United States Patent [19]

Sumi et al.

[11] **3,721,631**

[45] **March 20, 1973**

[54] **HUMIDITY SENSORS COMPRISING ALKALI METAL OXIDE, DIVANADIUM PENTOXIDE AND SILICON**

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[73] Assignee: **Shinyei Kaisha,** Ikuta-ku, Kobe shi, Japan

[22] Filed: **Aug. 16, 1971**

[21] Appl. No.: **172,055**

[52] **U.S. Cl.**.....**252/408,** 338/35, 117/169 R, 117/169 A, 117/221, 117/222, 117/223, 252/506, 252/507, 252/508, 252/509

[51] **Int. Cl.**.....**H01c 13/00,** G01n 31/06

[58] **Field of Search**.....338/35; 252/408; 117/169 R, 117/169 A; 252/506, 507, 508, 509

[56] **References Cited**

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Assistant Examiner—Roland E. Martin, Jr.
Attorney—Larson, Taylor & Hinds

[57] **ABSTRACT**

A humidity sensor having a negative relative humidity coefficient of resistivity comprises 0.10 to 12.00 mole percent of alkali metal oxide, 0.05 to 10.00 mole percent of divanadium pentoxide and the balance substantially all silicon.

10 Claims, 4 Drawing Figures

FIG. 1.

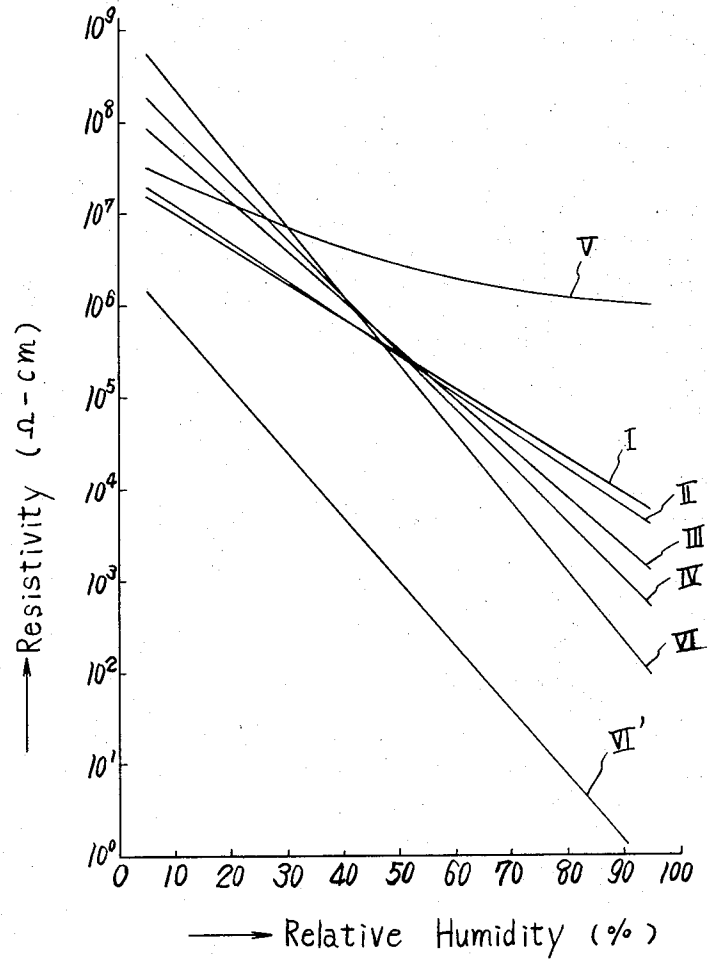

Resistivity (Ω-cm)
10⁹
10⁸
10⁷
10⁶
10⁵
10⁴
10³
10²
10¹
10⁰
0 10 20 30 40 50 60 70 80 90 100
Relative Humidity (%)
V
I
II
III
IV
VI
VI'

FIG. 2.

