Jan. 9, 1968 R. C. LANGLEY 3,363,090

ELECTRIC HEATING ELEMENT

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FIG. 1

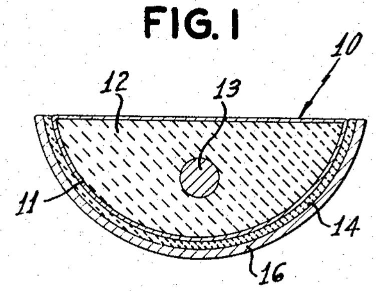
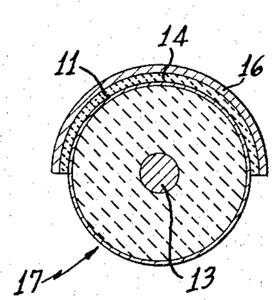


FIG. 2



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ELECTRIC HEATING ELEMENT

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ABSTRACT OF THE DISCLOSURE

This application discloses an electric heating element comprising an electrical resistance embedded in electrical insulation and enclosed in a metallic sheath which is provided with a low emissivity gold coating and a thin barrier layer of refractory oxide intermediate the sheath and the gold coating.

This invention relates to electric heating units, and more particularly to electric heaters of the sheathed type such as are employed in domestic appliances e.g. electric ranges, radiant heaters and the like.

The conventional electric or "strip" heater which is now in use includes a jacket which is normally formed of metal, heated by passing an electric current through a heating element disposed within the jacket. The jacket thereby becomes hot, and this heat, in the case of surface heaters, is transmitted to cooking utensils resting on one surface of the jacket which is fabricated in planar configuration for this purpose. In the case of broil heaters or radiant heaters, the jacket is normally cylindrical in cross section.

It is appreciated that such electric heaters are normally employed in applications wherein the heat output is usefully employed on only one side of the heater. Thus the surface area of the heater not in contact with the cooking utensil, or not facing the material to be heated as in radiant heaters, radiates useful heat wastefully. Various attempts have been made in the past to reduce this heat loss by directing this lost, radiant energy back in the useful direction by use of parabolic aluminum reflectors and by coating the heater on one side with a coating of low emissivity to reduce radiation from that side.

The present invention has as its principal object the provision of an improved electric heating element which will direct the major portion of the heat in one direction.

It is another object of the invention to provide a sheathed electric heater having an improved low emissivity coating upon the surface of one side to reduce radiation from that side.

These and other objects as will hereinafter appear will be apparent from the following description, the appended claims and the accompanying drawing, wherein

FIGURE 1 is a cross section of the electric heating element of the invention adapted for heating cooking utensils by conduction, and

FIGURE 2 is a cross section of the electric heating element of the invention adapted for radiant heating.

Referring now to the drawings, and more particularly to FIGURE 1, the strip heater which is designated by the reference character **10** comprises an elongated sheath of suitable metal **11**, such as stainless steel, nickel chromium alloy or other high temperature metal enclosing a compacted mass of refractory, electrical insulating heat conducting material **12** such as magnesium oxide, aluminum oxide, zirconium silicate or other suitable material. Embedded in the refractory material is a suitable electric heating element **13**. The upper surface of the heater **10** comprising the high temperature metal sheath is usually flat for maximum transfer of heat by conduction from the heater to the utensil which is superposed thereon in use.

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According to the present invention, the surface of the strip heater other than the top surface thereof is provided with a coating of low emissivity to reduce the loss of heat due to radiation in the undesired direction. Such coating consists of two layers, shown in greatly enlarged cross section as coating **14** and coating **16** in FIGURE 1. Coating **14**, applied directly to the metallic sheath of the heating element, comprises a thin barrier layer of a refractory material as more fully described hereinafter, and is interposed between the metal sheath **11** of the heater and coating **16** which comprises a low emissivity gold coating, for the purpose of preventing interdiffusion of the gold and the metal of the sheath.

Referring to FIGURE 2, wherein like numerals designate the same structural features as referred to in connection with FIGURE 1, a strip heater **17** of cylindrical cross section is shown in section. Such a heater is employed, for example, in oven heating units where the material to be heated is heated by radiant heat energy. In such heater, the coatings **14** and **16** are deposited upon the upper half of the strip heater, so as to prevent loss to heat in an upward direction. It will be appreciated that more or less of the exterior surface of the strip heater may be coated with the low emissivity coating, depending upon the particular requirements to which the heater is put, and that the particular shape of the heater, whether round, triangular, hemispherical or the like is similarly dependent upon such requirements and does not constitute a limitation upon the present invention.

