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[54] AGING-PROOF HUMIDITY SENSING ELEMENT AND METHOD FOR THE PRODUCTION THEREOF

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[51] Int. Cl.....H01c 13/00

[58] Field of Search 338/34, 35; 73/29, 73, 336.5

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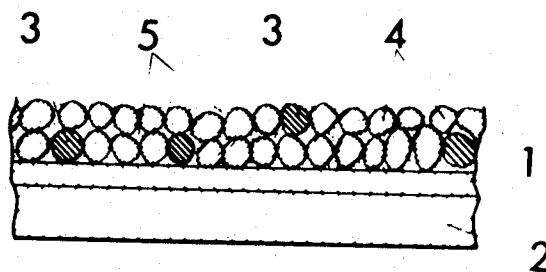
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[57]

ABSTRACT

A humidity sensing element comprises an insulating base plate provided with gold electrodes and a film or layer metal oxide particles or a mixture of metal oxide particles and carbon particles. The micro-gaps between said particles are filled up with a hydrophilic high polymer, thereby minimizing the deterioration by aging. The humidity sensing element can be produced by a method which comprises forming a film made of metal oxide particles or a mixture of metal oxide particles and carbon particles on an insulating base plate provided with gold electrodes, immediately whereupon said film is impregnated with a solution of a hydrophilic high polymer in a water-miscible volatile solvent and subsequently volatilizing off said solvent. The thus produced humidity sensing element shows a substantially constant electric resistance at a given humidity even with the passage of a long period of time, thereby enabling a hydrometer capable of exactly indicating humidity with high durability to be provided.

11 Claims, 5 Drawing Figures



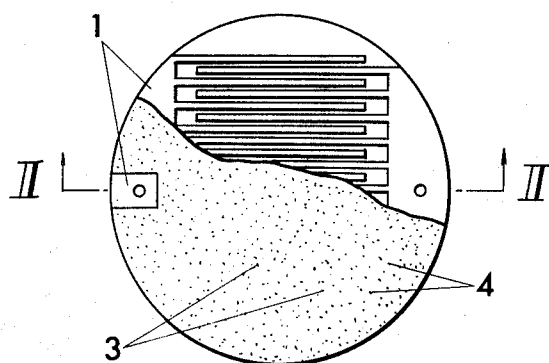


Fig. 1

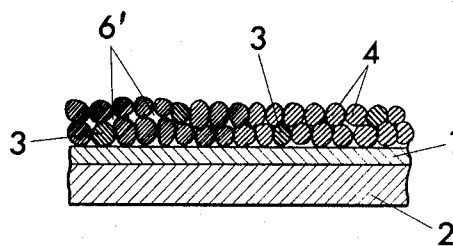


Fig. 2

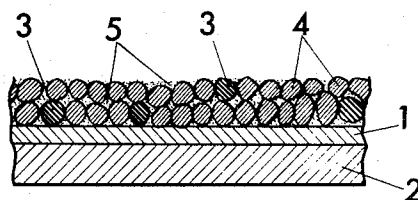


Fig. 3

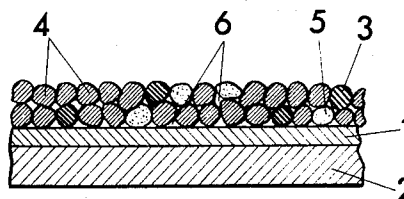


Fig. 4

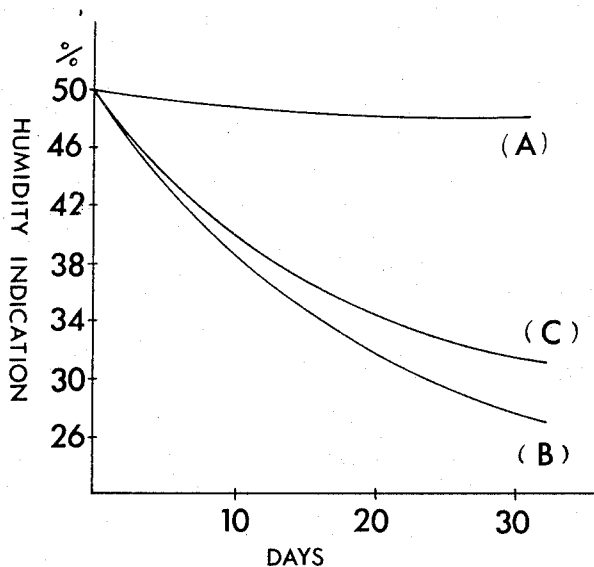


Fig. 5

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AGING-PROOF HUMIDITY SENSING ELEMENT AND METHOD FOR THE PRODUCTION THEREOF

This invention relates to a humidity sensing element and a method for producing the same, and more particularly to an aging-proof humidity sensing element and a method for the production thereof.