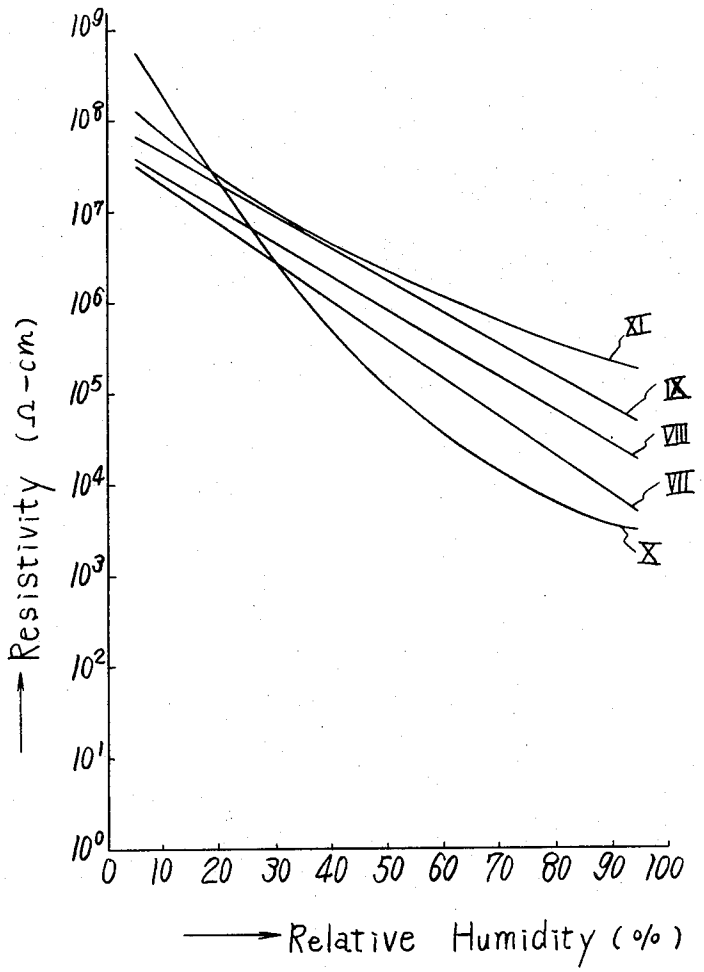

10^9
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
Resistivity (Ω-cm)
0 10 20 30 40 50 60 70 80 90 100
Relative Humidity (%)
XI
IX
VIII
VII
X

FIG. 3.

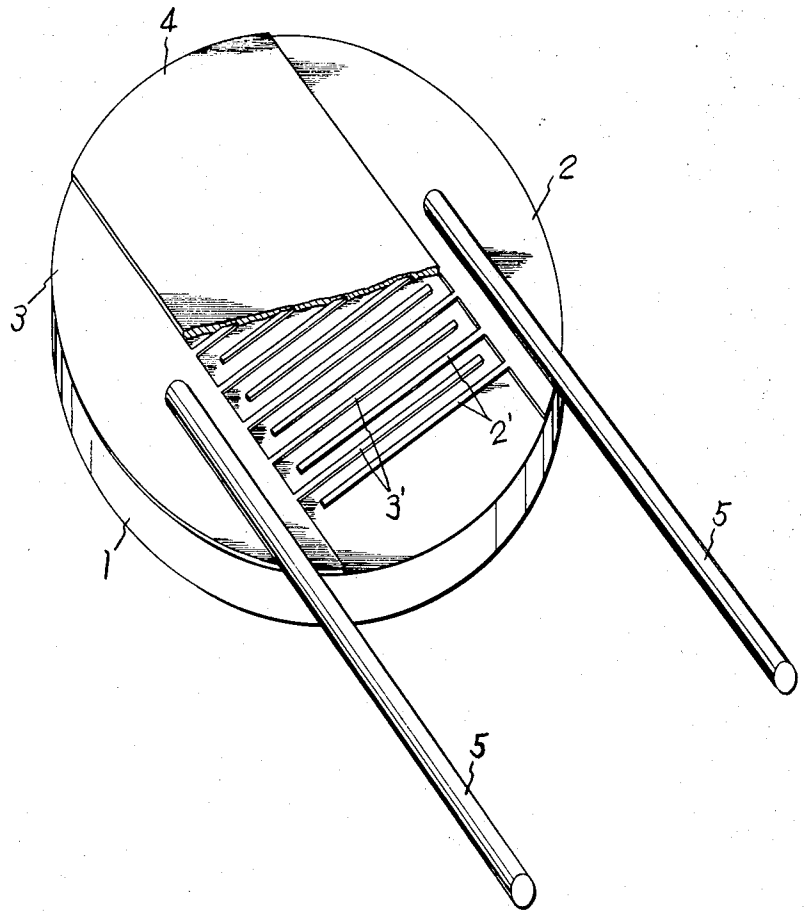
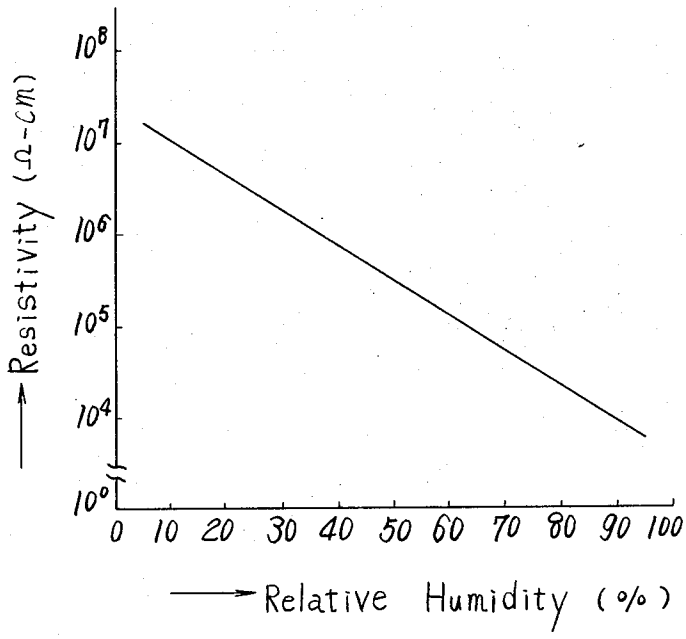


