
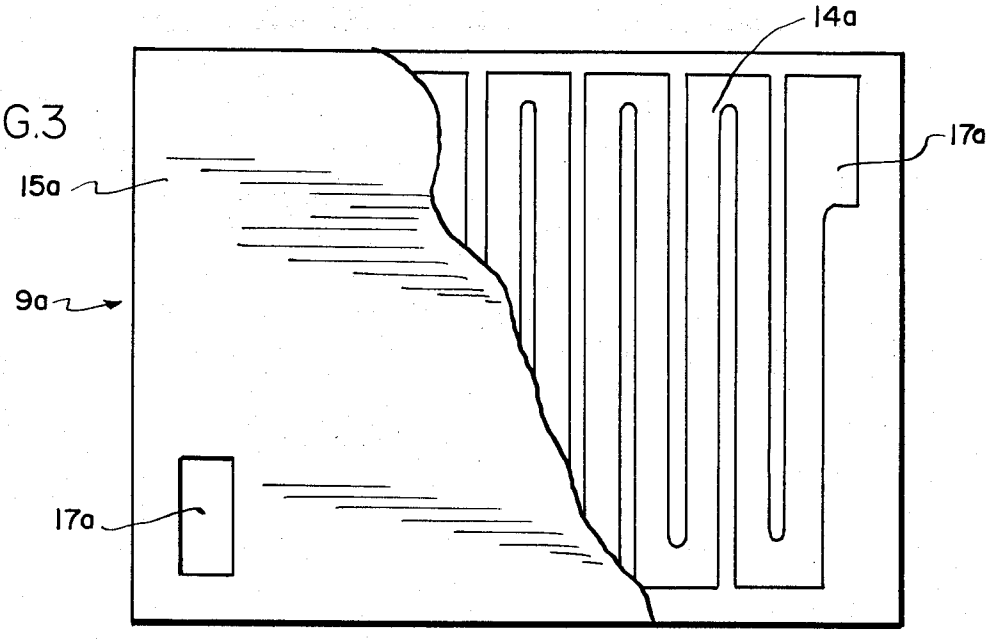


FIG.3



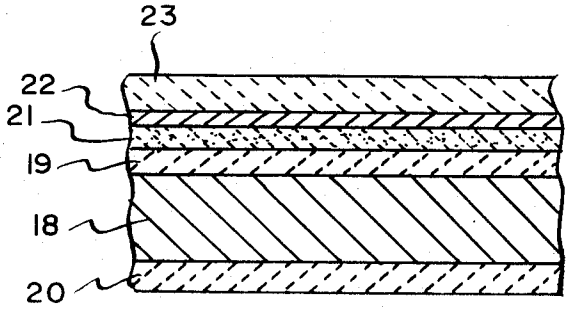


FIG.4

INVENTORS
JOHN K. BLATCHFORD
EDWARD C. PETERSON
JAN C. BURDA
BY Hofgren, Wegner, Allen, Stellman & McCord.
ATTORNEYS.

HEATING ELEMENT & METHOD OF MAKING

SUMMARY OF THE INVENTION

One of the features of this invention is to provide a method of making an improved heating element in which the heating member comprises a protected layer that is electrically conducting to function as a resistance heating element on a heat resistant support base.

Other features and advantages of the invention will be apparent from the following description of certain embodiments thereof taken in conjunction with the accompanying drawings. Of the drawings:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a fragmentary sectional view through a portion of a heating element embodying the invention with the layers thereof being magnified for clarity of illustration.

FIG. 2 is a fragmentary plan view of the heating element of FIG. 1.

FIG. 3 is a plan view of a second embodiment of the invention with the protective coating partly removed to illustrate details.

FIG. 4 is a view similar to FIG. 1 but illustrating another embodiment of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In preparing the heating element of the embodiment of FIG. 1 there is first provided a heat resistant base which may advantageously be a metal panel, for example, where the heating element **9** is to be used as an inner surface heating element in a cooking oven. Other applications include heated panels, heating utensils, heated counter tops, dryers, water heaters, space heaters and electric ranges.

The heat resistant base for heating element **9** could be ceramic instead of metal provided it was strong enough for the intended application.

In one embodiment the base comprises a sheet steel panel **10**. This metal panel **10** is coated on both sides with a first coating **11** and **12** of a fired on porcelain or other ceramic coating. Next, over one of these first coatings **11** there is applied a fired vitreous ceramic second coating **13** containing dispersed metal particles such as nickel particles distributed throughout with provision of enough particles to nucleate the plating applied to coating **13**. While nickel particles were utilized in the embodiment of FIGS. **1** and **2**, particles of copper, silver, or chromium-nickel could also be used. For coating **13** a useful composition has been found to be about 60% nickel to 40 percent porcelain, both by weight. In this composition Raney Nickel No. 28, a product of W. R. Grace & Company, Raney Catalyst Division, was used. Other nickels that can be used are Mond Nickel Powder Grade 128 MNP 696, average particle size 7–9 microns, a product of International Nickel Company (Mond) Ltd., London, England; and Nichrome Powder (Ni 80%; CR 20%) particle size less than **150** microns, a product of Varlacoid Chemical Company, Elizabeth, New Jersey. Other metals can also be used. Iron and cobalt can be used. Gold, platinum and palladium can also be used.

