# United States Patent [19]

**De Luca**

[11] **3,808,574**

[45] **Apr. 30, 1974**


[54] **MAGNESIUM AND MAGNESIUM OXIDE RESISTOR AND METHOD OF FORMING**


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[22] Filed: **May 7, 1973**

[21] Appl. No.: **358,070**

[52] **U.S. Cl.** .................... **338/258,** 29/613, 29/620, 117/118, 117/222

[51] **Int. Cl.** .................... **H01c 1/02**

[58] **Field of Search** .......... 338/258, 273; 117/222, 117/107 R, 118; 29/613, 620


[56] **References Cited**

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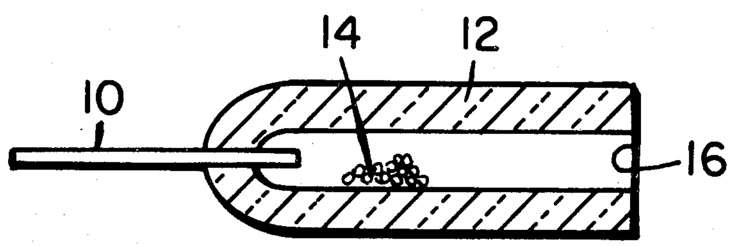
[57] **ABSTRACT**


An insulated electrical resistor comprising a glass tube having a conductive cermet layer on the inner surface thereof. A conductive lead wire is sealed to each end of the tube, the end of each lead wire extending into the tube and making electrical contact to the cermet layer. This resistor is formed by disposing a measured amount of magnesium in a glass tube and sealing the two lead wires thereto. The assembly so formed is heated to a temperature greater than 300°C but less than the softening point of the glass to cause the magnesium to vaporize and react with the oxygen within the sealed tube to reduce the pressure therein and to react with the inner surface of the tube to form the conductive cermet layer.


**13 Claims, 5 Drawing Figures**



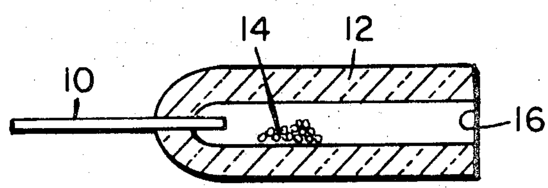



*Fig. 1*

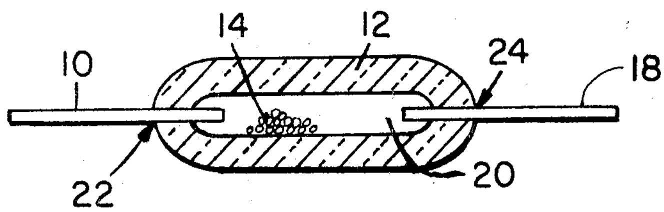



*Fig. 2*

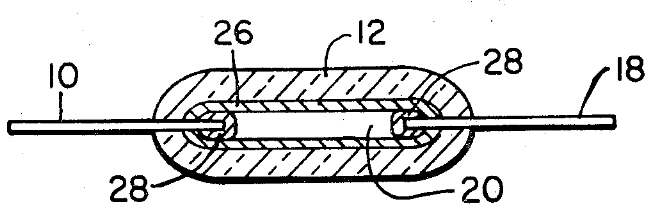



*Fig. 3*

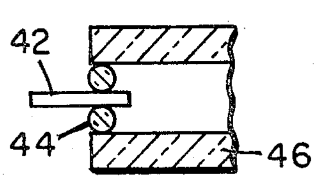



*Fig. 4*

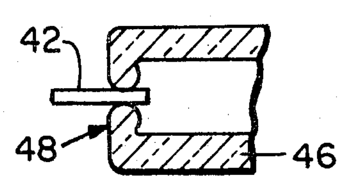



*Fig. 5*

# MAGNESIUM AND MAGNESIUM OXIDE RESISTOR AND METHOD OF FORMING

## CROSS-REFERENCES TO RELATED APPLICATIONS

This application is related to U. S. patent application Ser. No. 358,014 entitled "Encapsulated Impedance Element and Method" and Ser. No. 358,013 entitled "Method of Forming Conductive Layer on Oxide-Containing Surfaces" both filed on even date herewith.

## BACKGROUND OF THE INVENTION

This invention relates to an insulated electrical resistor and method of making the same.

