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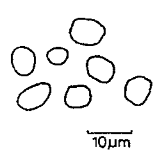
(54) **VOLTAGE NONLINEAR RESISTOR AND METHOD OF PRODUCING THE SAME.**

(57) A voltage nonlinear resistor essentially comprises inorganic semiconductor fine particles, and at least one of the oxides of metal elements of the groups IIIA, IIIB, IVA, IVB, VA, VIIB and VIII of the periodic table, and includes an inorganic insulating film layer that covers the surfaces of the semiconductor fine particles. The semiconductor fine particles are used as a starting material for the inorganic semiconductor, and are subjected to at least one time of baking step at a temperature higher than 1000°C and to at least one time of pulverizing step after at least one time of the baking step. The semiconductor fine particles are mixed with a starting compound that contains at least one of said metal elements and that forms inorganic oxides thereof, and the mixture is baked at a temperature higher than 1000°C such that an insulating film layer consisting essentially of at least one inorganic oxide of said metal element is formed on the surfaces of the semiconductor fine particles.

Fig.1A



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VOLTAGE NONLINEAR RESISTOR AND PROCESS FOR PRODUCING SAME

TECHNICAL FIELD

The present invention relates to a voltage nonlinear resistor and a process for producing the same. More particularly, the voltage nonlinear resistor of the present invention has a stable voltage-current characteristic and is useful for various applications such as an absorption of abnormally high voltage or a stabilization of voltages, and particularly suitable for use as a switching element for a matrix drive type of liquid crystal display device.

BACKGROUND ART

Numerous proposals have been made in the past regarding voltage nonlinear resistors, which are obtained by forming an insulating film on the surface of an inorganic semiconductor particulate.

For example, Japanese Unexamined Patent Publication (Kokai) No. 62-190808 discloses a voltage nonlinear resistor obtained by forming an inorganic insulating film of Bi_2O_3 on the fine particle surface of an inorganic semiconductor. The resistor element obtained from this resistor is characterized by having a large voltage nonlinear index α at the low current region and a small parallel static capacitance. Nevertheless, the inorganic semiconductor fine particulates used in the above-mentioned resistor are nonspherical in form, as shown in Fig. 1 of the above-mentioned unexamined patent publication, and in particular, include large amounts of block shaped fine particulates which are very different from each other in the length of the major axis and minor axis thereof. Further, the distribution of particle sizes is also wide.

Further, in the production of the above-mentioned resistor, Bi is easily evaporated during the firing process, and thus the problem arises of a large variation in the characteristics of the resultant resistors.

The above-mentioned extremely nonspherical inorganic semiconductor fine particulates cause no particular problem when the resultant remarkably nonspherical resistor is used as a voltage nonlinear resistor having a large thickness. Nevertheless, when this resistor is used as a switching element for an active matrix drive type of a liquid crystal display device such as liquid crystal television sets or office automation equipment displays, the area of contact of the fine particulate resistors with each other changes according to the direction of the nonspherical resistor fine particulates, so there are often fluctuations in the parallel static capacitance of the resultant devices or fluctuations in the numbers of resistor fine particulates arranged between electrodes, resulting in the problem of fluctuations in the varistor voltage, and therefore, the above-mentioned resistor is unsatisfactory in practical use.

Therefore, there is a demand for the development of a voltage nonlinear resistor having a superior voltage-current characteristic and small parallel static capacitance, and a process for producing same.

DISCLOSURE OF THE INVENTION

The present invention provides a voltage nonlinear resistor having a stable voltage-current characteristic and a small and stable parallel static capacitance, which is suitable for use in a thin film state, and a process for producing same.

The voltage nonlinear resistor of the present invention is characterized by including inorganic semiconductor particulates and an inorganic insulating film covering the surface of the particulates; the above-mentioned insulating film layer consisting essentially of at least one member selected from the group consisting of oxides of metallic elements of group IIIA, group IIIB, group IVA, group IVB, group VA, group VIIB, and group VIII of the Periodic Table.