An example of the preparation of a nickel containing porcelain enamel slip is as follows: 100 grams of porcelain enamel slip (60 percent solids 40 percent water) and 67.5 g. Raney Nickel No. 28 containing 37.5 percent water was mixed in a Waring Blender for 3–5 minutes. Potassium Nitrite in water was added until the mixture was the proper consistency for spraying. The nickel containing slip was then sprayed on a porcelain enameled steel panel in a layer of about 1 mil thick, dried and fired in a furnace for approximately three minutes at a temperature of 1,500°F.

It has been found desirable to add a reducing agent such as sodium hypophosphite (NaH_2PO_2), sodium borohydride ($NaBH_4$) or stannous oxide (SnO), in the amount of 1 percent to 10 percent by weight of the porcelain enamel slip used in the coating, to the material of the metal particle containing coating **13**, and to the vitreous ceramic coating **15** referred to below, before the firing of these coatings. The addition of a reducing agent to the wet slip of coating **13** prevents excessive oxidation of the metal of coating **13** during such firing.

Next, in a preferred embodiment, there is applied to this second coating a metal layer **14** in contact with the metal particles of the coating **13**. The metal particles of the coating **13** need not be present in sufficient quantity to provide an electrically conductive layer themselves. However, coating **13** must contain enough metal particles to nucleate the plating or application of metal layer **14**. The metal layer here may be nickel and is preferably applied by the well known electroless metal deposition process which involves chemical deposition of an adherent metal coating to the second coating substrate in the absence of an external electric source.

The utilization of porcelain coatings **11** and **12** is not essential providing that the metal particles in the layer adjacent the metal panel **10** are sufficient to give nucleating sites for the electroless plating to form metal layer **14**, but insufficient to give a conductive layer after firing.

In one method of applying the metal coating **14** the exposed surface of the particle containing coating **13** is abraded as with sand paper in order to expose metal particles.

Another way of exposing these metal particles is by chemical etching of which examples of etching solution are 1 percent hydrofluoric acid in water applied for 2 or 3 minutes, 2 percent by volume of sulfuric acid in water applied for the necessary time up to 10 minutes, or 4 percent phosphoric acid by volume in water for the necessary time up to 20 minutes. These times will of course vary in the well known manner depending upon the type of porcelain used.

When thusly exposed the metal such as nickel layer **14** is chemically bonded to the exposed nickel particles. This bonding provides secure anchoring of the metal layer to the porcelain layer **13** thereby providing considerable mechanical strength. Another very important advantage is that the chemically bonded metal film when heated electrically during use provides good distribution of heat as the particles that are bonded to the metal layer distribute heat throughout the panel structure. This results in a lower temperature of operation of the nickel layer. The bonding of the metal such as nickel layer **14** to the metal particles in layer **13** improves heat transfer throughout the heating element,

thereby reducing the possibility of developing hot spots or overheated areas with subsequent burn out.

An alternate method of applying the plated metal layer **14** is set forth below. Just prior to plating metal layer **14** the area of the metal panel containing the second coating **13** is sensitized as follows: The area of the metal panel containing coating **13** is well cleaned, and then the well cleaned surface is coated with an aqueous solution containing 10 g/liter stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$) and 40 ml/liter concentrated hydrochloric acid (37% HCl) for one minute. The solution is rinsed off well with water and the surface coated with an aqueous solution containing 0.3 g/liter palladium chloride ($PdCl_2$) and 3.0 ml/liter concentrated hydrochloric acid (37% HCl) for 1 minute. The last step with the palladium chloride solution is called activating. Platinum chloride can also be used for activation.

Sodium hypophosphite and a hydrazine solution can also be used for sensitizing.

After sensitizing and activating the metal plating by the electroless metal deposition process as described above may then be accomplished in a very short time which may be as little as 2 minutes.

After the metal layer **14** has been deposited, there is applied an overlying fired vitreous ceramic protective coating **15** that covers the metal layer **14** (except at terminal portions thereof as described below) and provides protection to metal layer **14**.

The fired ceramic coatings **11**, **12**, **13** and **15** may be porcelain. The ceramics of the various layers may be the same or may be different.

As stated above, coating **15** should preferably include a reducing agent and the addition of such reducing agent minimizes oxidation of metal layer **14** during the firing of layer **15**.

For low temperature applications, where metal layer **14** does not reach a temperature high enough for an objectionably rapid rate of oxidation to take place, protective coating **15** may be omitted.

An electric current may be conducted through the metal layer **14** by electric terminals **16** and **17** affixed to metal layer **14** at opposite ends of the heating element. In one embodiment the terminals **16** and **17** were provided by applying a layer of silver paint to the opposite ends of metal layer **14**. A suitable silver paint for terminals **16** and **17** is Engelhard Industries, Inc., Hanovia Liquid Gold Division, Squeegee Organic Silver No. 9124.