Heretofore, there has been known an electric resistance type hygrometer in which there is used an insulating plate provided with gold electrodes and a metal oxide film formed thereon, so that the electric resistance between said gold electrodes changes in response to a change of humidity (Japanese Patent No. 473306). Furthermore, the present inventors have disclosed in Japanese Patent Application No. 83043/1967 that an improved humidity sensing element, which comprises a steatite plate provided with gold electrodes and a graphite-containing γ -ferric oxide film formed thereon, has the advantage that it does not deteriorate on exposure to air under severe conditions of high temperature and high humidity, it requires no temperature compensation and it has an improved linear relationship between humidity and electric resistance.

The conventional humidity sensing element comprising a metal oxide film has, however, the severe disadvantage that it does not possess resistance to repeated great changes in humidity or aging resistance. Illustratively stated, when the humidity sensing element which comprises a porcelain, for example steatite base plate provided with gold electrodes and a film made of metal oxide particles or a mixture of metal oxide particles and carbon particles is exposed to an atmosphere of low humidity for a long time, its electric resistance, observed at a given humidity, increases more and more and, thus it will be unable to be used as a humidity sensing element. As a result of the present inventors' investigation on the aging of the conventional humidity sensing element, to wit, the change in the electric property (relationship between relative humidity and electric resistance) of the element on exposure to the air, it has been found that the difficulty stated above is due to a number of hairline cracks which are formed on the surface of the oxide film. These hairline cracks occasionally have a width of 1.5×10^{-3} mm and appear in a network form. Such hairline cracks causes the electric resistance to greatly change, thereby destroying the function of the humidity sensing element.

The unfavorable aging of the conventional humidity sensing element will be illustrated in Table 1 which is set forth later. As an example, when a titanium oxide film is employed as the metal oxide film, the humidity sensing element which shows, at the beginning, an electric resistance of 2.2×10^5 ohms at a relative humidity of 50 percent will change in quality after exposure to air (temperature: 15° to 25° C., humidity (R.H.): 30 to 50 percent for 3 weeks and show an electric resistance of 6.2×10^5 ohms at the same relative humidity as at the beginning. Such change of electric resistance will not cease even after an exposure for 5 weeks. When γ -ferric oxide is used, a similar change of electric resistance is observed. In this connection, it is noted that as the rate of such change of electric resistance of the humidity resistance element decreases with the passage of time of exposure, the element is occasionally employed in a hygrometer at the time when the rate of change of electric resistance has been minimized. However, because of the lack of reproducibility of the rate of change of the electric resistance with aging, it is difficult to obtain a humidity sensing element having a predictable property (relationship between relative humidity and electric resistance) only by regulating the period of time of exposure to the air. For this reason, the rate of production of acceptable products is less than 10 percent. Thus, it is disadvantageous in view of economic consideration.

As a result of intensive study by the present inventors, it has been found that a humidity sensing element capable of resisting repeated great changes of humidity can be obtained by filling up the gaps formed between the oxide particles in the oxide film with a hydrophilic high polymer. The present invention has been made on the basis of such novel finding.

Therefore, it is an object of the present invention to provide a humidity sensing element which is aging-proof and especially is capable of resisting repeated great changes of humidity.

It is another object of the present invention to provide a humidity sensing element of the character described which is capable of sensing humidity with certainty as well as with accuracy.

It is a further object of the present invention to provide a humidity sensing element of the kind described which can be mass-produced and sold at reasonable cost.

It is a still further object of the present invention to provide a method for producing a humidity sensing element of the kind described which is simple and is excellent in the rate of production of acceptable products.

