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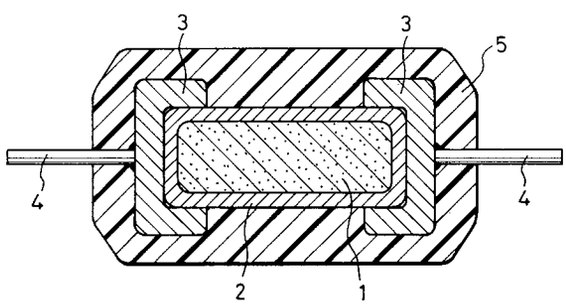
(54) **Metal oxide film resistor and method for producing the same.**

(57) A metal oxide film resistor having a resistance value in a wide range from 100Ω to 10 MΩ, a small variance in its resistance, and a positive and small temperature coefficient of resistance is made by comprising mainly indium oxide and auxiliarily an oxide of at least one metal added as an activator for covering the wide range of resistance. A method of producing the metal oxide film resistor comprises the steps of: preparing a solution composed of at least an inorganic indium salt, an organic compound capable of coordinating to indium, and an organic solvent capable of dissolving said components; applying said solution to an insulating substrate to form a coated film; firing the coated film to form an indium oxide film; and optionally subjecting said indium oxide film to a heat treatment under an inert gas atmosphere or a reducing gas atmosphere.

FIG.1



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BACKGROUNDS OF THE INVENTION

1. Field of the Invention

The present invention relates to a metal oxide film resistor which has wide applications for configuring circuits in various electric appliances, and a method for producing such metal oxide film resistors.

2. Description of the Related Art

Conventional metal oxide film resistors are generally configured with insulating substrates of rod-type made of mullite or alumina, metal oxide films comprising tin oxide or antimony tin oxide (ATO) formed on the surfaces of the substrates, pairs of metal cap terminals press-fitted on both ends of the substrates, lead wires welded to the terminals, and electrically insulating protective films formed on the surfaces of the resistors.

Of these metal oxide film resistors, those comprising a single phase of tin oxide have a very large temperature coefficient of resistance and their conditions for application are greatly limited, and are therefore not practical. For this reason, the ATO has now been put into practical use as the material for the metal oxide film in general.

The method for producing the metal oxide film is generally performed in a chemical film forming process such as spraying or chemical vapor deposition (CVD). In these processes, a film of ATO is formed on the surface of the substrate by spraying vapor of an aqueous solution or an organic solvent solution containing stannic chloride and antimony trichloride to the substrate of rod-type placed in a furnace elevated to 600 - 800 °C. Thereafter, a pair of metal cap terminals are press-fitted on both ends of the substrate, and a part of the film is cut or grooved in order to adjust the resistance of the film to have a desired value. The metal oxide film resistor is completed by welding a pair of lead wires to the metal cap terminals, and forming a resin protective coating film on these components.

However, the metal oxide film resistor using the ATO film has a disadvantage that it has a large variance or dispersion or scatter in its resistance value, presumably because the ATO film is formed by an unstable film forming process such as spraying process and the antimony therein is thermally unstable. In addition, since specific resistance of the ATO film is relatively low, e.g., about from 1×10^{-3} to 1×10^{-2} Ω • cm, the film thickness must be made considerably thin in a case wherein the final resistance value is 100 kΩ or above. When this inconvenience is put together with the above-mentioned disadvantage in the manufacturing process which represents the large variance in its resistance value, it has been difficult to obtain a metal oxide film resistor having a constant or uniform quality and a high reliability.

SUMMARY OF THE INVENTION

The present invention is proposed in order to overcome the above-mentioned disadvantages and deficiencies of the prior art, and has, as its object, a provision of a metal oxide film resistor having a resistance value in a wide range from 100Ω to 10 MΩ, and a small variance or dispersion or scatter in its resistance.

It is another object of the present invention to provide a method for producing a metal oxide film resistor having a constant film thickness, and a small variance in its resistance.

It is a further object of the present invention to provide a metal oxide film resistor which demonstrates a temperature coefficient of resistance of a positive and small value.

It is still another object of the present invention to provide a method for producing a metal oxide film resistor having a metal oxide film of a constant film thickness and a small variance in its resistance.

The present invention provides a metal oxide film resistor comprising: an insulating substrate, an indium oxide film formed on the surface of the insulating substrate, and a pair of terminals which are in contact with the indium oxide film.

The present invention also provides a metal oxide film resistor, wherein the indium oxide film further comprises an oxide of tin.

In a preferred embodiment of the present invention, the above-mentioned indium oxide film comprises, as an activator, an oxide of at least one metal selected from the group consisting of aluminum, magnesium, calcium, titanium, vanadium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, molybdenum, lanthanum and cerium, in place of the tin oxide or in addition to the tin oxide.

The present invention also provides a method for producing a metal oxide film resistor comprising the steps of:

preparing a solution composed of at least an inorganic indium salt, an organic compound capable of coordinating to indium, and an organic solvent capable of dissolving the inorganic indium salt and the organic compound,

applying the solution to an insulating substrate to form a coated film, and

firing the coated film to form an indium oxide film in the air or under an atmosphere containing oxygen.

In a preferred embodiment of the method for producing a metal oxide film resistor in accordance with the present invention, the solution further contains an organic salt of tin.

In a further preferred embodiment of the present invention, the solution further comprises an inorganic salt or an organic salt of a metal selected from the group consisting of aluminum, magnesium, calcium, titanium, vanadium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, molybdenum, lanthanum and cerium in place of the organic salt of tin or in addition to the organic salt of tin.

A method for producing a metal oxide film resistor in a preferred embodiment of the present invention comprises the steps of:

preparing a solution composed of at least an inorganic indium salt, an organic compound capable of coordinating to indium, and an organic solvent capable of dissolving the inorganic indium salt and the organic compound,

applying the solution to an insulating substrate to form a coated film,

firing the coated film to form an indium oxide film in the air or under an atmosphere containing oxygen, and

heat-treating the indium oxide film under an inert gas atmosphere or a reducing gas atmosphere.

In the above-mentioned method, a preferred inorganic indium salt employed is indium nitrate.

Further, the organic compound capable of coordinating to indium is preferably at least one compound selected from the group consisting of β-diketones, polyhydric alcohols and condensation products of polyhydric alcohols.

Further, the organic salt of tin is preferably a salt of dicarboxylic acid.

In a preferred embodiment of the present invention, the firing step is performed at a temperature ranging from 400 °C to 900 °C.

Further, in a preferred embodiment of the present invention, the heat-treating of the indium oxide film is performed at a temperature ranging from 200 °C to 600 °C.

In a preferred embodiment of the present invention, the inert gas or reducing gas atmosphere employed in the heat-treating of the indium oxide film is an atmosphere of at least one species or a mixed gas atmosphere of two or more species selected from the group consisting of nitrogen, argon and hydrogen.

In a preferred embodiment of the present invention, the step of applying the solution to the insulating substrate comprises the steps of:

accommodating a multiplicity of the substrates in a container having a multiplicity of apertures which are smaller than the substrate,

soaking or dipping the substrates in the solution while the container is being rotated, and

thereafter drying the substrates while the container is being rotated.

While the novel features of the present invention are set fourth particularly in the appended claims, the invention, both as to organization and content, will be better understood and appreciated, along with other objects and features thereof, from the following detailed description taken in conjunction with the attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG.1 is a cross-sectional side view showing a schematic configuration of the metal oxide film resistor built in accordance with an embodiment of the present invention.

FIG.2 is a diagram showing a relationship between the resistance value and the proportion of tin added to the film of a resistor configured with an indium oxide film also containing oxide of tin built in accordance with an embodiment of the present invention.