FIG. 4.


Resistivity (Ω-cm)
10^8
10^7
10^6
10^5
10^4
10^0
0 10 20 30 40 50 60 70 80 90 100
Relative Humidity (%)

HUMIDITY SENSORS COMPRISING ALKALI METAL OXIDE, DIVANADIUM PENTOXIDE AND SILICON

The present invention relates generally to humidity sensors, more particularly to humidity sensors having a negative relative-humidity coefficient and it is also concerned with a novel method of making these sensors.

Various humidity sensors have heretofore been known whereby changes in relative humidity in an atmosphere are detected in terms of changes in electrical resistivity (hereinafter referred to merely as "resistivity"). These humidity sensors have come into extensive use in recent years for humidity measurement and control devices.

With the humidity sensors to be used for this type of devices, it is required that the resistivity vary regularly with the changes in humidity over the entire range of the relative humidity.

Examples of the humidity sensors already known are a sensor prepared by coating a high molecular weight substance serving as an insulator with a thin film of a hygroscopic salt such as lithium chloride and a sensor prepared by impregnating a porous synthetic resin with a hygroscopic salt such as lithium chloride. In the case of these humidity sensors, the salt dries or wets in corresponding relation to the changes in the relative humidity of the atmosphere and, by virtue of the flow of current, the changes in the amount of moisture taken up is detected in terms of the changes in the resistivity of the humidity sensor. However, the above-mentioned hygroscopic salt, because of its properties dissolves in a highly humid atmosphere upon absorption of a large amount of moisture and becomes no longer serviceable as a resistive material, so that that the humidity sensors including such salt are subject to a large limitation in that they can be used only under restricted humidity conditions and have the drawback that the resistivity varies greatly with the changes in temperature.

Another humidity sensor is also known which is made by reacting an organic terpene compound with ozone gas and causing the resulting fuming substance to be adsorbed to the single crystal of oxidized anthracene. The product thus obtained is used as a humidity sensor as it is. Since this sensor is inherently very high in resistivity, it is applicable only to special devices which incorporate some other electrical elements having electrical characteristics corresponding to the high resistivity of the sensor. Moreover, the sensor has an inherent drawback that it is low in the reproductivity of the humidity changes in terms of the changes in resistivity, namely it fails to exhibit accurate performance as a humidity sensor.

Further in another sensor where magnetite is used as a resistive material, a colloidal liquid containing particles, for instance, with a particle size of about 100 A is prepared and the liquid is then applied or sprayed onto an insulating base plate to form a coating, since magnetite loses the humidity-resistance characteristics when fired to more than 150° C. However, the coating of the humidity sensor obtained is poor in mechanical strength, easy to peel off and becomes unusable once peeling takes place.

Accordingly, a primary object of this invention is to provide a humidity sensor which is capable of accurately detecting the changes in humidity in terms of the changes in resistivity over the entire range of the relative humidity.

Another object of this invention is to provide a humidity sensor which is free of deterioration in respect of the humidity-resistivity characteristics thereof even when used repeatedly in a very humid atmosphere.