The foregoing and other objects, features and advantages will be apparent in the following detailed description taken in connection with the accompanying drawing in which:

FIG. 1 is a partly cut-away plan view of a humidity sensing element according to the present invention;

FIG. 2 is an enlarged sectional view taken along the line II—II, showing the condition prior to application of the treatment according to the present invention;

FIG. 3 is a view similar to FIG. 2, showing the condition following the application of the treatment according to the present invention;

FIG. 4 is a view similar to FIG. 2, in which a humidity sensing film, for comparison purposes, is formed by spraying a suspension containing metal oxide particles, graphite particles and a hydrophilic high polymer; and

FIG. 5 is a diagram showing the characteristics of the respective humidity sensing elements having the structures of FIGS. 2, 3 and 4.

According to the present invention, there is provided a humidity sensing element which comprises an insulating base plate provided with gold electrodes and metal oxide particles or a mixture of metal oxide particles and carbon particles, and forming a film on the base plate. The micro-gaps between said particles are filled up with a hydrophilic high polymer, thereby enabling the deterioration by aging to be minimized. Such a humidity sensing element can be produced by a method which comprises forming a film made of metal oxide particles or a mixture of metal oxide particles and carbon particles on an insulating base plate provided with gold electrodes, immediately whereupon said film is impregnated with a solution of a hydrophilic high polymer in a water-miscible volatile solvent and subsequently volatilizing off said solvent. In this connection, it should be noted that the application of said hydrophilic high polymer to the film must be carried out immediately after the film is formed. Accordingly, said application of the hydrophilic high polymer is conducted at the time when the moisture still remains in the film. For this reason, the volatile solvent to be used for the preparation of a solution of the hydrophilic high polymer should be selected from the solvents of the kinds which are easily miscible with water. The hydrophilic high polymers which can be used in the present invention embrace various high molecular weight compounds; for example, polyvinyl acetate or cellulose acetate may be employed with advantage. As the solvent for these high polymers, acetone or ethyl acetate may suitably be employed. In applying a solution of the high polymer, when the concentration of the solution is too high, too thick a film of the high polymer is formed on the surface of metal oxide, leading to a lowering of the sensibility of metal oxide to humidity. Therefore, the concentration of the solution is of importance and is suitably in the range of 1 to 5 percent by weight, preferably 2 to 4 percent. As to a method for impregnating the metal oxide film with the solution of high polymer, dipping or spraying using a spray gun is preferably employed. In this connection, it is to be noted the purpose of application of the solution of high polymer is not to simply coat the metal oxide film nor to simply adhere the metal oxide to the base plate, but rather is to fill up the micro-gaps between the component particles of the metal oxide film. Ac-

cordingly, a method in which the suspension prepared by dispersing the metal oxide particles in the solution of high polymer is sprayed onto the insulating base plate for form a humidity sensing film or a method in which the concentrated solution of high polymer is sprayed onto the metal oxide film to form a simply strong film, can not achieve the desired purpose. On the other hand, for example when the solution of high polymer is sprayed onto the film using a spray gun, when the position of the spray gun is too high, the volatile solvent, e.g., acetone, volatilizes and dissipates before reaching the metal oxide film, hence only the high polymer is sprayed onto the metal oxide film while the surface is in a dry condition. As a result, the purpose of filling up the micro-gaps between the component particles of the oxide film is not achieved and the desired product can not be obtained. Accordingly, it is necessary to hold the surface of the metal oxide film always wet with the solution.