FIG.3 is a diagram showing a relationship between the resistance value as well as its temperature coefficient and the proportion of tin added to the film of a resistor configured with an indium oxide film containing oxide of tin in another embodiment of the present invention.

FIG.4 is a perspective view showing a schematic configuration of an apparatus used for coating a metal oxide film-forming composition in accordance with an embodiment of the present invention.

FIG.5 is a front view showing a state of holding the substrate by a grasping device used in Comparative Example 4.

FIG.6 is a front view showing a state of holding the substrate by a grasping device used in Examples 1 - 6 of the present invention and in Comparative Example 5.

FIG.7 is a perspective view showing a resistor whose metal oxide film has a spiral groove for adjusting its resistance.

FIG.8 is a diagram showing a relationship between the number of turns of the spiral groove provided on the metal oxide film and its resistance value in the resistor shown in FIG.7.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Specific resistance of single phase indium oxide which constitutes the body of the metal oxide film resistor of the present invention is in a range from about $4 \times 10^{-4}\Omega \cdot$ cm to about $1 \times 10^{-1}\Omega \cdot$ cm depending on the amount of oxygen imperfections or defects present in the oxide film. However, by adequately adjusting the species and the amount of metal element to be added to the indium oxide film, it is possible to obtain an indium oxide film that has a resistance value in a wide range. A film composed of indium oxide including tin has a specific resistance in a range from about $1 \times 10^{-4}\Omega \cdot$ cm to about $1 \times 10^{-1}\Omega \cdot$ cm, and a temperature coefficient of resistance value of ±200 ppm/°C, depending on the amount of the added tin. By adequately adjusting the species and the amount of metal element to be added to the indium oxide in addition to tin, it is further possible to obtain an indium oxide that has a resistance value in a very wide range as compared with the ATO film, of a specific resistance in a range from about $1 \times 10^{-4}\Omega \cdot$ cm to about $1 \times 10^{2}\Omega \cdot$ cm.

Moreover, in the production method of the present invention, a solution composed of at least an inorganic indium salt, an organic compound capable of coordinating to indium, and an organic solvent capable of dissolving the inorganic indium salt and the organic compound is employed as a composition for forming the metal oxide film. In preparing this composition, it is preferable to reflux the above-mentioned components at a temperature where the organic solvent can be refluxed. This refluxing treatment is performed in order to promote a reaction of the indium salt or another salt of metal M further added as an activator with the organic compound capable of coordinating to indium, and is not necessarily indispensable for the preparation of the solution. In a case of employing an activator having a very low solubility at room temperature, however, the refluxing treatment is an effective means for the preparation of the solution.

The organic compound capable of coordinating to indium has a function of suppressing possible hydrolysis of the indium salt by forming a coordination compound with indium. During a thermal decomposition process, a situation where a deposition of the above-mentioned indium salt takes place simultaneously with its thermal decomposition is produced. This is because a part of the organic compound capable of coordinating to indium, which had failed to form a coordination compound with indium and remained after an evaporation of the organic solvent, functions as an auxiliary solvent for the above-mentioned indium salt until the thermal decomposition of the above-mentioned indium salt is actually completed. Thanks to the presence of the organic compound capable of coordinating to indium in the solution, it is possible to obtain a very fine and dense film.

Further, in a case of adding another metal M salt as an activator to the solution in order to cause the other metal M to be included in the finished indium oxide film, a deposition and a thermal decomposition of both of the above-mentioned indium salt and the activator take place simultaneously. Since a metal oxide film having a very small deviation of composition can be produced by the above-mentioned function of the organic compound capable of coordinating to indium, it is possible to produce a metal oxide film resistor having a very small variance in its resistance value in a stable operation.

As previously described, the organic compound capable of coordinating to indium greatly participates in the thermal decomposition process of the indium salt, and thus the characteristics of the obtained film are greatly influenced by the property (for instance, boiling point) of the compound. Therefore, an adequate selection of the species of the organic compound is important.

As a method for applying the metal oxide film-forming composition prepared in the above-mentioned manner to the surface of the substrate, a dip-coating process, a spraying method, a dispenser method and the like are employed.

The substrate employed in the present invention should have an electrically insulating property at least on its surface, and is preferably exemplified as ceramic materials such as mullite, alumina, forsterite, steatite and cordierite.

The coated film of the composition for forming the metal oxide film is dried, and then fired to form the metal oxide film comprising indium oxide or the one comprising indium oxide as its principal component and other oxide(s) of the metal M. The temperature of performing the firing step is above a temperature at which the composition for forming the metal oxide film is thermally decomposed and is below a

temperature at which the substrate deforms, and is preferably in a range from 400 °C to 900 °C. The atmosphere under which the above-mentioned firing step is performed is air or an atmosphere including oxygen. The thickness of the metal oxide film formed in this manner is usually in a range from several tens nm to several hundreds nm.

It is preferable that the above-mentioned oxide film is subjected to a heat treatment under an inert gas atmosphere or a reducing gas atmosphere. By this heat treatment, a desorption of oxygen which had been chemically adsorbed on the surface of the oxide film and a formation of vacant hole of oxygen in the crystals of the indium oxide occur. A resistor having a smaller variance in the resistance value is given by this treatment.

The heat treatment is preferably performed under a nitrogen gas atmosphere or a mixed gas atmosphere of nitrogen and hydrogen.

Although the resistance value of the metal oxide film after the firing treatment becomes constant within several hours, that of the metal oxide film after the above-mentioned heat treatment under an inert gas or reducing gas atmosphere necessitates several days until the value becomes constant. It is believed that behavior of the metal oxide film of inuniform resistance value is attributable to oxygen gas which had been adsorbed on the film during the firing process. By this heat treatment under an inert gas or reducing gas atmosphere, the oxygen gas which had been adsorbed during the firing process desorbs therefrom and releases or emits conductive electrons. In this heat treatment, since a thermodynamically stable amount of oxygen is left in adsorbed state, the variance or scatter of the resistance value attributable to the variance or scatter in the amount of the adsorbed oxygen decreases.

Incidentally, indium oxide is a semi-conductor which has a large band gap of 3.3 eV or larger, and also a transparent conductive material which has a high carrier (conductive electron) concentration. Therefore, by the above-mentioned heat treatment under the inert gas or the reducing gas atmosphere, the carrier concentration of the indium oxide increases and the resistance value decreases by as much as the portion of the conductive electrons released or emitted as a result of the desorption of the oxygen gas which has been adsorbed during the firing process. And, it is believed that, since the amount of the conductive electrons in the conduction band becomes very large, the electrons in the lower band (valence band) are hardly excited to the conduction band even with the increase in the temperature. On the contrary, the resistance value rather increases by a scattering of the conductive electrons induced by a lattice vibration, and thus the metal oxide film after the above-mentioned heat treatment under the inert gas or reducing gas atmosphere demonstrates a positive temperature coefficient of resistance value which is analogous to that of a metal.

As mentioned in the foregoing, if the temperature during the heat treatment under the inert gas or reducing gas atmosphere is lower than a certain extent, the adsorbed oxygen is hardly desorbed. On the contrary, if the temperature during the heat treatment under the inert gas or reducing gas atmosphere is higher than a certain extent, the metal oxide film demonstrates a positive and large temperature coefficient of resistance value, because the metal oxide film is reduced during the heat treatment and thus a deposition or precipitation of a metal takes place. The degree of reduction may differ with the species of the inert gas or the reducing gas, and an upper limit of the heat treatment temperature falls if a gas is of a high reducing ability. Preferably, this heat treatment is performed at a temperature ranging from 200 °C to 600 °C.