Electrical resistor elements usually consist of an electrically conductive wire wound on the surface of an insulating substrate or an electrically conductive film disposed on the substrate surface. To form a completed resistor from such an element lead wires are attached to the ends of the electrically conductive wire or film and the element is provided with a nonconductive sleeve or coating which hermetically seals and electrically insulates the element.

Hermetically sealed resistors have been made by forming a resistive film on the inner surface of a glass or ceramic tube. U.S. Pat. No. 2,717,946 issued Sept. 13, 1955 to D. B. Peck teaches a resistor which is formed by passing a reducing gas such as hydrogen, methane, illuminating gas, or the like through a heated tube of reducible material, preferably lead oxide or bismuth oxide. After the inside surface of the tube is reduced to provide a resistance coating, terminal wires may be inserted in the ends of the tube which are sealed to provide a finished resistor. The method of the Peck patent requires that the material from which the tube is formed contain at least one oxide that is reducible by one of the aforementioned reducing gases and further requires that lead wires be connected to the ends of the tube after the reducing step is performed.

Another prior art method of forming a resistance film on the inner surface of a tube is taught in U.S. Pat. No. 2,961,352 issued Nov. 22, 1960 to W. Grattidge et al. That patent teaches the formation of a resistive film on the inner surface of a hollow ceramic cylinder by spraying that surface with a solution of an easily reducible oxide such as $Fe_2O_3$, $TiO_2$ or $ZrO_2$. A pair of metallic end caps are affixed to the ends of the cylinder by placing the assembled parts in an evacuated container while increasing the temperature thereof to about 1,000°C. During the high temperature treatment, hydrogen is released from some portion of the combination such as a nickel shim and reduces the oxide coating. This method is disadvantageous in that it requires that the inner surface of a hollow ceramic cylinder be initially coated with an oxygen bearing compound which is reducible by hydrogen, and it must be performed in an evacuated chamber.

## SUMMARY OF THE INVENTION

It is an object of the present invention to provide an inexpensive method of forming insulated electrical resistors.

Another object of the present invention is to provide an insulated electrical resistor having a resistive film formed by the reaction of magnesium vapor with an oxide-containing surface such as glass, glass-ceramic and ceramic.



Briefly, the resistor of the present invention comprises a hollow, hermetically sealed enclosure of oxide-containing material such as glass, glass-ceramic and ceramic. A pair of electrically conductive lead wires extend through the enclosure at spaced locations. A conductive cermet layer including magnesium and magnesium oxide is disposed on the inner surface of the enclosure, the cermet layer contacting that portion of each of the lead wires which extends into the enclosure.

This resistor is formed by providing a hollow enclosure of oxide-containing material having a pair of apertures therein. A measured amount of magnesium is disposed in the enclosure. An electrically conductive lead wire is sealed in each of the apertures to form a hermetically sealed cavity, an end of each of the lead wires extending into the cavity. The assembly so formed is heated to a temperature greater than 300°C which is sufficient to cause the magnesium to vaporize and react with oxygen within the cavity to reduce the pressure therein and to form a conductive cermet layer in the inner surface of the enclosure, the cermet layer making electrical connection to both of the lead wires.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. **1, 2** and **3** illustrate the steps of the preferred method of the present invention. FIGS. **1** and **2** illustrate the sealing of magnesium into a glass tube having a pair of lead wires extending therefrom. FIG. **3** shows the finished resistor.

FIGS. **4** and **5** illustrate an alternative method of sealing lead wires to the end of a tube.

## DETAILED DESCRIPTION

FIGS. **1, 2** and **3** illustrate the steps of the preferred method of the present invention. As shown in FIG. **1**, lead wire **10** is sealed to one end of glass tube **12**, and a measured amount of magnesium **14** is then inserted into aperture **16** in the opposite end thereof. A second lead wire **18** is then inserted into aperture **16** and that end of tube **12** is heated and caused to seal thereto, thereby forming a hermetically sealed enclosure containing cavity **20**. The lead wires may be sealed in the ends of tube **12** by inserting an end of each wire into the tube while applying sufficient heat thereto to cause the end thereof to soften and collapse onto the adjacent wire, thereby forming seals **22** and **24** of FIG. **2**.