The process of the present invention for producing the above-mentioned voltage nonlinear resistor comprises at least one step of firing at a temperature of 1000 °C or more, and at least one pulverizing step after at least one said firing step, to a material for producing inorganic semiconductor therefrom to provide inorganic semiconductor particulates; mixing the above-mentioned semiconductor particulates with a material compound including at least one member selected from oxides of metallic elements of group IIIA, group IIIB, group IVA, group IVB, group VA, group VIIB, and group VIII of the Periodic Table, and capable of producing inorganic oxides thereof; and firing the mixture at a temperature of 1000 °C or more to form insulating film layers consisting essentially of least one member selected from metallic elements on the surfaces of the above-mentioned semiconductor particulates.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1A is a reproduction of an electron microscopic photograph showing the shape of particulates of the voltage nonlinear resistors of the present invention observed by an electron microscope;

Fig. 1B is a reproduction of an electron microscopic photograph showing the shape of particulates of conventional voltage nonlinear resistor observed by an electron microscope;

Fig. 2 is a view of the voltage-current characteristic voltage nonlinear devices produced from voltage nonlinear resistors of the present invention and of a prior art;

Fig. 3 is a sectional explanatory view showing the constitution of an example of a liquid crystal display panel apparatus using the voltage nonlinear resistors of the present invention; and

Fig. 4A, Fig. 4B, and Fig. 4C are, respectively, explanatory views of examples of the connection of picture element electrodes and signal electrodes in the above-mentioned liquid crystal display panel apparatus through voltage nonlinear resistors.

BEST MODE OF CARRYING OUT THE INVENTION

The voltage nonlinear resistor of the present invention comprises inorganic semiconductor particulates and an inorganic insulating film layer covering the surface of the semiconductor particulates.

The type of the inorganic semiconductor usable for the present invention is not particularly limited, but preferably, as main components, at least one member selected from zinc oxide, barium titanate, and silicon carbide, etc., is used. The size of the inorganic semiconductor particulates is not particularly limited, but in general the average particle size is preferably from 0.1 to 20 µm, more preferably from 3 to 10 µm.

In the resistor of the present invention, the inorganic semiconductor particulates preferably have a substantially spherical shape, the ratio of the length 1_1 of the major axis and the length 1_2 of the minor axis being preferably from 1:1 to 1:3. More preferably, the ratio $1_1/1_2$ is 1:1 to 1:1.5, particularly closer to 1:1, i.e., most preferably close to a sphere.

In the resistor of the present invention, an inorganic insulating films are formed on the surfaces of the semiconductor particulates. The insulating films are formed from an insulating inorganic oxide. The insulating film of the resistor of the present invention consist essentially, of at least one member selected from oxides of metallic elements of group IIIA, group IIIB, group IVA, group IVB, group VA, group VIIB, and group VIII of the Periodic Table.

The above-mentioned oxides usable for the present invention are preferably selected from oxides of Al, Ga and In (group IIIA), La and Dy (group IIIB), Si, Ge and Sn (group IVA), Ti, Zr and Hf (group IVB), Sb and Bi (group VA), Mn (group VIIB), Co, Rh, Ir, Fe, Ru, Ni, Pd, and Pt (group VIII).

In the resistor of the present invention, the weight and the thickness of the insulating film layer are not particularly limited. In general, the weight of the insulating film layer preferably is 10^{-4} to 30 mol%, more preferably 10^{-3} to 2.0 mol%. Also, in general, the thickness of the insulating film layer is preferably 0.001 to 5 µm, more preferably 0.01 to 1 µm.

In one embodiment of the resistor of the present invention, the insulating film layer consists essentially of oxides of Mn, Ni, and Al. In this case, there is no special limitation to the content of the respective metallic oxides in the said insulating film layer, but in general, preferably the content of MnO with respect to the molar weight of the semiconductor particulates is 0.1 to 10 mol%, the content of NiO is 0.1 to 10 mol%, and the content of Al_2O_3 is 10^{-4} to 1 mol%.

Further, in another embodiment of the resistor of the present invention, the insulating film layer consists essentially of oxides of Mn, Co, and Al. In this case, the content of the respective metallic oxides in the said insulating film layer is not particularly limited, but in general, preferably the content of MnO with respect to the molar weight of the semiconductor particulates is 0.1 to 10 mol%, the content of Co_2O_3 is 0.1 to 10 mol%, and the content of Al_2O_3 is 10^{-4} to 1 mol%.

Further, in still another embodiment of the resistor of the present invention, the insulating film layer consists essentially of oxides of Mn, Co, La, and Al. In this case, the content of the respective metallic oxides in the insulating film layer is not particularly limited, but in general, preferably the insulating film-layer includes 0.1 to 10 mol% of MnO, 0.1 to 10 mol% of Co_2O_3, 0.1 to 10 mol% of La_2O_3, and 10^{-4} to 1 mol% of Al_2O_3 with respect to the molar weight of the semiconductor particulates.

The resistor of the present invention, having an insulating film layer comprising oxides of Mn, Co, La, and Al, exhibits a stable voltage-current characteristic, a small parallel static capacitance, and a high pulse resistance, and further, a resistor element obtained from this resistor exhibits an extremely low varistor voltage fluctuation rate.