Any of inorganic indium salts can be employed as far as it contains a ligand that can be exchanged or substituted with the organic compound capable of coordinating to indium; and indium chloride, indium sulfate and the like are employed as the inorganic indium salt in addition to the exemplified indium nitrate. As the organic salt of tin, a salt of carboxylic acid, a salt of dicarboxylic acid, complex salt with acetylacetone and the like can be used, of which the most preferable is the salt of dicarboxylic acid.

The organic compound capable of coordinating to indium is necessary for giving a solubility in the organic solvent to the indium by partly forming a coordination compound with indium; and any of β-diketones such as acetylacetone, polyhydric alcohols such as ethylene glycol and trimethylene glycol, condensation products of polyhydric alcohol such as diethylene glycol and triethylene glycol can be employed.

Any of organic solvents can be employed as far as it can dissolve the organic compounds and inorganic compounds used in the present invention, and may be exemplified as aromatic hydrocarbons such as toluene and xylene, alcohols such as methanol, ethanol and isopropanol, acetic acid esters such as ethyl acetate and butyl acetate, ketones such as acetone and diethylketone, ethers such as methoxyethanol and ethoxyethanol, tetrahydrofuran, and the like.

The activator is a metal salt added to the film-forming composition in order to adjust the resistance value and the temperature coefficient of resistance of the finished indium oxide film; and the metal element in the salt can be exemplified as aluminum, magnesium, calcium, titanium, vanadium, manganese, iron,

cobalt, nickel, copper, zinc, yttrium, zirconium, molybdenum, lanthanum and cerium, in addition to the above-mentioned tin. These metals are employed as their inorganic salts such as nitrate, chloride, sulfate and fluoride, carboxylic acid salts such as 2-ethylhexylic acid salt, dicarboxylic acid salts such as oxalic acid salt, complex salts with acetylacetone, and the like, of which the most preferable are the dicarboxylic acid salts.

It is believed that each of these metal elements forms a solid solution or a complex oxide with indium oxide in a manner similar to that in the case with tin, or becomes a metal oxide, thereby to create a state wherein it is mixed with indium oxide.

This belief is further illustrated in detail as follows. The metal oxide film in accordance with the present invention can be considered to be in a state wherein the following three local states are mixed.

1. A state wherein the oxide of the various metals other than indium is in a solid solution with the indium oxide.
2. A state wherein the above-mentioned oxide of the various metals forms a compound with the indium oxide.
3. A state wherein both of the above-mentioned oxide of the various metals and the indium oxide exist discretely without forming a solid solution and/or a compound.

In a case wherein the amount of the metal oxide of the various metals is small for indium oxide, the metal oxide is completely dissolved in the indium oxide in a solid state, but the respective metal oxides may differ from each other with respect to their solubilities. And the indium oxide added with the metal oxide of the various metals exists in a single phase. In a case wherein the amount of the metal oxide of the various metals is large for indium oxide, all of the metal oxide is not completely dissolved in the indium oxide in a solid state, and a part of the metal oxide is deposited or precipitated in the interface of the grains. And the metal oxide of the various metals exists in a dispersed state by making the indium oxide added with the other metal oxide as a matrix. A part of the metal oxide reacts with the indium to form a compound of the spinel form such as MIn_2O_4 or $InMO_3$ type. And in a case wherein the amount of the metal oxide of the various metals is small for indium oxide, a complex oxide composed of the metal oxide and the indium oxide exists in a single phase. In a case wherein the amount of the metal oxide of the various metals is large for indium oxide, the metal oxide is deposited or precipitated in the interface between the grains of the indium oxide, and exists in a dispersed state in a matrix of the complex compound composed of the metal oxide and the indium oxide.

The following examples and comparative examples are provided for the purpose of further illustrating the present invention with reference to the attached drawings, but are in no way to be taken as limiting.

EXAMPLE 1

FIG.1 shows a schematic configuration of the metal oxide film resistor built in accordance with an embodiment of the present invention.

Synthesis of Metal Oxide Film-Forming Composition

To 45 g of indium nitrate ($In(NO_3)_3 \cdot 3H_2O$) weighed and placed in a conical flask of 1 L. volume, added were 50 g of acetylacetone, and the mixture was blended in room temperature to dissolve the indium nitrate in the acetylacetone. To each of the solutions thus obtained, added were an acetylacetone complex salt of each of the various metals M weighed in a manner that a value represented by the formula: M/(In + M) and converted in terms of mole number of the metals becomes 0.05 and 260 g of acetone, and refluxed at 60 °C. The solutions obtained after the refluxing were cooled to around room temperature to prepare the metal oxide film-forming compositions.

Coating of Substrate with the Composition

Next, a substrate 1 was coated with each of the metal oxide film-forming compositions prepared in the above-mentioned manner by a dip-coating process. The substrate 1 was configured cylindrical and is made of a ceramic containing 92 wt% of alumina with a balance of silica, having a diameter of 2 mm and a length of 10 mm. In this dip-coating process, a grasping device composed of a pair of calipers 18 and 19 equipped with a compression spring 20 shown by FIG.6 was employed. The grasping device holds the substrate at its both ends in a manner that the lengthwise direction of the substrate 16 was in horizontal position while it was soaked or dipped in and then withdrawn from the composition.

After drying the coated film of the above-mentioned metal oxide film-forming composition at 60 °C for 5 minutes, it was fired in the air at 800 °C for 10 minutes to form a metal oxide film 2 with a thickness of about 50 nm consisting mainly of indium oxide.

Assembly of Resistor

A pair of cap terminals 3, 3 made of stainless steel plated with tin were press-fitted on both ends of the substrate 1 having been formed with the above-mentioned metal oxide film 2 and a pair of copper lead wires 4, 4 plated with tin were welded to the cap terminals 3, 3. As the cap terminals 3, any terminals may be used as far as they can be ohmically connected to the metal oxide film 2; and as the lead wires 4, any lead wires may be used as far as they can be ohmically connected to the cap terminals 3.

Next, the surface of the above-mentioned metal oxide film 2 was coated with a paste of a thermosetting resin, dried and then cured by heating at 150 °C for 10 minutes to form an electrically insulating protective film 5 for completing the metal oxide film resistor of the present invention. As the protective film 5, any resin material which may include any inorganic filler may be used as far as it has an electrically insulating property and a humidity-resistant property; and its curing may be performed by using an irradiation of visible light, ultraviolet light, or the like in addition to the heat.

The characteristics of the metal oxide film resistors produced with the respective compositions are summarized in Table 1 below.

COMPARATIVE EXAMPLE 1

A metal oxide film-forming composition was obtained by mixing stannic chloride ($SnCl_4 \cdot 5H_2O$), antimony trichloride ($SbCl_3$) and methanol in a proportion of 100 g, 6.4 g, and 10 ml, respectively. This composition was heated at 110 °C to be converted into a state of smoke, and blown onto a substrate kept at 650 °C to form a metal oxide film consisting of the ATO on the substrate. A pair of cap terminals made of stainless steel plated with tin were press-fitted on both ends of the substrate having been formed with the above-mentioned ATO film; and then a pair of copper lead wires plated with tin were welded to the cap terminals. Finally, the surface of the above-mentioned ATO film was coated with a paste of a thermosetting resin, dried and then cured by heating at 150 °C for 10 minutes to form an electrically insulating protective film for completing the metal oxide film resistor.

The characteristic of the resistor of the Comparative Example is also shown in Table 1 below.