Unlike low emissivity enamel layers which have heretofore been taught as suitable for reducing radiant heat loss from portions of the surface of electrical strip heaters, the diffusion barrier layer **14** is essentially a thin layer of thickness between about 200 and about 1000 Angstrom Units, and preferably between about 400 and about 800 Angstrom Units in thickness. Such thin diffusion barriers provide materially better bonding of the low emissivity coating to the metallic base despite inherent differences between these layers in expansion and contraction due to thermal cycling of the heater. Further, such thin diffusion barriers are entirely unlike thicker enamel coatings which tend to spall and flake off of the heater due to differential expansion effects.

The low emissivity coating **16** which constitutes the outermost layer of the heater of this invention comprises a thin gold film, consisting essentially of gold or alloys of gold containing up to about 10% by weight platinum or palladium. Gold is the preferred coating for low emissivity, and gold with minor amounts of rhodium added for thermal stability is particularly advantageous. Excellent results have been obtained with metal films consisting of gold—5% by weight palladium, gold—10% palladium plus 0.05% rhodium and gold—0.5% rhodium.

The preparation method for producing the electric strip heater, in its broadest aspects, involves applying a thin layer of a refractory oxide onto the metallic sheath of the heater, for example stainless steel or nickel-containing alloy such as "Inconel," followed by applying over the diffusion barrier of refractory oxide a thin coating of a liquid gold containing composition comprising a soluble thermally decomposable organo-compound of gold, compatible compounds of fluxing elements, an organic solvent for the organo compound of gold and one or more soluble thermally decomposable organo cmpounds of platinum group metals where it is desired to form a gold alloy film. The gold containing composition is fired on the diffusion barrier at a temperature sufficiently elevated to decompose the organo compounds of the metals and to form a thin low emissivity gold film on the surface of the heating element.

The emissivity of a material is an intrinsic property, though it varies somewhat with surface finish and with temperature. In the case of very thin gold films, it has been found that emissivity reaches its minimum value when transparency to infrared radiation becomes a minimum, that is, when the thickness of the film is just sufficient to transmit no infrared energy; this thickness is about 1200 A. Greater thicknesses, e.g., 2500 A., give no improvement in emissivity and thus are wasteful of material, but such thicknesses can be used when desirable for some other reason, e.g., greater resistance to abrasion or to chemical attack.

For the particular application of the present invention, it is preferred that the gold film be from about 1000 A to about 0.2 mils thick. It is particularly desirable that the thickness be from 1200 to 1800 A. since this range is obtainable in a single application of an organic gold solution, and also assures a minimum emissivity value.

The liquid gold composition which is applied over the barrier layer to form the low emissivity coating is preferably a liquid bright gold composition. "Liquid bright gold" is well known in the art as a solution of an organo-gold compound, for instance a gold sulforesinate, in an organic decorating vehicle containing essential oils, and also containing minor amounts of compatible compounds of fluxing elements, for instance of rhodium, bismuth and chromium. A gold mercaptide can be utilized in place of the gold sulforesinate. The liquid bright gold, when applied to a refractory substrate or surface and fired to drive off or burn off the organic material present, results in lustrous thin films. Liquid bright golds are described in Chemnitus, J. Prakt. Chem. 117, 245 (1927) and by Ballard in U.S. Patent 2,490,399.

Liquid bright gold compositions generally contain the organo gold compound in amount equivalent to about 7–20 percent gold by weight, with the compatible compounds of the other fluxing elements or metals, for instance rhodium, chromium and bismuth, normally contained therein being present in relatively minor quantities. The organo compound of the rhodium is usually present therein in amount equivalent to about 0.03–0.10 percent Rh by weight, the organo compound of chromium in amount equivalent to about 0.02–0.06 percent Cr_2O_3, and the organo compound of bismuth in amount equivalent to about 0.10–0.50 percent Bi_2O_3 with the remainder being the vehicle. Where it is desired to produce a gold alloy film containing up to 10% by weight platinum or palladium, organo compounds of these metals may be substituted for a part of the organo gold compound but the film will then have a bright silvery appearance, rather than a gold color. Such compositions are commercially available as Bright White Gold. Organo compounds of nickel and cobalt can replace the compounds of chromium and bismuth as fluxing elements in the formulation if desired. In place of the soluble organo compounds of the rhodium, chromium, bismuth or other fluxing elements in the liquid bright gold, compatible inorganic compounds can be used including rhodium chloride, chromium chloride and bismuth trichloride or nitrate.