Further, in a further embodiment of the resistor of the present invention, the insulating film layer consists essentially of oxides of Mn, Hf, and Al. In this case, there is no particular limitation to the content of the respective metallic oxides in the insulating film layer, but in general, preferably the insulating film layer includes 0.1 to 10 mol% of MnO, 0.1 to 10 mol% of HfO_2, and 10^{-4} to 1 mol% of Al_2O_3 with respect to the molar weight of the semiconductor particulates.

Further, in the other embodiment of the resistor of the present invention, the insulating film layer consists essentially of oxides of Mn, Dy, and Al. In this case, there is no particular limitation on the content of the respective metallic oxides in the insulating film layer, but in general, preferably 0.1 to 10 mol% of MnO, 0.1 to 10 mol% of Dy_2O_3, and 10^{-4} to 1 mol% of Al_2O_3 are contained with respect to the molar weight of the semiconductor particulates.

The above-mentioned mixtures of oxides of Mn, Ni, and Al, mixtures of oxides of Mn, Co, and Al, mixtures of oxides of Mn, Co, La, and Al, mixtures of oxides of Mn, Hf, and Al, and mixtures of oxides of Mn, Dy, and Al do not all melt at the firing temperature of 1000° C or more, but are solid solved in the surfaces of the semiconductor particulates, to form stable insulating film layers on the surfaces of the semiconductor particulates.

The inorganic semiconductor-forming material usable for the process of the present invention comprises at least one member selected from, for example, since compounds such as zinc oxide, zinc hydroxide and zinc carbonate and barium titanate, silicon carbide, and the like.

In the present invention, the inorganic semiconductor-forming material, for example, a material consisting of at least one member selected from zinc oxide, zinc hydroxide and the like, is subjected to at least one firing step at a temperature of 1000° C or more, preferably 1000° C to 1400° C, more preferably 1150° C to 1250° C, preferably for 1 to 5 hours, and to at least one pulverizing step to be carried out after the at least one firing step, to manufacture the inorganic semiconductor particulates.

Namely, the steps of producing the inorganic semiconductor particulates may comprise a single firing step and a single pulverizing step applied after the same, or two firing steps and at least one pulverizing step performed between the two firing steps. Alternatively, a preliminary pulverizing step may be applied before a single firing step, or a finishing pulverizing step may be applied after the final firing step.

Further, a classifying step following each pulverizing step may be incorporated thereto.

By the above-mentioned firing step and pulverizing step, the semiconductor-producing material is converted to the fore-mentioned semiconductor, and simultaneously, fine particulates having a substantially spherical shape and having a ratio $1_1/1_2$ of the length 1_1 of the major axis to the length 1_2 of the minor axis in the range of 1:1 to 1:3, and preferably having an average particle size of 1 to 20 μm, are obtained.

Next, the semiconductor particulates are mixed with the insulating inorganic oxide-producing material compounds. In this mixing step, preferably, the oxide-producing material compounds are convertible to inorganic metallic oxides for constituting a predetermined insulating film by the later mentioned firing step, and are selected from oxides, carbonates, nitrates, and hydroxides of predetermined metallic elements. The total weight of the oxide-producing material compounds is preferably 10^{-4} to 30 mol%, more preferably 10^{-3} to 2.0 mol%, in terms of oxides, based on the weight of the inorganic semiconductor particulates.

Next, the mixture is fired at a temperature of 1000° C, preferably 1000 to 1400° C, more preferably 1100 to 1250° C. In this firing process, the inorganic oxide-producing material compounds are converted to corresponding inorganic oxides which are solid-dissolved in the surface portions of the semiconductor particulates to provide insulating films.

The weight and thickness of the insulating films are as mentioned earlier.

There is no special limitation to the time of the firing step, and the firing time is suitably set in consideration of the type of material compounds used and the firing temperature. In general, the firing time is preferably from 1 to 5 hours.

The resistor particles obtained from the firing step are subjected to a classifying step, if necessary, to classify the particles into predetermined particle sizes.

The resistors obtained by the above-mentioned process have a substantially spherical shape as shown, for example, in Fig. 1A, and exhibit stable varistor voltages.

Therefore, the voltage nonlinear resistor particles of the present invention are useful as constituent elements of switching elements for liquid crystal display apparatuses.

EXAMPLES

The present invention will be explained in further detail using the following examples.