Table 1

Metal M	Resistance value(kΩ)
None	100
Al	150
Mg	6000
Ca	8000
Ti	100
V	320
Mn	12000
Fe	440
Co	15000
Ni	740
Cu	3800
Zn	6000
Y	860
Zr	14
Mo	460
Sn	2.0
La	1200
Ce	1600
C.E.	0.15

C.E.: Comparative Example 1

EXAMPLE 2

Synthesis of Metal Oxide Film-Forming Composition

To 45 g of indium nitrate ($In(NO_3)_3 \cdot 3H_2O$) weighed and placed in a conical flask of 1 L. volume, added were 50 g of acetylacetone, and the mixture was blended in room temperature to dissolve the indium nitrate in the acetyl acetone. To the solution thus obtained, added were stannous oxalate (SnC_2O_4) weighed in a manner that a value represented by the formula: Sn/(In + Sn) becomes from 0.025 to 0.30 and 260 g of acetone, and refluxed at 60 °C. The solution obtained after the refluxing was cooled to around room temperature to prepare the metal oxide film-forming composition.

Coating of Substrate with the Composition

Next, a substrate similar to that in Example 1 was coated with the composition by a dip-coating process in a manner similar to that in Example 1. The coated film of the composition was dried at 60 °C for 5 minutes, and then fired at 800 °C for 10 minutes to form a metal oxide film with a thickness of about 50 nm consisting mainly of indium oxide also containing tin oxide. Thereafter, a pair of cap terminals as well as lead wires were attached to the substrate in a manner similar to that in Example 1, and a protective film consisting of a thermosetting resin was formed on these components.

The relationships between the resistance values of the metal oxide film resistors thus obtained, and the proportion of tin added to the composition are summarized in FIG. 2. As clearly seen from FIG.2, by selecting the film consisting indium oxide also containing tin oxide as the resistor element, it is possible to obtain the metal oxide film resistor having a resistance value in a wide range.

EXAMPLE 3

In a manner similar to that in Example 2, a series of metal oxide film-forming compositions was synthesized by using indium nitrate, acetyl acetone, and stannous oxalate of such an amount that satisfies Sn/(In + Sn) = 0.15, and each of acetyl acetone complex salts of the various metals M of such an amount that satisfies M/(In + M) = 0.10, as well as 260 g of acetone. By using these compositions, the resistors having the indium oxide films containing oxide of tin, or oxide of tin as well as the oxide of the various

metals M were obtained in a manner similar to that in Example 2. The characteristics of the respective metal oxide film resistors are summarized in Table 2 below. As clearly seen from Table 2, by properly selecting the species of the various metals M, it is possible to obtain the metal oxide film resistors having a resistance value in a wide range.

TABLE 2

Metal M	Resistance value(kΩ)
None	0.60
Al	1.80
Mg	45.0
Ca	1500
Ti	0.90
V	3.60
Mn	250
Fe	15.0
Co	450
Ni	120
Cu	900
Zn	2.70
Y	1.60
Zr	1.20
Mo	2.20
La	8.00
Ce	10.0

EXAMPLE 4

Synthesis of Metal Oxide Film-Forming Composition

To 45 g of indium nitrate ($In(NO_3)_3 \cdot 3H_2O$) weighed and placed in a conical flask of 1 L. volume, added were 50 g of acetylacetone, and the mixture was blended in room temperature to dissolve the indium nitrate in the acetyl acetone. To each of the solutions thus obtained, added were an acetyl acetone complex salt of the various metals M in such an amount that satisfies M/(In + M) = 0.05, as well as 260 g of acetone, and refluxed at 60 °C. The solutions obtained after the refluxing were cooled to around room temperature to prepare the respective metal oxide film-forming compositions.

Coating of Substrate with the Composition

Next, a substrate similar to that in Example 1 was coated with one of the compositions by the dip-coating process in a manner similar to that in Example 1. The coated film of the composition was dried at 60 °C for 5 minutes, and then fired in the air at 800 °C for 10 minutes to form a metal oxide film consisting mainly of indium oxide. Thereafter, a pair of cap terminals as well as lead wires were attached to each of the substrates in a manner similar to that in Example 1.

Next, each of the substrates thus obtained was heat-treated at 300 °C for 3 hours. The atmosphere under which this heat treatment is performed may be any of an inert gas or reducing gas, and is preferably an atmosphere of at least one selected from the group consisting of nitrogen, argon and hydrogen, or a mixed gas atmosphere of at least two selected from the group. It is preferable that the heat treatment is performed at a temperature in a range from 200 °C to 600 °C.

Finally, the metal oxide film resistors of this example were completed by forming electrically insulating protective films consisting of a thermosetting resin on the surfaces of the metal oxide films in a manner similar to that in Example 1.

The characteristics of the metal oxide film resistors added with the various metals M as the activator are summarized in Table 3 below. The temperature coefficient of resistance was calculated based on the difference of resistances between 25 °C and 125 °C. As clearly seen from Table 3, it was found that the metal oxide film resistors having a resistance value in a wide range and a small variance in the resistance

value were obtained by this process.

Table 3

Activator	Resistance value (kΩ)	Variance (%)	TCR (ppm/°C)
Sn	0.2	±5	300
Mo	1.0	±5	300
Ce	3.3	±5	300
Zn	50	±5	400
Ni	1200	±5	400
Mn	5000	±5	400
Mg	12000	±5	500
TCR: Temperature Coefficient of Resistance			

EXAMPLE 5

A metal oxide film resistor was produced in an identical manner with that in Example 4 except for the use of stannous oxalate (SnC_2O_4) as the activator in such an amount that satisfies Sn/(In + Sn) = 0.05.

COMPARATIVE EXAMPLE 2

A metal oxide film resistor was produced in an identical manner with that in Example 4 except for the use of tin acetylacetonate as the activator in such an amount that satisfies Sn/(In + Sn) = 0.05, and an omission of the heat treatment under inert gas atmosphere.

COMPARATIVE EXAMPLE 3

A metal oxide film resistor was produced in an identical manner with that in Example 4 except for the use of zinc acetylacetonate as the activator in such an amount that satisfies Zn/(In + Zn) = 0.05, and an omission of the heat treatment under inert gas atmosphere.

Table 4 summarizes the characteristics of the metal oxide film resistors produced in Example 5, and Comparative Examples 2 and 3. As clearly seen from Table 4, the resistors obtained by Comparative Examples 2 and 3 show a very large variance in the resistance value which is three times as large as that obtained by Example 5, and the value of the temperature coefficient of resistance of the resistors of Comparative Examples 2 and 3 is about three times as large as that obtained by Example 5.

Table 4

	Resistance value (kΩ)	Variance (%)	TCR (ppm/°C)
Example 5	0.2	±5	300
Comparative Example 2	0.5	±15	-800
Comparative Example 3	110	±15	-1000
TCR: Temperature Coefficient of Resistance			

EXAMPLE 6

Synthesis of Metal Oxide Film-Forming Composition

To 36 g of indium nitrate ($In(NO_3)_3 \cdot 3H_2O$) weighed and placed in a conical flask of 1 L. volume, added were 32 g of ethylene glycol ($HOCH_2CH_2OCH_2CH_2OH$), and the mixture was blended at room temperature to dissolve the indium nitrate in the ethylene glycol. To the solution thus obtained, added were stannous oxalate weighed in such an amount that satisfies Sn/(In + Sn) = 0.025 --- Sn/(In + Sn) = 0.3, as well as

260 g of acetone, and refluxed at 60 °C. The solutions obtained after the refluxing were cooled to around room temperature to prepare the respective metal oxide film-forming compositions.