The assembly shown in FIG. **2** is heated to a temperature greater than 300°C but below the softening point of glass tube **12** to vaporize the magnesium and cause it to react with the oxygen in cavity **20** to reduce the pressure therein and to form cermet layers **28**. The magnesium vapor also reacts with the inner surface of glass tube **12** to form cermet layer **26**. Whereas layers **28** contain only MgO and Mg, layer **26**, which is disposed on the inner surface of the oxide-containing walls of tube **12**, also contains reaction products resulting from the reduction of those oxides, i.e., magnesium intermetallic compounds and the metallic constituents of the oxides of glass tube **12**. A sufficient amount of magnesium should be used to form a cermet layer having a thickness between 0.1 and 10 micrometers.

Lead silicate glass has been reacted with magnesium vapor at temperatures as low as 300°C. The reaction of such a glass at a temperature between 300°C and 330°C results in the formation of $Mg_2Pb$, $Mg_2Si$ and MgO. The same glass reacts with magnesium at a temperature between 330°C and 440°C to form Pb, MgO, $Mg_2Si$ and Si. If the temperature of this reaction is increased to 500°–600°C the resultant cermet will contain Pb, MgO and Si. At temperatures under 300°C magnesium metal was deposited on the glass surface from the vapor produced by heating a magnesium source, but the metal did not reduce the glass.

For the reaction of magnesium vapor and the glass surface to proceed at a reasonable rate, the tube should be heated to at least 640°C. However, care should be taken not to exceed the softening point of the glass tube, since the reduced pressure within the sealed tube due to the magnesium-oxygen reaction can collapse a glass tube which has been heated to this point. For example, a tube of boro-silicate sealing glass collapsed due to reduced internal pressure when heated to 600°C.

The specific temperature to which the combination of FIG. 3 is subjected depends upon the material from which tube **12** is constructed, the desired rate of reaction and the desired resistance of the resultant device. This process can conceivably be applied to the formation of resistors with values between 1 ohm and several megohms, the resistance being a function of resistor size and geometry, glass composition, amount of magnesium used, and the temperature and time of reaction.

If the magnesium cermet layer has a higher thermal expansion coefficient than the glass substrate, the cermet may fracture during cooling from the high temperature reduction process, the resultant resistor being unstable and having a high voltage coefficient of resistance due to electrical breakdown across fissures in the cermet layer. A large mismatch between thermal expansion coefficients in the glass tube and cermet layer could also result in a fracturing process occuring over longer periods of time, thus causing a gradual increase in resistance with the passage of time. It is therefore preferred that tube **12** consist of a relatively high expansion material to match that of the cermet layer which appears to have an expansion coefficient greater than $90 \times 10^{-7}$ per degree C. Moreover, lead wires **10** and **18** should consist of a conductive material having a thermal coefficient of expansion that is compatible with that of tube **12** and cermet layers **22** and **24**.

Hermetically sealed glass resistors were formed in accordance with the following specific example. The following glass composition, which was used in forming tube **12**, is set forth as calculated from the glass batch in weight percent on the oxide basis: 57% $SiO_2$, 19% $Al_2O_3$, 13% $Na_2O$, 4% $K_2O$, 2% MgO, 3% CaO and 1% $As_2O$. The thermal coefficient of expansion of this glass is about $92 \times 10^{-7}$/°C, and it therefore formed a good seal with the copper clad nickel wire which was employed for lead wires **10** and **18.** After one lead wire was sealed to a first end of the glass tube, the inside diameter of which was about 50 mils, the tube was charged with 10 milligrams of magnesium ribbon. After the second dumet lead wire was sealed to the tube, the overall length thereof was about one inch. The resultant composite body was fired at 640°C for 200 minutes, resulting in the formation of a hermetically sealed resistor having a resistance of about 800 ohms.

Various modifications can be made to the preferred method described hereinabove without departing from the scope of the present invention. For example, the magnesium may be present in any convenient form



such as ribbon, wire, granules or the like. Also, the magnesium could be disposed in the tube prior to sealing any lead thereto, and thereafter, the leads could be simultaneously or consecutively sealed to the tube.

Whereas a glass tube has been described hereinabove, The resistor enclosure may be formed in other geometrical shapes or from other oxide-containing materials such as glass-ceramic or ceramic materials. If glass-ceramic materials are used, the lead wires could be sealed to the ends of tube **12** as shown in FIG. **2** while tube **12** is in its vitreous state. Thereafter, during the cermet-forming step or in a separate ceramming step, the glass tube could be converted to a crystalline or semicrystalline structure to enhance the strength of the resultant resistor.