Another object of this invention is to provide a humidity sensor which will undergo hardly any change in resistivity when subjected to varying temperatures.

Another object of this invention is to provide a humidity sensor having resistivity in a practical range and which therefore does not require the use of a special device including some other special electrical elements.

Another object of this invention is to provide a humidity sensor having excellent mechanical strength.

Still another object of this invention is to provide a method for manufacturing a humidity sensor having the above characteristics.

These and other objects of this invention will become more apparent from the following description.

In principle, the present invention provides a humidity sensor having a negative relative humidity coefficient of resistivity which comprises 0.10 to 12.00 mole percent of alkali metal oxide, 0.05 to 10.00 mole percent of divanadium pentoxide and the balance substantially all silicon.

It has been found that the humidity sensor of this invention is capable of accurately detecting relative humidity since the resistivity thereof varies regularly in the exponential functional relation to the change in humidity over the entire relative humidity range; that repeated use in a very humid atmosphere does not impair the humidity-resistivity characteristics thereof; that the changes in temperature do not produce any substantial change in resistivity; that the sensor can be used for usual humidity measurement and in control devices since the changes in resistivity over the range of relative humidity of **0** to 100 percent are in a relative low range of about $10^9\Omega$-cm to $10^2\Omega$-cm; and that the sensor has excellent mechanical strength.

With the humidity sensor of this invention, the amounts of the alkali metal oxide and divanadium pentoxide are critical in achieving the effects described above.

In the first place, it is required that the alkali metal oxide content be 0.10 to 12.00 mole percent. If it is lower than 0.10 mole percent, an exponential functional relation will not be obtained between the relative humidity and the resistivity, while if it is in excess of 12.00 mole percent, the resistivity may be in an exponential functional relation to the relative humidity but varies also with the changes in temperature with high sensitivity. Accordingly, it is not suitable to use the alkali metal oxide in an amount out of the above-emntioned range. More preferably, the alkali metal oxide may be used in an amount of 0.20 to 10.00 mole percent. The alkali metal oxide may be sodium oxide, potassium oxide or the like. Sodium oxide is particularly preferable.

It is essential that the divanadium pentoxide content be 0.05 to 10.00 mole percent. If it is less than 0.05 mole percent or in excess of 10.00 mole percent, there will be no exponential functional relation nor any other regular relation between the relative humidity and the resistivity, this rendering the sensor unusable. More preferably, the divanadium pentoxide content may be 0.10 to 5.00 mole percent.

Furthermore it has been found that insofar as these oxide components are within the foregoing ranges, a certain kind of metal oxide can be substituted for part of silicon depending upon the purpose. Thus, ZrO_2 and/or SiO_2 may be substituted for 0.02 to 7.00 mole percent of silicon to impart improved chemical durability to the humidity sensor obtained.

The humidity sensor can be improved in mechanical strength by substituting Al_2O_3 for 0.01 to 5.00 mole percent of silicon.

Substitution of CaO and/or MgO for 0.01 to 2.00 mole percent of Si further gives improved water resistance to the humidity sensor.

The method of making a humidity sensor in accordance with this invention primarily comprises steps of providing a compact of mixed powders consisting essentially of 0.10 to 12.00 mole percent of alkali metal oxide, 0.05 to 10.00 mole percent of divanadium pentoxide and the balance substantially all silicon, firing the compact at about 500° C to about 800° C and thereafter cooling the compact to room temperature.

It is necessary to conduct firing at about 500° C to 800° C. A temperature lower than 500° C fails to impart sufficient mechanical strength to the humidity sensor, whereas if the firing temperature is higher than 800° C, the resultant product will be vitrified to markedly increase the resistivity thereof, rendering it incapable of exhibiting the desired change in resistivity. Accordingly, the firing temperature should be as set forth above. The firing temperature may preferably be in the range of 600°C to 750°C.

The firing gives a compact exhibiting semiconductivity with satisfactory mechanical strength imparted to the humidity sensor obtained. The firing time may generally be in the range of 10 to 60 minutes, more preferably 20 to 40 minutes.

In accordance with a preferred example of the above process, the alkali metal oxide, divanadium pentoxide and silicon are mixed together, along with the previously mentioned metal oxide substituting for part of the silicon when so desired, and a binder is then added to the mixture. The resultant mixture is thereafter kneaded in usual manner to prepare a pasty composition, which is directly molded or applied to an insulating base plate made of steatite porcelain, alumina porcelain or glass and equipped with electrodes. After drying, the product is placed in a furnace for firing in a surrounding atmosphere of air.