Coating of Substrate with the Composition

Next, a substrate similar to that in Example 1 was coated with one of the compositions by a dip-coating process in a manner similar to that in Example 1. The coated film of the composition was dried at 60 °C, and then fired in the air at 800 °C for 10 minutes to form a metal oxide film having a thickness of about 50 nm consisting mainly of indium oxide also containing tin oxide. Thereafter, a pair of cap terminals as well as lead wires were attached to each of the substrates in a manner similar to that in Example 1.

Next, each of the substrates thus obtained was heat-treated under a nitrogen gas atmosphere at 500 °C for 5 hours. Thereafter, the metal oxide film resistors of this example were completed by being provided with a pair of cap terminals as well as lead wires and by being formed of electrically insulating protective films consisting of a thermosetting resin on the surfaces of the metal oxide films in a manner similar to that in Example 1.

The relationships between the resistance value as well as its temperature coefficient of the thus obtained metal oxide film resistors, and the proportion of tin added to the metal oxide film-forming composition are shown in FIG.3. As clearly seen from FIG.3, it is found that the metal oxide film resistors having a resistance value in a wide range and a small and positive temperature coefficient of resistance were obtained by adequately selecting a film consisting indium oxide also containing tin oxide as the resistor element.

EXAMPLE 7

In this example, a description will be made on a method of coating the substrate with the film-forming composition and drying which is suited for a mass-production of the metal oxide film resistor.

FIG.4 shows a container 10 used for coating the substrate with the film-forming composition and drying. The container 10 is a combination of a cylindrical barrel 12 made of polyfluorocarbon resin provided with a multiplicity of apertures 11 whose sizes are smaller than that of the substrate so as to prohibit an escape of the substrate from the container 10, with a pair of lids 14 made of polyfluorocarbon resin and fitted on both ends of the cylindrical barrel 12. Each of the lids is provided with a rotating axis 15 supported by a suitable supporting means as well as a multiplicity of small pores 13. The container 10 is configured to be rotatable around the rotating axis 15 by a suitable driving means.

The container 10 accommodating a multiplicity of the substrates is first soaked or dipped in the metal oxide film-forming composition and the surfaces of the substrates are coated with the above-mentioned composition by rotating the container 10. Then, by withdrawing the container 10 from the composition and rotating the container in a drier, a coated film of uniform thickness is formed on each of the surfaces of the substrates. Although polyfluorocarbon resin is used for configuring the cylindrical barrel 12 and the lids 14, polyethylene and/or polypropylene may similarly be used with the same advantage.

In this example, 20 pieces of the substrates identical with those used in Example 1 were accommodated in the cylindrical barrel container 10 having a diameter of 4 cm and a length of 20 cm, and the film-forming composition identical with that in Example 4 was prepared. After being soaked or dipped in the composition for 5 seconds while the container 10 being rotated around its center axis at 12 rpm, the container 10 was withdrawn from the composition at a velocity of 60 cm/minute while being similarly rotated, and its content was dried at 60 °C for 10 minutes while being similarly rotated.

Next, the above-mentioned soaking or dipping and drying were repeated again. In this manner, the substrates which had been formed of the coated film of the composition were taken out from the container 10, and fired at 850 °C for 10 minutes to form the metal oxide films having a thickness of about 100 nm consisting mainly of indium oxide.

Then, after the substrates thus obtained were heat-treated under nitrogen atmosphere at 300 °C for 3 hours, a pair of the cap terminals and lead wires were attached to each of the substrates in a manner similar to that in the foregoing examples. Thereafter, the metal oxide film resistors of this example were completed by forming electrically insulating protective films consisting of a thermosetting resin on the surfaces of the metal oxide films in a manner similar to that in Example 1.

The characteristics of the metal oxide film resistors consisting mainly of indium oxide added with the various activators are summarized in Table 5 below. As apparently seen from Table 5, it is appreciated that each of the resistors of this example has a small variance in the resistance value and a small temperature coefficient of resistance.

Table 5

Activator	Resistance value (kΩ)	Variance (%)	TCR (ppm/°C)
Sn	0.1	±5	300
Mo	1.0	±5	300
Ce	2.5	±5	300
Zn	30	±5	400
Ni	800	±5	400
Mn	3000	±5	400
Mg	9000	±5	500
TCR: Temperature Coefficient of Resistance			

EXAMPLE 8

A procedure analogous to that in Example 7 was repeated by using a metal oxide film-forming composition comprising cerium as the activator M in an amount which satisfies M/(In + M) = 0.05, to produce a resistor which has no protective film composed of a thermosetting resin.

COMPARATIVE EXAMPLE 4

By holding a substrate 16 with a pair of vacuum-absorption tweezers (or a suction chuck) 17 so that the lengthwise direction of the substrate 16 was in perpendicular as shown by FIG.5, the substrate 16 was first soaked or dipped in the metal oxide film-forming composition which was identical with that of Example 8. Then the substrate 16 was withdrawn from the composition at a velocity of 60 cm/minute, dried at 60 °C for 10 minutes, and then fired and heat-treated under the conditions identical with that in Example 7 to produce a resistor which has no protective film composed of a thermosetting resin.

COMPARATIVE EXAMPLE 5

By holding a substrate 16 on its both ends with a grasping device composed of a pair of calipers 18 and 19 equipped with a compression spring 20 so that the lengthwise direction of the substrate 16 was in horizontal as shown by FIG.6, the substrate 16 was first soaked or dipped in the same metal oxide film-forming composition as the above-mentioned. Then the substrate 16 was withdrawn from the composition at a velocity of 60 cm/minute, dried at 60 °C for 10 minutes, and then fired and heat-treated under the conditions identical with those in Example 7, to produce a resistor which has no protective film composed of a thermosetting resin.

On each of the metal oxide films 2 formed on the resistors obtained in Example 8, and Comparative Examples 4 and 5, a spiral groove 6 was provided by a diamond cutter as shown by FIG.7. By selecting a first point P_0 as a base point of one of the terminal regions which is also a starting point of the spiral groove 6, selecting a second point $P_{0.5}$ as a point of the film whereto the groove turns half (0.5) time around the cylindrical substrate, selecting a third point $P_{1.0}$ as a point of the film whereto the groove turns one (1.0) time around the cylindrical substrate and so on, the resistance values of the metal oxide film between the points P_0 and $P_{0.5}$, and between the points P_0 and $P_{1.0}$, and so on were measured. The results of the resistance value measurements up to the position where the groove 6 turns five times around the cylindrical substrate are summarized in FIG.8.

As clearly shown in FIG.8, the resistor obtained by Example 8 demonstrates a linear relationship between the number of turns and the resistance value, because the coating film of the metal oxide film-forming composition is formed uniformly. In the resistor obtained by Comparative Example 5, the thickness of part of the coating film which had been at the bottom of the substrate during the dip-coating process was large and that of the coating film which had been at the top of the substrate was small, as apparent from the position of the substrate during the dip-coating process shown by FIG.6. The rate of increase of the resistance value of this resistor changes for every half (0.5) turn of the groove 6. On the other hand, the resistor obtained by Comparative example 4 varies its increase rate in the resistance value with the increase in the turn number of the groove 6, because the thickness of the coating film of the composition varies along its lengthwise direction as apparent from the position of the substrate during the dip-coating process

shown by FIG.5.

Although the present invention has been described in terms of the presently preferred embodiments, it is to be understood that such disclosures are not to be interpreted as limiting. Various alterations and modification will no doubt become apparent to those skilled in the art to which the present invention pertains, after having read the above disclosure. Accordingly, it is intended that the appended claims be interpreted as covering all alterations and modifications as fall within the true spirit and scope of the invention.

Claims

1. A metal oxide film resistor comprising: an insulating substrate, an indium oxide film formed on the surface of said insulating substrate, and a pair of terminals which are in contact with said indium oxide film.