Referring now to FIGS. 1 to 3, the metal oxide film is formed by, for example, applying, using a spray gun, a suspension prepared by colloiddally dispersing 1 to 4 percent by weight of metal oxide particles 4 (diameter: 10^{-5} to 10^{-7} cm) containing carbon particles e.g. graphite particles 3 of 0 to 40 percent, preferably 10 to 20 percent, by weight based on the weight of the metal oxide particles in water onto a porcelain base plate e.g. steatite plate 2 provided with a pair of comb-shaped symmetrical gold electrodes 1, 1. As the metal oxide, γ -ferric oxide, titanium oxide, tri-iron tetroxide, silicon oxide, aluminum oxide, chromium oxide or the like may suitably be employed. Yet, γ -ferric oxide is most preferably employed because of its lower electric resistance as well as its high resistance to deterioration by oxidation. Thus, the metal oxide particles and graphite particles are fixed onto the base plate thereby to form a film having an electric conductivity. The metal oxide film containing graphite particles may preferably be 5 to 10×10^{-3} mm thick. In order to obtain such thickness, it is preferable to make a film by spraying a suspension of a regulated concentration (1 to 4 percent by weight) two or more times. During the spraying operation, the base plate is preferably maintained at a temperature above room temperature, preferably 40° to 60° C. Subsequently, the temperature of the base plate having the metal oxide film thereon is lowered to room temperature, whereupon a 1 to 5 percent by weight solution of a hydrophilic high polymer in a water-miscible volatile solvent is applied onto the metal oxide film by spraying or dipping thereby to fill up the micro-gaps 5 between the component particles of the metal oxide film. The amount of high polymer employed is suitably in the ratio of 1:2 to the weight of metal oxide film. The thus obtained humidity sensing element is placed in a room with a ventilator and then is allowed to stand at room temperature for 3 weeks. As a result, the volatile solvent is completely volatilized and dissipated to obtain the desired product in which the micro-gaps between the component particles of the film are completely filled up with the high polymer 6.

When the treatment according to the present invention is not applied, the mixture of metal oxide particles 4 and graphite particles 3 forms a film on the steatite base plate 2 leaving micro-gaps 6' therebetween as depicted in FIG. 2. On the other hand, when the suspension prepared by dispersing a mixture of metal oxide particles 4 and graphite particles in a solution of the high polymer in the solvent is sprayed onto the base plate 2 to form a film, the high polymer is caused to be mixedly present between the metal oxide particles 4 and the graphite particles 3 as depicted in FIG. 4.

As is clearly seen in FIG. 5, a comparison of the characteristics of these three kinds of humidity sensing elements is as follows: The humidity sensing element according to the present invention A (FIG. 3) shows almost no change in the humidity indication at a given humidity with the passage of days. By contrast, the humidity sensing element not subjected to the treatment of this invention B (FIG. 2) and the humidity sensing element produced by spraying the suspension prepared by dispersing the mixture of metal oxide particles 4

and graphite particles in a solution of the high polymer in the solvent C (FIG. 4) both show great changes in the humidity indication at a given humidity with the passage of days.

Furthermore, it is to be noted that the remarkable effect of the present invention is a noticeable improvement in the rate of production of desired products. According to the actual example, the products capable of standing use for more than one year can be obtained at a rate of production of desired products of 85 percent or more according to this invention, while the conventional humidity sensing element having a film composed only γ -ferric oxide particles containing graphite particles capable of standing use for a half year can be obtained at a rate of production of desired products of 10 percent or less.

The present invention is illustrated by the following Examples.

EXAMPLE 1

An aqueous suspension containing 3.2 percent by weight of a mixture of γ -ferric oxide particles and graphite particles (15 percent by weight based on the weight of γ -ferric oxide particles) was sprayed three times onto a steatite base plate provided with a pair of comb-shaped symmetrical gold electrodes to form a fixed film having a thickness of 7×10^{-3} mm. During the spraying operation, the temperature of the base plate was maintained at 50° C. Subsequently, the temperature of the base plate having the metal oxide film thereon is returned to room temperature, whereupon a 2 percent by weight acetone solution of polyvinyl acetate was sprayed, using a spray gun, onto the metal oxide film three times in such manner that each-spraying operation was conducted for 3 seconds, followed by drying and such spraying operation was repeated three times. The thus obtained product was placed in a room with a ventilator at room temperature for 3 weeks thereby to completely volatilize and dissipate acetone, and the desired product was obtained.

EXAMPLE 2

The same operation as in Example 1 was repeated with exception that titanium oxide was employed in place of γ -ferric oxide. Thus, a desired product was obtained.

EXAMPLE 3

The same operation as in Example 1 was repeated with exception that cellulose acetate was employed in place of polyvinyl acetate. Thus, a desired product was obtained.