Since tubes of ceramic or crystalline glass-ceramic materials cannot be softened and deformed to cause the ends of the tube to seal to the lead wires in the manner described in conjunction with FIGS. **1, 2** and **3**, the method illustrated in FIGS. **4** and **5** can be used to connect the lead wires to tubes made of these materials. As shown in FIG. **4,** the end of lead wire **42,** which is surrounded by a toroidially shaped, fusible element or bead **44,** is inserted into the end of a glass-ceramic or ceramic tube **46.** The thermal coefficients of expansion of lead wire **42,** bead **44** and tube **46** should be compatible. The application of heat to bead **44** causes it to seal to both lead wire **42** and tube **46** to form the junction seal **48** shown in FIG. **5.** Although this method has been described in connection with sealing lead wires to rigid tubes, it could also be used to seal lead wires to glass tubes.

I claim:

**1.** An insulated electrical resistor comprising

a hollow, hermetically sealed enclosure of oxide-containing material selected from the group consisting of glass, glass-ceramic and ceramic, said enclosure having a cavity therein,

a pair of electrically conductive lead wires extending through said enclosure at spaced locations, and

a conductive cermet layer disposed on the inner surface of said enclosure, said cermet layer including magnesium and magnesium oxide, said cermet layer contacting that portion of each of said lead wires which extends into said cavity.

**2.** A resistor in accordance with claim **1** wherein the pressure within said cavity is lower than ambient pressure.

**3.** A resistor in accordance with claim **2** wherein said cermet layer further comprises reaction products that result from reduction of said oxide-containing material by magnesium.

**4.** A hermetically sealed resistor comprising

an elongated tube of oxide-containing material selected from the group consisting of glass, glass-ceramic and ceramic,

an electrically conductive lead wire disposed in each end of said tube,

means for sealing each end of said tube to its respective lead wire, thereby forming a hermetically enclosed cavity, and end of each of said lead wires extending into said cavity,

a conductive cermet layer disposed on the inner surface of said tube, said cermet layer including magnesium and magnesium oxide, said cermet layer contacting that portion of said lead wires which extend into said cavity.

**5.** A resistor in accordance with claim **4** wherein the pressure within said cavity is lower than ambient pressure.

**6.** A resistor in accordance with claim **5** wherein said cermet layer further comprises reaction products that result from reduction of said oxide-containing material by magnesium.

**7.** A resistor in accordance with claim **6** wherein the thickness of said conductive cermet layer is between 0.1 and 10 micrometers.

**8.** A resistor in accordance with claim **7** wherein the thermal expansion of said oxide-containing material is greater than $90 \times 10^{-7}$ per degree C.

**9.** A method of forming an insulated electrical resistor comprising the steps of

providing a hollow enclosure of oxide-containing material having a pair of apertures therein,

disposing a measured amount of magnesium in said enclosure,

sealing an electrically conductive lead wire in each of said apertures to form a hermetically sealed cavity, an end of each of said lead wires extending into said cavity, and

heating the assembly so formed to a temperature greater than 300°C which is sufficient to cause said magnesium to vaporize and react with oxygen within said cavity to reduce the pressure therein and to form a conductive cermet layer on the inner surface of said enclosure, said cermet layer making electrical connection to both of said lead wires.

**10.** A method in accordance with claim **9** wherein said enclosure is made from a material selected from the group consisting of glass, glass-ceramic and ceramic, and wherein the step of heating is performed at a temperature sufficient to cause the vapor from said magnesium to reduce said oxide-containing material, said conductive cermet layer further comprising reaction products resulting from the reduction of said oxide-containing material by magnesium.

**11.** A method of forming an insulated electrical resistor comprising the steps of

providing an elongated tube of oxide-containing material selected from the group consisting of glass, glass-ceramic and ceramic,

disposing a measured amount of magnesium in said enclosure,

sealing an electrically conductive lead wire in each end of said tube, thereby forming a hermetically enclosed cavity, an end of each of said lead wires extending into said cavity, and

heating the assembly so formed to a temperature greater than 300°C which is sufficient to cause said magnesium to vaporize and react with oxygen within said cavity to reduce the pressure therein and to form a conductive cermet layer on the inner surface of said tube, said cermet layer making electrical connection to both of said lead wires.

**12.** A method in accordance with claim **11** wherein the step of heating is performed at a temperature sufficient to cause the vapor from said magnesium to reduce said oxide-containing material, said conductive cermet layer further comprising reaction products resulting from the reduction of said oxide-containing material by magnesium.

**13.** A method in accordance with claim **12** wherein said oxide-containing material is glass and wherein the step of heating is performed at a temperature less than the softening point of said glass.

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