2. A metal oxide film resistor in accordance with claim 1, wherein said indium oxide film contains an oxide of tin.

3. A metal oxide film resistor in accordance with claim 1, wherein said indium oxide film comprises an oxide of at least one metal selected from the group consisting of aluminum, magnesium, calcium, titanium, vanadium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, molybdenum, lanthanum and cerium.

4. A metal oxide film resistor in accordance with claim 2, wherein said indium oxide film further comprises an oxide of at least one metal selected from the group consisting of aluminum, magnesium, calcium, titanium, vanadium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, molybdenum, lanthanum and cerium.

5. A method for producing a metal oxide film resistor comprising the steps of;
   preparing a solution composed of at least an inorganic indium salt, an organic compound capable of coordinating to indium, and an organic solvent capable of dissolving said inorganic indium salt and said organic compound,
   applying said solution to an insulating substrate to form a coated film, and
   firing the coated film to form an indium oxide film in the air or under an atmosphere containing oxygen.

6. The method for producing a metal oxide film resistor in accordance with claim 5, wherein said solution further contains an organic salt of tin.

7. A method for producing a metal oxide film resistor comprising the steps of;
   preparing a solution composed of at least an inorganic indium salt, an organic compound capable of coordinating to indium, and an organic solvent capable of dissolving said inorganic indium salt and said organic compound,
   applying said solution to an insulating substrate to form a coated film,
   firing the coated film to form an indium oxide film in the air or under an atmosphere containing oxygen, and
   heat-treating said indium oxide film under an inert gas atmosphere or a reducing gas atmosphere.

8. The method for producing a metal oxide film resistor in accordance with claim 7, wherein said solution further contains an organic salt of tin.

9. The method for producing a metal oxide film resistor in accordance with claim 5, 6, 7 or 8, wherein said inorganic indium salt is indium nitrate.

10. The method for producing a metal oxide film resistor in accordance with claim 5, 6, 7 or 8, wherein said organic compound capable of coordinating to indium is at least one compound selected from the group consisting of β-diketones, polyhydric alcohols and condensation products of polyhydric alcohols.

11. The method for producing a metal oxide film resistor in accordance with claim 5, 6, 7 or 8, wherein said solution further comprises an inorganic salt or an organic salt of a metal selected from the group consisting of aluminum, magnesium, calcium, titanium, vanadium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, molybdenum, lanthanum and cerium.

12. The method for producing a metal oxide film resistor in accordance with claim 6 or 8, wherein said organic salt of tin is a salt of dicarboxylic acid.

13. The method for producing a metal oxide film resistor in accordance with claim 5, 6, 7 or 8, wherein said firing step is performed at a temperature ranging from 400 °C to 900 °C.

14. The method for producing a metal oxide film resistor in accordance with claim 7 or 8, wherein said heat-treating said indium oxide film is performed at a temperature ranging from 200 °C to 600 °C.

15. The method for producing a metal oxide film resistor in accordance with claim 7, wherein said inert gas or reducing gas is at least one species selected from the group consisting of nitrogen, argon and hydrogen.

16. The method for producing a metal oxide film resistor in accordance with claim 5, 6, 7 or 8, wherein said step of applying said solution to the insulating substrate comprises the steps of:

accommodating a multiplicity of said substrate in a container having a multiplicity of apertures which are smaller than the substrate,

soaking or dipping said substrates in said solution while said container is being rotated, and

thereafter drying said substrates while said container is being similarly rotated.

