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Carron et al.

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[54] **METHOD OF FABRICATION OF A PROBE FOR A HYGROMETER**

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[52] **U.S. Cl.**..... **204/38 A,** 73/335, 73/336.5, 204/33, 204/129.9, 204/195 W, 324/65 M

[51] **Int. Cl.** **C23f 17/00,** C23b 3/06, G01r 27/02

[58] **Field of Search**..... 204/33, 38 A, 129.9, 37 R

[56] **References Cited**

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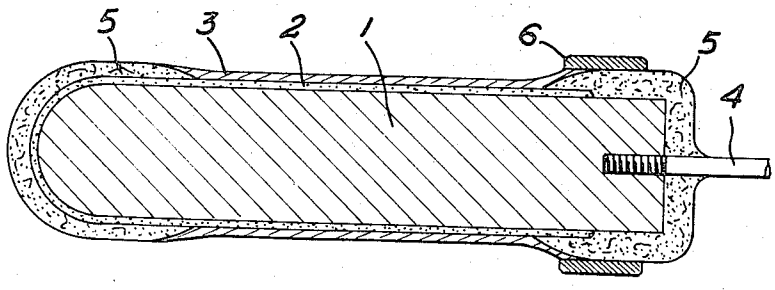
[57] **ABSTRACT**

The hygrometer probe is fabricated in successive steps which consist in forming a probe body having an aluminum base, in subjecting the probe body to a surface treatment comprising at least one mechanical polishing operation and one electrochemical polishing operation, in carrying out anodic oxidation of the probe body and in subjecting the film-layer of alumina thus formed to a hygrothermal treatment, in depositing a metallic film-layer by vacuum evaporation, and in placing the necessary connections on the probe.

17 Claims, 2 Drawing Figures



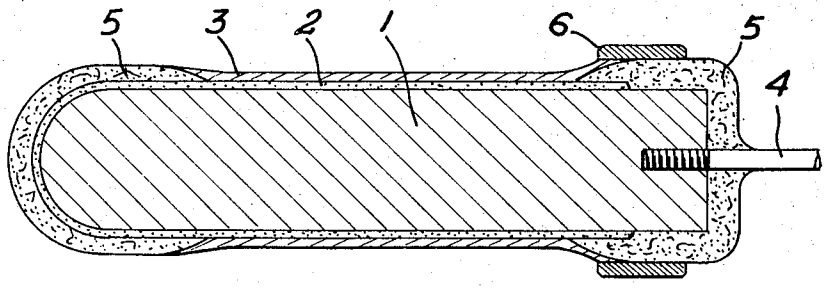


FIG. 1

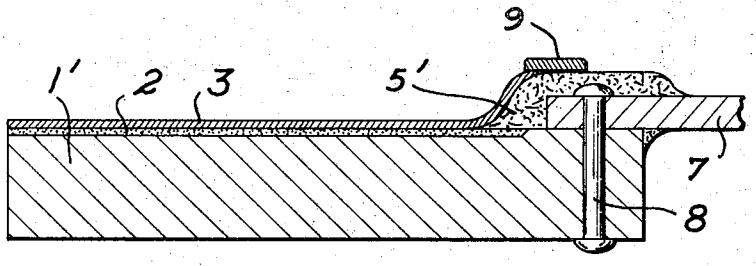


FIG. 2

METHOD OF FABRICATION OF A PROBE FOR A HYGROMETER

This invention relates to measurements of water-vapor contents and more precisely to the fabrication of a hygrometer probe for performing said measurements.

The invention is primarily directed to a method of fabrication of a probe for a hygrometer of the type which is based on the principle of adsorption of water vapor on a film-layer of porous alumina, the method being essentially carried out in successive steps which consist in fabricating a probe body having an aluminum base, in subjecting said probe body to a surface treatment comprising at least one mechanical polishing operation and one electrochemical polishing operation, in carrying out anodic oxidation of the probe body and in subjecting the film-layer of alumina thus formed to a hygrothermal treatment, in depositing a metallic film-layer by vacuum evaporation, and in placing the necessary connections on the probe.