The aging test (Condition: temperature 0° to 20° C., Relative humidity (R.H.) 20 to 60 percent) was conducted on the respective products obtained in Examples 1, 2 and 3. The test results are summarized in Table 1, in comparison with the test results of the convention humidity sensing elements not subjected to the treatment of this invention. Table 1

Aging test (Electric resistance in R.H. 50 percent)

TABLE 1
Aging test (electric resistance in R.H. 50%)

Days	Titanium oxide		γ -Ferric oxide (containing graphite)			
	Non-treated, Ω	Treated I, Ω	Non-treated, Ω	Treated II, Ω		
0	2.2×10^5	2.1×10^5	2.2×10^4	1.8×10^4	1.2×10^5	
7	4.9×10^5	2.8×10^5	1.1×10^5	3.8×10^4	1.35×10^5	
14	5.2×10^5	3.3×10^5	2.1×10^5	4.3×10^4	1.45×10^5	
21	6.2×10^5	3.6×10^5	2.8×10^5	4.3×10^4	1.50×10^5	
23	7.2×10^5	3.6×10^5	4.0×10^5	4.3×10^4	1.50×10^5	
35	8.4×10^5	3.6×10^5	4.4×10^5	4.3×10^4	1.50×10^5	

NOTE.—Treated I: Polyvinyl acetate is used as a high polymer; Treated II: Cellulose acetate is used as a high polymer.

As described, according to the present invention, an aging-proof humidity sensing element can be obtained which is capable of giving a substantially constant humidity indication at a given humidity even with the passage of time.

What is claimed is:

1. A humidity sensing element, comprising:

- an insulating base plate having gold electrodes thereon;
 a thin layer of particles on said electrodes, said layer being
 of substantially uniform thickness and consisting essen-
 tially of particles selected from the group consisting of
 (1) γ -ferric oxide particles and (2) a mixture of γ -ferric
 oxide particles and up to 40 per cent by weight of carbon
 particles based on the weight of said γ -ferric oxide parti-
 cles, said particles being of a size in the range of about
 10^{-5} to 10^{-7} cm and there being micro-gaps between the
 particles throughout the depth of said layer, and
 a hydrophilic high polymer filling the micro-gaps between
 the particles throughout the entire depth of said layer for
 improving the resistance to aging of said element.
2. A humidity sensing element as claimed in claim 1 in
 which said layer has a thickness in the range of $5-10 \times 10^{-3}$ mm.
 3. A humidity sensing element as claimed in claim 1, in
 which the weight ratio of said high polymer to said particles is
 about 1:2.
 4. A humidity sensing element as claimed in claim 1, in
 which said hydrophilic high polymer is disposed substantially
 entirely in the micro-gaps between said particles.
 5. A humidity sensing element as claimed in claim 1,
 wherein said hydrophilic high polymer is selected from the
 group consisting of polyvinyl acetate and cellulose acetate.
 6. A humidity sensing element as claimed in claim 1,
 wherein said gold electrodes comprises a pair of comb-shaped
 symmetrical gold electrodes.
 7. A method for preparing a humidity sensing element,
 which comprises the steps of:
 applying a suspension of particles in water onto an insulat-
 ing base plate having gold electrodes thereon to form a

- thin layer of particles thereon, said particles being
 selected from the group consisting of (1) γ -ferric oxide
 particles and (2) a mixture of γ -ferric oxide particles and
 up to 40 per cent by weight of carbon particles based on
 the weight of γ -ferric oxide particles, said particles being
 of a size in the range of about 10^{-5} to 10^{-7} cm,
 immediately thereafter and while said layer still contains
 said water, applying onto said layer a solution containing
 about 1 to 5 per cent by weight of a hydrophilic high
 polymer dissolved in a water-miscible volatile solvent so
 that the hydrophilic high polymer enters the micro-gaps
 between the particles, and then
 Volatilizing the water and solvent to obtain a humidity
 sensing element in which said micro-gaps are filled with
 said high polymer.
8. A method as claimed in claim 7, in which said high
 polymer is selected from the group consisting of polyvinyl
 acetate and cellulose acetate and said solvent is selected from
 the group consisting of acetone and ethyl acetate.
 9. A method as claimed in claim 8, in which said solution is
 applied to said layer by spraying.
 10. A method as claimed in claim 8, in which said solution is
 applied by dipping said base plate having the layer thereon
 into said solution.
 11. A method as claimed in claim 8, in which said suspen-
 sion contains in the range of about 1 to 4 per cent by weight of
 said particles and in which said plate is at a temperature in the
 range of about 40° to 60° C., when the suspension is applied
 thereto and said plate is at room temperature when said solu-
 tion is applied thereto.

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