The binder permits the composition to retain its shape during molding and imparts adhesion to the mixture when it is applied to the base plate. The binder includes water, volatile organic solvents such as lower alcohols like methanol, ethanol, etc., aqueous solutions or volatile organic solvent solutions of high molecular weight substances such as sodium carboxymethyl cellulose. The solution may contain 3 to 10 wt percent of the high molecular weight substance. The binder is generally used in an amount of 5 to 20 wt parts per 100 wt parts of the mixture.

The electrical characteristics of the humidity sensor of this invention will become more apparent from the examples below and drawing showing the results obtained in the examples;

FIG. 1 is a chart bearing seven curves representing resistivity-relative humidity data showing the beneficial effect of alkali metal oxide in the compositions of this invention;

FIG. 2 is a chart bearing five curves illustrating resistivity-relative humidity data indicating the effect of divanadium pentoxide in these compositions;

FIG. 3 is an enlarged perspective view showing a semiconducting element used in determining the data given in FIG. 1; and

FIG. 4 is a chart illustrating resistivity-relative humidity data obtained with an embodiment of this invention.

EXAMPLE 1

A base plate used has a structure as shown in FIG. 3 comprising a steatite porcelain disk 1 measuring 19.7 mm in diameter and 2.4 mm in thickness and about 50 micron thick gold electrodes 2 and 3, said electrodes 2 and 3 respectively having nine and eight comblike projections 2' and 3' having a width of 0.2 mm. The projections 2' and 3' are spaced apart by 0.5 mm. To 4 wt parts of each of powder compositions Nos. I to VI containing the predetermined amounts of respective components as listed in Table 1 was added 1 wt part of a binder comprising 94.2 wt percent of diethylene glycol monobutyl ether, 5 wt percent of ethyl cellulose and 0.8 wt percent of tannic acid, and the mixture was kneaded for 24 hours by a kneader to prepare a paste, which was applied by screen printing to the base plate into an approximately 12mm-wide space between the gold electrodes 2 and 3 to a thickness of about 94 microns. The paste was dried at 100° C for about 30 minutes and then fired in the air at 680° C for 40 minutes to form a semiconductor film 4, and to the gold electrodes 2 and 3 were attached copper wires 5, 0.8 mm in diameter, whereby a humidity sensing resistive element was obtained.

TABLE 1

Composition Nos.		Proportions of components (mole %) Si	Na_2O	V_2O_5
Present invention	I	98.87	0.10	1.03
	II	96.41	2.56	1.03
	III	94.00	4.97	1.03
	IV	86.97	12.00	1.03
Comparison	V	98.92	0.05	1.03
	VI	83.97	15.00	1.03

The sample thus prepared was then placed in a constant temperature and constant humidity chamber, wherein the relative humidity was gradually varied with the temperature kept at 20° C to measure the changes in resistivity corresponding to the humidity changes by a universal bridge having a standard frequency of 1 KHz. The results are given in FIG. 1.

The vital necessity for a minimum of 0.10 mole percent and a maximum of 12.00 mole percent of sodium oxide in the resistor of this invention will be apparent from the data presented in FIG. 1. With the resistors containing 0.10 to 12.00 mole percent of sodium oxide prepared from the Compositions Nos. I to IV in accordance with this invention, the resistivity varies in ex-

ponential functional relation to the changes in the relative humidity, this indicating that they have satisfactory properties as sensors for humidity measurement and control devices. In contrast, the resistor prepared from Comparison Composition containing 0.05 mole percent of sodium oxide does not exhibit an exponential functional relation between the relative humidity and the resistivity. Although the sample prepared from the Comparison Composition VI with a sodium oxide content of 15.00 mole percent indicates an exponential functional relation between the relative humidity and the resistivity, the resistivity varies also with the temperature changes with high sensitivity. For instance, when the humidity is varied at a constant temperature of 100° C, the sample shows the humidity-resistivity characteristics as represented by Curve VI', which is markedly distinct from Curve VI at 20° C. Thus it is seen that the sample is not serviceable for humidity measurement and control devices.

Approximately the same results as above will be obtained with the use of oxides other than sodium oxide for the alkali metal oxide. However, from the viewpoint of accurate detection of the changes in resistivity, it is most preferable to use sodium oxide.