The barrier layer, which is applied over the metallic sheath prior to application of the low emissivity gold layer, is essential for preventing interdiffusion of the gold and the metallic base. In the absence of such a diffusion barrier, the gold of the low emissivity coating will interdiffuse with the metallic sheath to the extent of actual disappearance of the gold, and concomitant increase in the emissivity of the coated portion of the electric heating element. The material of the diffusion barrier layer is a refractory oxide, and exemplary of such materials are cerium oxide, aluminum oxide, nickel oxide and the like. Cerium oxide is preferred.

The material of the diffusion barrier is preferably a dielectric material, i.e. a material non-conductive to electricity or having an electrical resistivity of at least 50,000 ohms. The reason for this is that metals do not diffuse in dielectric solids or do so at rates materially lower than diffusion rates of metals in non-dielectric materials.

The refractory oxides which are employed as diffusion barriers can be applied to the metallic sheath of the heater by conventional methods, provided however that the resultant coating is extremely thin i.e. of the order of 200 to 1000 Angstrom Units in thickness. For example, cerium oxide can be applied on the metallic base by vacuum deposition, aluminum oxide by flame spraying and nickel oxide by electroplating followed by heating the nickel-plated sheath in air. These application methods are conventional and well known. A preferred way of applying the refractory oxide is to prepare a solution of an organo compound of the metal in an organic solvent, then to spray or brush the solution over the metal sheath as a thin layer, followed by firing the sprayed on layer in air at temperatures of 300–800° C. to drive off organic matter and to convert the organo metal compounds to their respective oxides. The latter method is particularly preferred in the practice of the present invention in order to prepare thin, adherent barrier films which will not spall or flake due to differential thermal expansion on thermal cycling of the electric heater.

As hereinbefore set forth, the electric strip heater of this invention, except for the low emissivity coating and barrier layer, is of conventional construction and need not be further described. The sheath of such heaters is normally of stainless steel, nickel-chromium alloy, or the like high temperature resistant metals having high emissivity, and suitable for the application of the diffusion barrier layer and low emissivity gold coating as described herein.

The following examples further illustrate the invention.

Example 1

An electric strip heater of hemispherical shape as shown in FIGURE 1 and having an Inconel sheath was coated on the cleaned curved bottom side with a solution of cerium resinate having the following composition:

Ingredient:	Parts by weight
Cerium resinate dissolved in a mixture of oil of rosemary, nitrobenzene and toluene (5% CeO_2)	36.0
Rosin dissolved in oil of turpentine (50% rosin)	27.0
Oil of rosemary	9.0
Hexalin	9.0
Toluene	9.0
	90.0

The resulting clear brown solution contained 2.0% cerium calculated as CeO_2.

The film was heated in air to about 700° C. by passing electric current through the heater to form a thin layer of cerium oxide of approximately 500 Angstroms thickness.

Thereafter, the following liquid bright gold solution was brushed over the cerium oxide layer:

Ingredient:	Parts by weight
Gold tert-dodecyl mercaptide dissolved in cyclohexanone (35% Au)	286
Rhodium resinate dissolved in a mixture of essential oils and hydrocarbons (1% Rh)	50
Bismuth resinate dissolved in a mixture of essential oils (4.5% Bi)	70
Chromium resinate dissolved in a mixture of cyclohexanone and oil of turpentine (2.05% Cr)	20
Asphalt dissolved in oil of turpentine (30% asphalt)	200

Ingredient: Continued	Parts by weight
Rosin dissolved in oil of turpentine (50% rosin)	200
Chloroform	100
Nitrobenzene	70
Oil soluble red dye	4
Total	1000

The clear dark red solution containing about 10% gold, 0.5% rhodium, 0.32% bismuth, 0.4% chromium, 6% asphalt and 10% rosin was applied by brushing, and the gold film developed thermally at about 300° C. using the resistance wire of the electric strip heater as the source of heat. Heating was then continued to 700° C. to firmly bond the film to the cerium oxide diffusion barrier. The gold film was about 1200 Angstroms thick, and of a bright lustrous gold color.