FIG.1

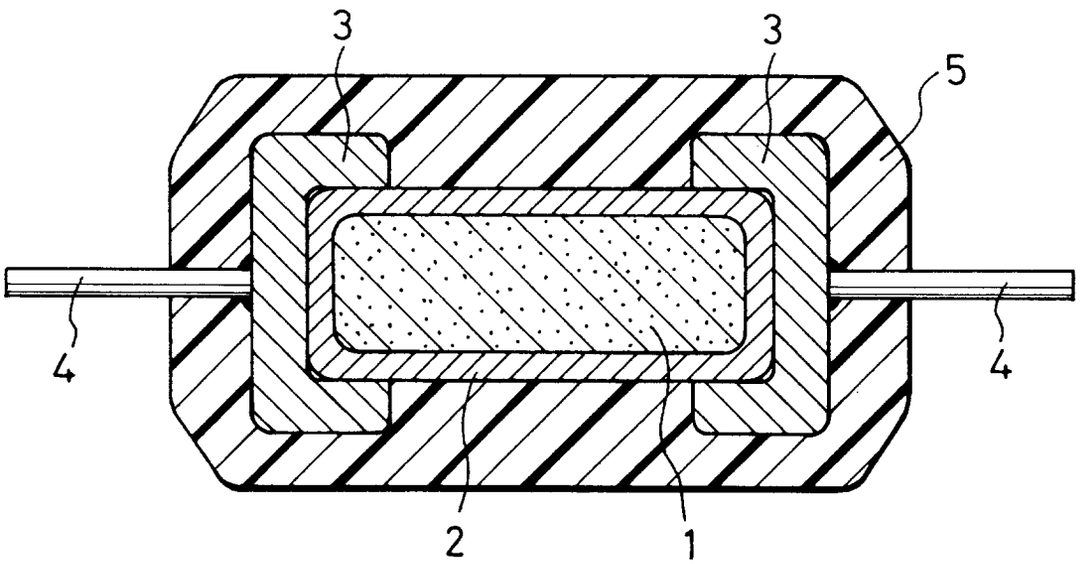


FIG. 2

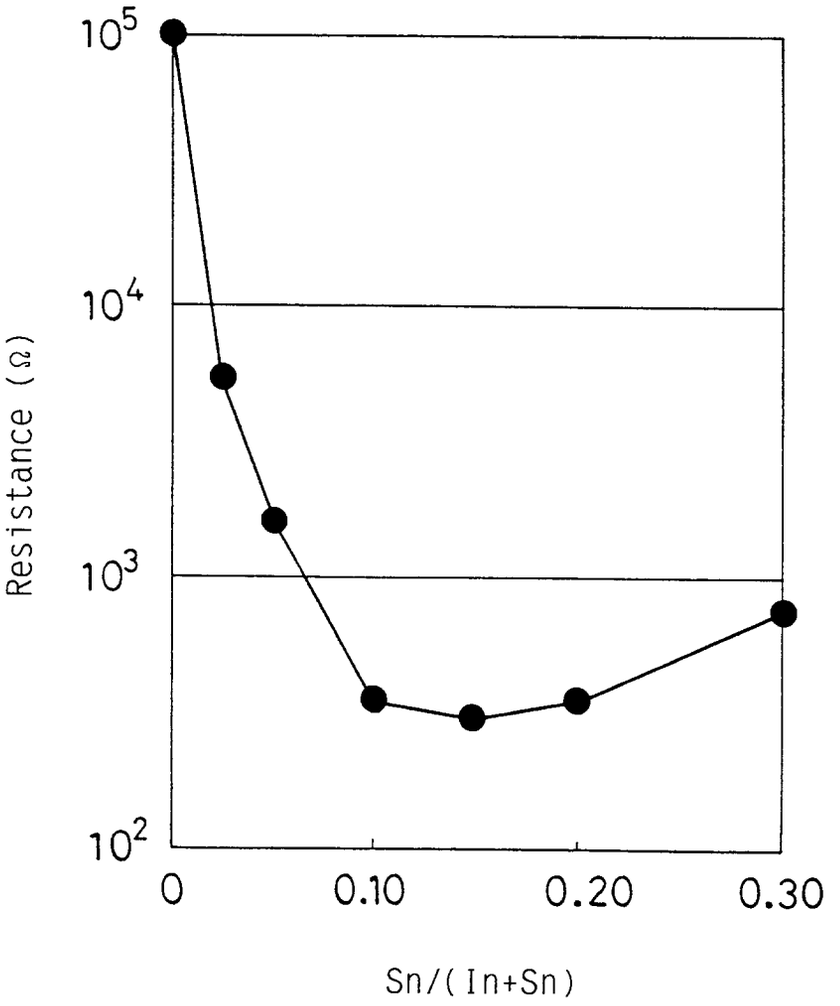


FIG.3

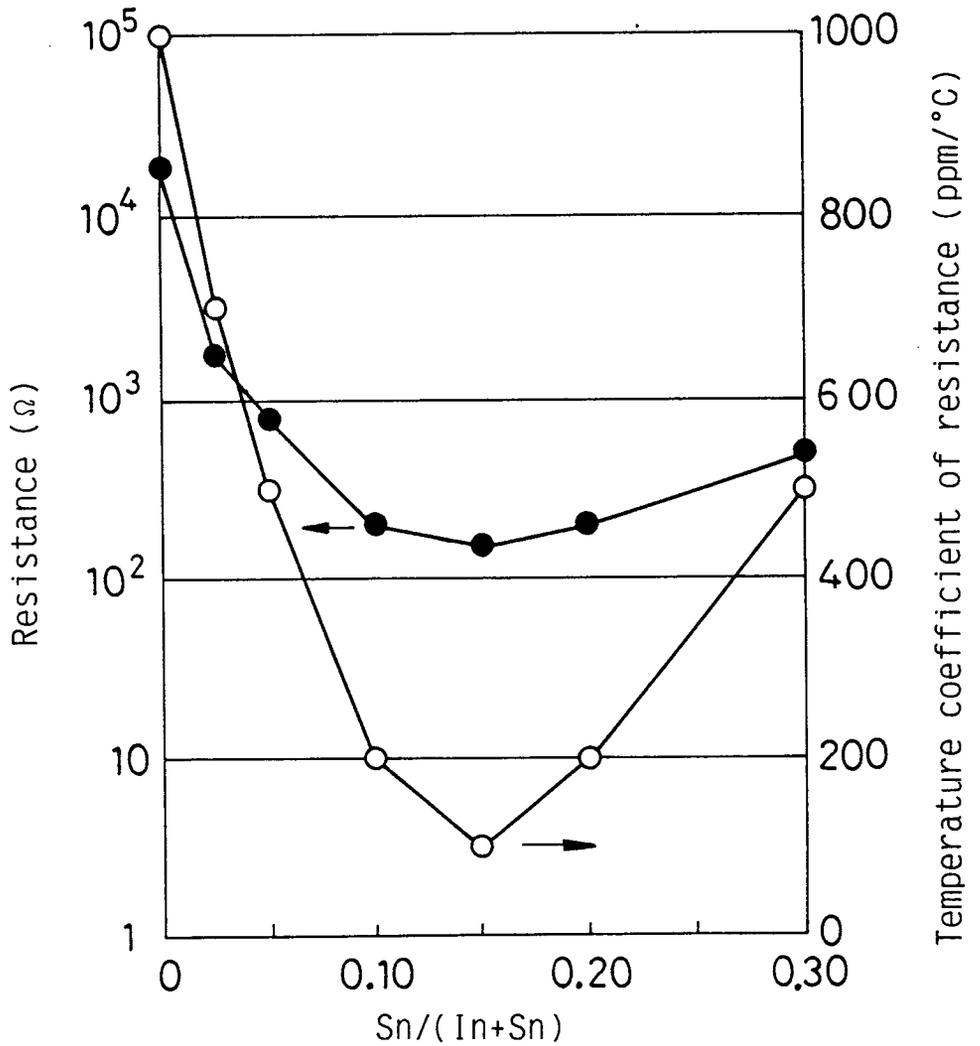

10^5
10^4
10^3
10^2
10
1
Resistance (Ω)
1000
800
600
400
200
0
Temperature coefficient of resistance (ppm/°C)
0
0.10
0.20
0.30
Sn/(In+Sn)

FIG.4

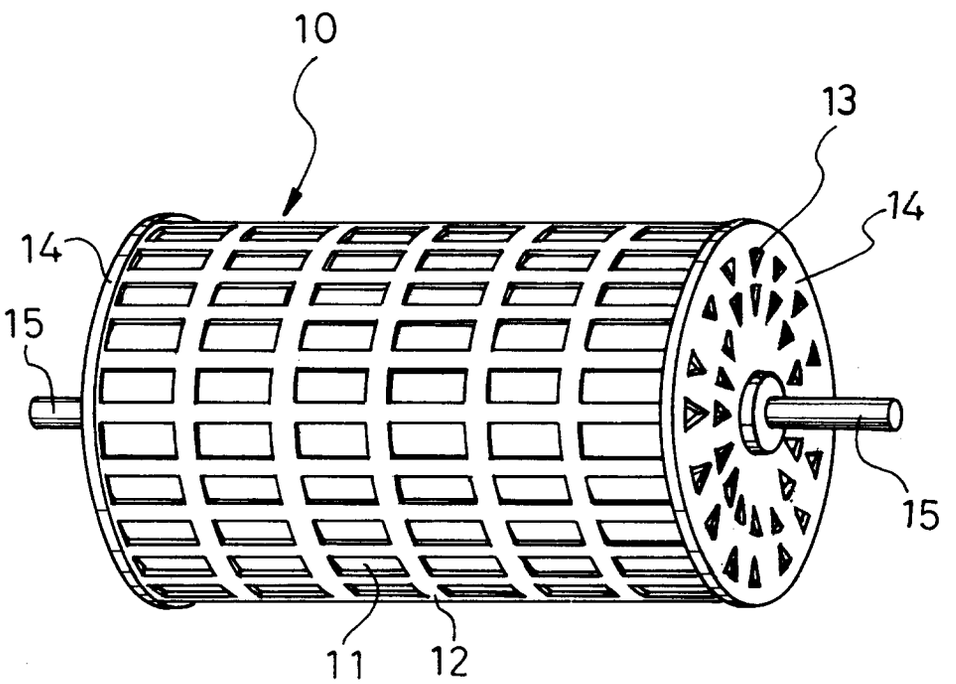


FIG.5

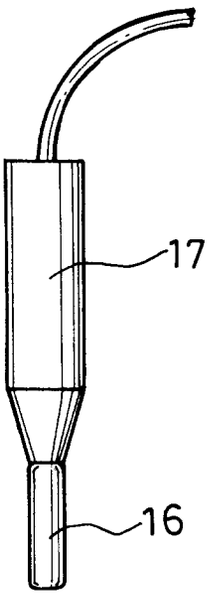
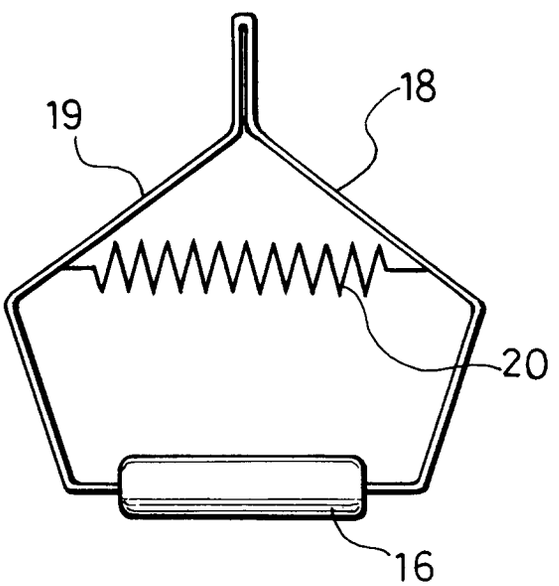