EXAMPLE 2

Humidity sensors were prepared in the same manner as above by using Compositions Nos. VII to IX of this invention and Comparison Compositions Nos. X to XI with component proportions as given in Table 2.

TABLE 2

Composition Nos.		Proportions of Components (mole %) Si	V_2O_5	Na_2O
Present invention	VII	97.39	0.05	2.56
	VIII	92.44	5.00	2.56
	IX	87.44	10.00	2.56
Comparison	X	97.41	0.03	2.56
	XI	82.44	15.00	2.56

The humidity sensors were then tested for the determination of the relation between the relative humidity and the resistivity. The results are shown in FIG. 2.

The effect of divanadium pentoxide on the electrical resistivity and relative humidity coefficient of various ceramic compositions is clearly shown in the data represented by several curves of FIG. 2. With the samples of this invention prepared from Compositions VII to IX containing 0.05 to 10.00 mole percent of divanadium pentoxide, the resistivity varies in exponential functional relation to the changes in the relative humidity, whereas in the case of the samples prepared from the Comparison Compositions X and XI containing 0.03 mole percent and 15.00 mole percent respectively of divanadium pentoxide, there is found no exponential functional relation nor any other regular relation between the relative humidity and the resistivity. The samples are therefore unusable for humidity measurement and control devices.

EXAMPLE 3

To 4 wt parts of a composition consisting of 94.10 mole percent of Si, 2.50 mole percent of Na_2O, 1.00 mole percent of V_2O_5, 0.65 mole percent of ZrO_2, 0.75 mole percent of Al_2O_3 and 1.00 mole percent of CaO was added 1 wt part of a binder consisting of 94.2 wt percent of diethylene glycol monobutyl ether, 5 wt percent of ethyl cellulose and 0.8 wt percent of tannic acid, and the mixture was kneaded by a kneader for 24 hours to prepare a pasty composition. The composition was applied to a base plate as shown in FIG. 3 to prepare a humidity sensor of this invention in the same manner as in Example 1.

The humidity-resistivity characteristics of this humidity sensor were measured in the same manner as in Example 1 with the results shown in FIG. 4. It is apparent that the sensor is capable of accurately indicating the changes in resistivity over the entire range of relative humidity.

Although the invention has been described with respect to certain specific examples, it will be appreciated that many modifications and changes may be made by those skilled in the art without departing from the spirit of the invention.

What we claim is:

1. A humidity sensor having a negative relative humidity coefficient of resistivity which comprises 0.10 to 12.00 mole percent of alkali metal oxide, 0.05 to 10.00 mole percent of divanadium pentoxide and the balance substantially all silicon.

2. The humidity sensor as set forth in claim 1 wherein said alkali metal oxide is sodium oxide.

3. The humidity sensor as set forth in claim 1 wherein said alkali metal oxide is contained in the amount of 0.20 to 10.00 mole percent.

4. The humidity sensor as set forth in claim 1 wherein said divanadium pentoxide is contained in the amount of 0.10 to 5.00 mole percent.

5. The humidity sensor as set forth in claim 1 wherein at least one of ZrO_2 and SiO_2 is substituted for 0.02 to 7.00 mole percent of said silicon.

6. The humidity sensor as set forth in claim 1 wherein Al_2O_3 is substituted for 0.01 to 5.00 mole percent of said silicon.

7. The humidity sensor as set forth in claim 1 wherein at least one of CaO and MgO is substituted for 0.01 to 2.00 mole percent of said silicon.

8. A method of producing a humidity sensor having a negative relative humidity coefficient of resistivity, which comprises the steps of providing a compact of mixed powders consisting essentially of 0.10 to 12.00 mole percent of alkali metal oxide, 0.05 to 10.00 mole percent of divanadium pentoxide and the balance substantially all silicon, firing said compact at 500° C to 800° C and thereafter cooling the fired compact to room temperature.

9. The method as set forth in claim 8 wherein said alkali metal oxide is sodium oxide.

10. The method as set forth in claim 8 wherein said firing temperature is in the range of 600°C to 750°C.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,721,631 Dated March 20, 1973

Inventor(s) Kiyoshi Sumi and Osamu Asakura

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

In the heading insert

--Claims priority of Japanese Application Serial No. 73579, filed August 21, 1970.--

Signed and sealed this 14th day of August 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents

FORM PO-1050 (10-69)

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