The emissivity of the uncoated electric strip heater was tested by comparison with oxidized Inconel working standards available from the National Bureau of Standards. The metal sheath of the heater (uncoated top surface) had an emissivity of 0.8. The coated surface prepared as above had an emissivity of about 0.05.

Electric strip heaters coated as above were tested for 5000 hours at temperatures of 1050°, 1250° and 1450° F. The samples tested at 1450° F. showed a slight deterioration in the emissivity of the coated surface. Those tested at 1050° and 1250° F. showed no change.

In contrast, an electric strip heater which was coated with liquid bright gold in the absence of the cerium oxide diffusion layer showed low emissivity when first heated, but failed due to a rapid rise in emissivity of the coated surface after heating at 1050° F. for less than 50 hours.

Example 2

It is known that a thin film which contains 95:5 Au:Pd by weight has a slightly lower emissivity than a pure gold film. Commercial solutions, known as Bright White Gold, are available. These are made by substituting palladium for part of the gold in a liquid bright gold solution. For example, the solution of Example 1 is repeated with the same amount of solvents, but only 271.7 grams of the gold solution are used. 25 grams of a 20% Pd solution made by dissolving dichloro-bis di n-butyl sulfide Pd II in toluene are added. The fired film obtained from this solution will contain a 95:5 Au:Pd alloy by weight.

A flat piece of Inconel, two inches square, was honed to a surface finish of about 5 microinches. Cerium oxide was applied by vacuum deposition in a uniform, semi-bright film which weighed 3.4 mg./cm.^{2}.

A Bright White Gold solution was applied over the vacuum deposited cerium oxide film and developed to the metallic state by firing gradually in air to a peak temperature of 600° C. An adherent white metal film having the characteristic white metallic color of Au:Pd alloys resulted. The film was about 1300 Angstroms thick and had, at elevated temperatures, a slightly lower emissivity than that of pure gold films. Interdiffusion of the White Gold film and the substrate is prevented for prolonged periods at elevated temperature by the cerium oxide diffusion barrier applied in this way.

Example 3

Effective diffusion barriers can be made with refractory oxides other than cerium oxide.

To obtain very thin aluminum oxide diffusion barriers, the following solution was made:

Ingredient:	Parts by weight
Aluminum resinate dissolved in a mixture of oil of rosemary, nitrobenzene and toluene (5% Al_2O_3)	33.3
Rosin dissolved in oil of turpentine (50% rosin)	33.3
Oil of rosemary	11.1
Hexalin	11.1
Toluene	11.2
	100.0

The dark brown, fluid solution resulting after mixing contained 1.67% aluminum calculated as Al_2O_3.

Three thin coats of this solution were applied by spraying to a honed Inconel specimen as in Example 2. Each coat was fired gradually to 600° C. in air. The iridescent film which resulted was about 1000 Angstroms thick. A 95:5 Au:Pd alloy was applied over this diffusion barrier in the same manner as described in Example 2. When tested at 600° C. for 50 hours, there was no change in the optical properties of the Au:Pd film.

It has been determined that lowering the emissivity of of the underside surface of range-top burners of semicircular design as shown in FIGURE 1 from 0.8 even to 0.55 significantly lowers the loss of energy by radiation, and that a coating having an emissivity of 0.55 achieves a burner temperature 150° F. higher with the same input of power, or achieves the same operating temperature with substantially lower power consumption. The present invention permits manufacture of electrical strip heaters in which designated portions of the surface have, and maintain for long periods of time at elevated temperatures, emissivity of less than 0.1, thus offering substantial economic and engineering advantages in the design and utilization of such heating units.

What is claimed is:

1. An electric heating element including a sheathed tubular heating unit having an electrical resistance embedded in electrical insulation and enclosed in a metal sheath, said sheath having a portion of its surface provided with a low emissivity gold coating, and a thin barrier layer of a refractory oxide intermediate said sheath and said gold coating, said barrier layer being between about 200 and about 1000 Angstrom Units in thickness.

2. The electric heating element of claim **1** wherein said barrier layer comprises cerium oxide.

3. The electric heating element of claim **1** wherein said barrier layer comprises aluminum oxide.

4. The electric heating element of claim **1** wherein the gold coating comprises gold and alloys thereof containing up to 10% by weight of a member of the group consisting of platinum and palladium.

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