In fact, this method consists in forming an aluminum-alumina-metal sandwich in which the variation in impedance is detected by means of a standard multivibrator assembly, said variation being dependent on the characteristics of the medium in which the hygrometer is placed.

The surface treatment of the probe body is intended to prepare this latter for the desired formation of a film-layer of alumina.

The electrochemical polishing operation which is performed after mechanical polishing of the probe body is advantageously carried out in a bath comprising a mixture of orthophosphoric acid, chromic anhydride and sulphuric acid, this mixture being brought to an operating temperature corresponding to a viscosity of 5 to 7 centipoises at 4 to 5 volts.

In order to eliminate the undesirable alumina which is formed at the time of electrochemical polishing of the probe body, the chemical polishing operation which is then carried out preferably consists in immersing the probe body in a bath constituted by a mixture of phosphoric acid, chromic anhydride and water.

The optimum effect of this bath is obtained at a bath temperature of the order of 80° C, the time of immersion of the probe body being approximately 5 to 10 minutes.

When the probe body is completely ready to receive the intended film-layer of alumina, at an alternating current of 2.5 to 3.3 A/dm^3 or a direct current of 1.2 to 1.6 A/dm^3, the bath being at a temperature of approximately 30° C and the probe body being immersed in said bath for a period of approximately 10 minutes.

The operating conditions are chosen so as to obtain an alumina film having a thickness of approximately 4 μm.

The stabilization of said alumina film is obtained by subjecting the aluminized probe body to a hygrothermal treatment which can advantageously be carried out in an autoclave at 100° C or preferably at 250° C.

The alumina film-layer is then in readiness for receiving a porous metallic film-layer after the two ends of the body have been coated with a layer of insulating resin. Said metallic film is advantageously obtained by vacuum evaporation of a metal such as NiCr or Cr which has good adherence on the alumina film and can have a thickness of 200 to 300 A.

Connections are then formed on the probe body in order that the two electrodes constituting the probe, namely the body and the metallic film-layer, may accordingly be connected to a measuring assembly of standard type.

The probe body can be either of polycrystalline aluminum or of monocrystalline aluminum or alternatively of a monocrystalline aluminum alloy such as, for example, an alloy of aluminum and titanium.

By making use of the probe body fabricated from monocrystalline aluminum, it is subsequently possible to obtain a film of alumina having ordered and uniform porosity as well as characteristics of hydroscopicity which are distinctly superior to those of an alumina which is prepared from a polycrystalline support. This results in an appreciable reduction in the response time and a substantial attenuation of the hysteresis phenomenon.

Thus it follows by way of example that, by making use of a probe body of monocrystalline aluminum and by subjecting said body to anodic oxidation at an alternating current of 3 A/dm^2, there is formed a film of alumina having a thickness of approximately 4 μ. The porosity of this alumina film is such that the response time of the probe is distinctly less than one second.

Furthermore, when making use of a probe body formed of a monocrystalline aluminum alloy, there is obtained as a result of the proposed hygrothermal treatment a film-layer of mixed oxide which is subject to only very slight modification in the course of time.

A more complete understanding of the invention will be obtained from the following description of two slightly different embodiments of a probe in accordance with the invention.

Reference is made to FIGS. **1** and **2** of the accompanying drawings in which the probe is illustrated in cross-section along the axis and in which the thicknesses are highly exaggerated for the sake of enhanced clarity.

The probe which is illustrated in FIG. **1** essentially comprises a body **1** in the form of a stick of aluminum which is coated with a film **2** of alumina. Each extremity is coated with an insulating resin **5** designated by the trade name "Colloplex" and this latter overlaps the alumina film-layer to a distance of 2 to 3 mm. A connection consisting of a metal rod **4** is screwed into one extremity of the body **1**. A metallic film **3** is laid on the alumina and the insulating resin over a width of 5 to 6 mm. A metallic ring **6** of greater thickness is then placed over the resin in order to form a second connection which can be joined by microwelding or simply by application of mechanical pressure.