FIG.6



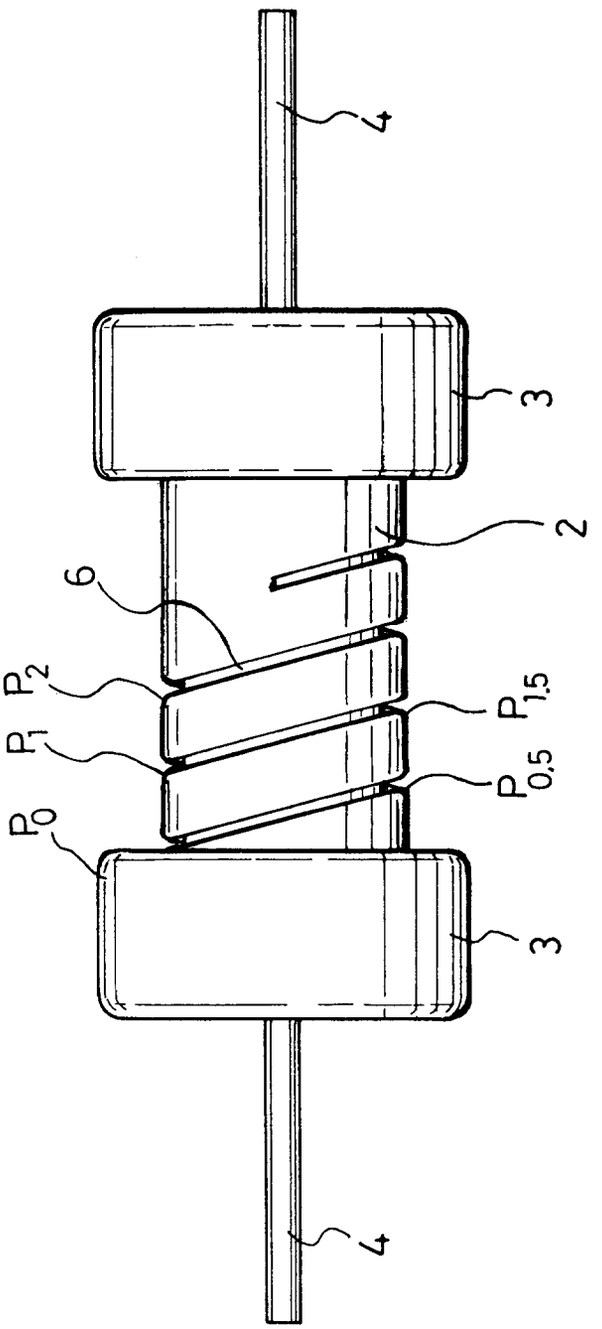
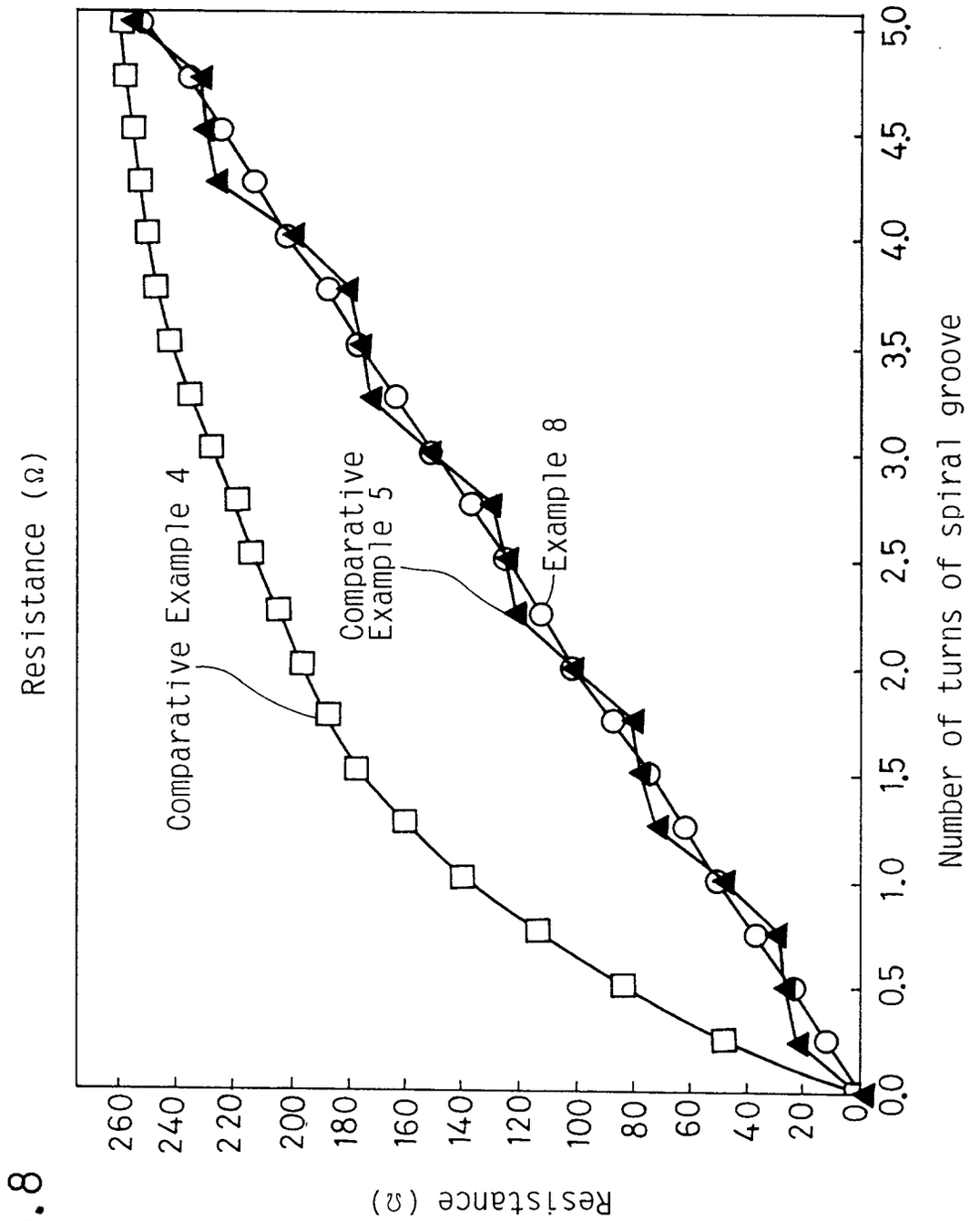


FIG.7

FIG.8


Resistance (Ω)
Comparative Example 4
Comparative Example 5
Example 8
Resistance (Ω)
Number of turns of spiral groove
0
20
40
60
80
100
120
140
160
180
200
220
240
260
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0

European Patent Office

EUROPEAN SEARCH REPORT

Application Number EP 94112212.9

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)
A	EP - A - 0 337 134 (TAIYO YUDEN) * Abstract; claims 1-3 * --	1-5,7	H 05 B 3/12 H 05 B 3/16 H 01 C 7/00
A	GB - A - 2 086 142 (RCA) * Abstract * --	1	
A	US - A - 4 737 757 (SENDA) * Abstract; fig. * ----	1-3	

TECHNICAL FIELDS SEARCHED (Int. Cl. 6)

H 01 C 1/00
H 01 C 7/00
H 01 C 8/00
H 01 C 17/00
H 05 B 3/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	30-11-1994	TSILIDIS

CATEGORY OF CITED DOCUMENTS

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