In FIG. **2** a portion of coating **15** is removed to illustrate the relationship of electrically conductive metal layer **14** to the underlying metal particle containing coating **13**. Additionally, FIG. **2** illustrates that protective coating **15** partially overlies edge portions of terminals **16** and **17** for added protection for the edge portions of the terminals.

In some applications the voltage specifications of the current source or other reasons may make it advantageous to provide a heating element **9*a*** with a metal layer **14*a*** in the form of a serpentine path as illustrated in FIG. **3**. The serpentine path is obtained by dipping or spraying over a porcelain enamel coating on a steel panel a conventional photosensitive resist material and then hardening and baking the resist in the absence of ultraviolet light.

Then, using a photographic negative in which the black areas are the serpentine path areas to be plated, the photo resist coated panel is exposed to ultraviolet light through the negative.

The photo resist is selectively removed from those areas not receiving light by washing the exposed panel with a developing agent which will remove the photo resist.

After a short bake to harden the photo resist the exposed areas are plated by the electroless metal deposition process referred to above. The unwanted photo resist material along with any plating that has occurred on it is then removed with a suitable photo resist remover.

An alternative method to obtain the serpentine path is to use a positive photographic film having the desired serpentine path image in the exposure process on a panel which has been plated with nickel prior to coating with photo resist. Then the nickel layer in the unwanted areas is etched away with an etching solution such as nitric acid.

The end portions of serpentine metal layer **14*a*** may advantageously be enlarged to form terminals as indicated at **17*a***. Heating element **9*a*** may then be coated with a protective fired vitreous ceramic coating **15a**.

FIG. **4** is similar to the FIG. **1** embodiment in that there is also provided a heat resistant base **18** which may be a metal panel and a fired vitreous ceramic first coating **19** and **20** as indicated in FIG. **4**. Then on one of these coatings **19** there is sprayed a masked area of porcelain enamel slip. The porcelain enamel slip particles need not contain dispersed metal particles since the porcelain coating will accept a layer of metal deposited by electroless metal deposition following treating of the coating as described below.

The mask is removed and the dried porcelain enamel slip or bisque is partially fired to provide a coating **21** having a porous surface. This porous surface is activated with stannous chloride solution, washed, and sensitized with a palladium chloride solution as described above and then electroless metal plated using nickel, for example, to give a nickel layer **22** capable of being heated electrically. The porosity of the surface of coating **21** facilitates the plating process by providing indentations in which the nickel is received providing positive adhesion between coating **21** and metal layer **22**. A cover coat of porcelain enamel **23** is applied over the nickel layer **22** leaving exposed areas (not shown) at each end which may be coated with a silver paint and used as the terminal connections similar to the terminals **16** and **17** of FIGS. **1** and **2**.

Having described our invention as related to the embodiments disclosed in the accompanying drawings, it is our intention that the invention be not limited by any of the details of description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

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

1. A heating element, comprising: a heat resistant base; fixed thereto a fired vitreous ceramic coating containing dispersed metal particles; a plating metal layer in contact with metal particles in said coating, said metal particles being present in sufficient quantity

to nucleate said plating metal layer; and an overlying fired vitreous ceramic protective coating.

2. The heating element of claim 1 wherein said heat resistant base comprises a metal panel having a pair of opposite surfaces, a first coating is fixed to both said surfaces, and said coating containing said metal particles is fixed to one only of said first coatings.

3. The method of making an electrical resistance heating element, comprising: applying to a heat resistant base a fired vitreous ceramic coating containing dispersed metal particles; treating the coating so that it will accept a layer of metal deposited by electroless metal deposition; and applying over said ceramic coating by electroless metal deposition a layer of metal.

4. The method of claim 3 wherein the treatment applied to said coating comprises partial removal of surface portions to increase surface exposure of said metal particles in said coating.

5. The method of claim 3 wherein said coating is partially fired to provide a porous surface to receive said metal layer and the treatment applied to said coating comprises sensitizing and activating the surface of said coating.

6. The method of making a heating element, comprising: applying to a heat resistant base a fired vitreous ceramic first coating; applying over said first coating a fired vitreous ceramic second coating containing dispersed metal particles; plating over said second coating a metal layer in contact with metal particles in said second coating, said metal particles being present in sufficient quantity to nucleate said plating metal layer; and applying over said plating metal layer a fired vitreous ceramic protective coating.

7. The method of claim 1 wherein said dispersed metal particles are protected from oxidation by incorporating in said vitreous ceramic second coating prior to firing a reducing agent activated during the firing of said second coating to minimize oxidation of the metal particles.

8. The method of claim 1 wherein said heat resistant base comprises a metal panel having a pair of opposite surfaces, said first coating is applied to both said surfaces, and said second coating is applied to one of said first coatings.

9. The method of claim 1 wherein said second coating is partially removed to increase the surface exposure of said particles prior to applying said metal layer.

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