The probe shown in FIG. **1** is fabricated in accordance with the invention from a cylindrical body **1** formed of aluminum which is at least 99.99 % pure.

Said body **1** is first subjected to a surface treatment consisting of:

mechanical polishing to a grit size of 400,

electrochemical polishing in a bath having a composition per 380 liters of mixture, of 357 liters of 85 % orthophosphoric acid, 45 kg of chromic anhydride, and 21 liters of 66° Be. sulphuric acid. The temperature of the bath is adjusted so as to obtain a viscosity of 5 to 7 centipoises at 4 to 5 volts. The

conditions of utilization of the bath can vary in particular as a function of the hardness of the aluminum employed,

chemical polishing which is intended to remove the alumina which is formed at the time of electrochemical polishing, by dissolution in a bath having a composition per 1000 cm^3, of 35 cm^3 of phosphoric acid, 20 grams of chromic anhydride and water in a sufficient quantity to make-up 1000 cm^3.

The operation consists in maintaining the probe body in the aforesaid bath for a period of 5 to 10 minutes, said bath having previously been brought to a temperature of the order of 80° C and maintained at this temperature throughout the operation.

On completion of the surface treatment, the probe body is ready to undergo oxidation with a view to coating said body with an adherent film-layer of alumina having predetermined values of thickness and porosity.

The alumina is obtained by anodic oxidation with a direct current of 1.2 to 1.6 A/dm^3 or with an alternating current of 2.5 to 3.3 A/dm^3 in a bath of 30 wt % sulphuric acid which is maintained at a temperature of the order of 25° to 30° C, the probe body being immersed in said bath for a period of about 10 minutes.

With an alternating current of 2.5 A/dm^3, there is obtained on the probe body after approximately 10 minutes a thickness of alumina of 4±0.5 μ having a porosity within the range of 50 to 500 A.

After this oxidation process, stabilization of the aluminum film is then carried out by means of a hygrothermal treatment which is advantageously performed in an autoclave at 100° C or preferably at 250° C.

The probe body which is coated with its film of alumina is coated at each extremity with a layer of insulating resin and is then ready to receive a metallic film. Said film is obtained by vacuum evaporation of Ni or NiCr having good adherence on the alumina, the thickness of said film being within the range of 200 to 300 A.

In order to connect the probe to the measuring assembly, the probe is provided with two connections constituted:

in one case by a metal rod of copper, for example, which is screwed into the probe body,

in the other case by a metallic coating deposited on the metallic film-layer at that point of this latter which is insulated from the alumina by the resin known commercially as "Colloplex".

The probe which is illustrated in FIG. 2 essentially comprises a body 1' constituted by a circular or rectangular plate of monocrystalline aluminum. The top face of the body 1' is coated with a film-layer 2 of alumina. An aluminum rod 7 which constitutes a first connection of the probe is rigidly fixed to one extremity of the body 1' by means of a rivet 8. An insulating layer 5' of Plexiglas adhesive which is applied by dipping partially covers the alumina layer 2 and the aluminum rod 7. A metallic film-layer 3 is laid over the alumina layer 2 and partially covers the insulating layer 5'. A terminal contact 9 of copper having a thickness of 4000 A and constituting the second probe connection is placed over the insulating layer 5'.

In an alternative form of this embodiment, the probe body 1' is provided with a layer of alumina and a metallic layer on both faces. In another alternative form of this embodiment, it is possible to have two alumina layers of different porosity on the two faces of the probe body by making use of two different oxidation baths.

It is readily apparent that the invention is not limited to the forms of construction of the probe which have been described in the foregoing. If so required, recourse may be had to other embodiments and methods of application of the invention without thereby departing either from the scope or the spirit of the invention.

What we claim is:

1. A method of fabrication of a probe for a hygrometer of the type in which water vapor is adsorbed on a film-layer of porous alumina, wherein said method is carried out in successive steps which consist in fabricating a probe body having an aluminum base, in subjecting said probe body to a surface treatment comprising at least one mechanical polishing operation and one electrochemical polishing operation, in carrying out anodic oxidation of the probe body and in subjecting the film-layer of alumina thus formed to a hygrothermal treatment in vapor phase at a temperature above 100°C. and at about 250°C. to stabilize the layer of alumina, in depositing a metallic film-layer by vacuum evaporation, and in placing the necessary connections on said probe.

2. A method according to claim **1**, wherein the electro-chemical polishing operation is followed by a chemical polishing operation.

3. A method according to claim **1**, wherein the electrochemical polishing of the probe body is carried out in a bath comprising a mixture of orthophosphoric acid, chromic anhydride and sulphuric acid, said mixture being brought to an operating temperature corresponding to a viscosity of 5 to 7 centipoises at 4 to 5 volts.

4. A method according to claim **3**, wherein the mixture constituting the electrochemical polishing bath has a composition, for approximately 380 liters of said mixture, of approximately 357 liters of 85 % orthophosphoric acid, 45 kg of chromic anhydride and 21 liters of 66° Be. sulphuric acid.

5. A method according to claim **2**, wherein the chemical polishing of the probe body is carried out in a bath constituted by a mixture of phosphoric acid, chromic anhydride and water for effecting the dissolution of the alumina which has formed during the electrochemical polishing operation.

6. A method according to claim **5**, wherein the mixture of the chemical polishing bath has a composition, for 1000 cm^3 of said mixture, of 35 cm^3 of phosphoric acid, 20 grams of chromic anhydride and water in a sufficient quantity to make-up 1000 cm^3.

7. A method according to claim **5**, wherein the probe body is immersed in the chemical polishing bath for a period of 5 to 10 minutes, said bath being brought to and maintained at a temperature of approximately 80° C during this operation.

8. A method according to claim **1**, wherein the anodic oxidation of the probe body is carried out in a bath of 30 wt % of sulphuric acid with an alternating current of 2.5 to 3.3 A/dm^3 or a direct current of 1.2 to 1.6 A/dm^3, the bath being at a temperature of approximately 30° C and the probe body being immersed in said bath for a period of approximately 10 minutes.

9. A method according to claim **1**, wherein the metallic film-layer which is deposited by vacuum evapora-

tion is of metal such as NiCr or Cr which has good adherence on the alumina and has a thickness of 200 to 300 A.

10. A method according to claim **1**, wherein the probe body is formed of polycrystalline aluminum.

11. A method according to claim **1**, wherein the probe body is formed of pure monocrystalline aluminum.

12. A method according to claim **1**, wherein the probe body is formed of a monocrystalline aluminum alloy.

13. A method according to claim **12**, wherein the probe body is formed of an alloy of aluminum with titanium.

14. A method according to claim **1**, wherein the connection corresponding to the metallic film-layer is formed by the superposition of a metallic film having a thickness greater than 4000 A at one extremity which has previously been coated with an insulating resin, said metallic film-layer being clamped by means of a metal ring.

15. A method according to claim **1**, wherein the connection corresponding to the metallic film-layer is constituted by a copper contact having a thickness of 4000 A.

16. A method according to claim **1**, wherein one of the probe connections is constituted by a metal rod which is screwed into the probe body.

17. A method according to claim **1**, wherein one of the probe connections is constituted by a metal rod which is riveted to the probe body.

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CERTIFICATE OF CORRECTION

Patent No. 3,821,093 Dated June 28, 1974

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Foreign Application Priority Data

June 18, 1971 France 7122299

Signed and sealed this 29th day of October 1974.

(SEAL)
Attest:

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Attesting Officer

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Commissioner of Patents

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