Example 1

A zinc oxide powder having a particle size of 0.05 to 1 µm was shaped into pellets, then subjected to a primary firing step at 1200 °C for 2 hours. Next, the product of the primary firing step was pulverized and classified to provide angular particles having a size of 5 to 10 µm. Next, the pulverized product was subjected to a secondary firing step at 1200 °C for 1 hour, then the product was further lightly pulverized. Substantially spherical semiconductor particulates with a particle size of 2 to 20 µm, an average particle size of 5 to 10 µm, and a ratio in length of major axis 1_1 to minor axis 1_2 of from 1 to 1.5 were obtained.

Bi_2O_3 in an amount of 0.5 molar% was admixed with the above-mentioned zinc oxide particles. This admixture was fired at 1200 °C for 1 hour, then lightly pulverized and classified to provide voltage nonlinear resistors having a particle size of 5 to 10 µm. Figure 1A is a reproduction of an electron microscopic photograph showing the shape of the particles of the above-mentioned voltage nonlinear resistors as seen in an electron micrograph. As is clear from Fig. 1A, the resistor particles are substantially spherical and the particle sizes thereof are substantially uniform.

The above-mentioned voltage nonlinear resistors were added with 50 percent by weight of glass particles, 5 percent by weight of a binder, and 40 percent by weight of a solvent to provide a paste. The paste was printed in a predetermined pattern on the substrate. The printed substrate was subjected to a heat treatment at a temperature of 450 °C to prepare voltage nonlinear elements.

The voltage nonlinear elements had voltage-current characteristics as shown by curve A of Fig. 2. When the element area was 1 mm^2 and the distance between electrodes was 30 µm, the voltage nonlinear index α was 11 which is large in the low current region. The varistor voltage of the elements at a current of 10^{-6} A was 28 ± 3 V at the number of the elements of 50, and was substantially uniform.

Examples 2 to 7

In Examples 2 to 7, the same procedures as in Example 1 were performed except that the oxides shown in Table 1 were used in the amounts shown in Table 1, instead of Bi_2O_3.

The production conditions and electrical characteristics of the voltage nonlinear resistors are as shown in Table 1.

Comparative Example 1

The same procedures as in Example 1 were performed except that the pulverization and secondary firing operations were not performed. That is, a zinc oxide powder with a particle size of 0.05 to 1 µm was shaped into pellets, then subjected to a primary firing operation at 1200 °C for 2 hours. The resultant particles had a size of 2 to 20 µm, an average particle size of 5 to 10 µm, and a major axis/minor axis ratio ($1_1/1_2$) of 1 to 3.

Next, 0.5 mol% of Bi_2O_3 was added to and mixed with the zinc oxide powder, and the admixture was fired at 1200 °C for 1 hour, then lightly pulverized and classified, to provide voltage nonlinear resistors having a particle size of 5 to 10 µm. Figure 1B is a reproduction of an electron microscopic photograph showing the shape of the particles of the voltage nonlinear resistors as observed by an electron micrograph.

The voltage-current characteristic of the voltage nonlinear elements obtained from the voltage nonlinear resistors is shown by curve B of Fig. 2. When the element area was 1 mm^2 and the distance between electrodes was 30 µm, in the same way as Example 1, the voltage nonlinear index α was 6 which was a small value in the low current region. The varistor voltage of the elements at a current of 10^{-6} A was 27 ± 7 V at the number of the elements of 50.

Table 1

Ex. No.	Item	Metal oxide for insulating film layer: Type	Amt (mol%) (*)	Primary firing temp. (°C)	Secondary firing temp. (°C)	Voltage nonlinear index α
Example	1	Bi	0.5	1200	1150	11
	2	Co	0.5	1200	1250	5
	3	Mn	0.5	1200	1200	8
	4	Sb	0.5	1200	1230	7
	5	Bi Co	0.5 0.5	1200	1180	19
	6	Bi Mn	0.5 0.5	1200	1180	23
	7	Bi Co Mn Sb Ti Al	0.5 0.5 0.5 0.5 0.5 0.005	1200	1150	27
Comp. Ex.	1	Bi	0.5	1200	None	6

Note: (*) Molar% of metal oxides based on the molar weight of semiconductor particulates.

Example 8

A zinc oxide powder having a particle size of 0.05 to 1 µm was shaped into pellets, then fired at 1200° C for 2 hours, pulverized, and classified to provide fine particulates having a particle size of 5 to 10 µm, an average particle size of 7 µm, and an $1_1/1_2$ ratio of 1:1.5.

Next, 0.5 mol% each of MnO and NiO and 0.005 mol% of Al_2O_3 were added to and mixed with the zinc oxide particulates, the admixture was fired at 1200° C for 1 hour, then lightly pulverized and classified to provide voltage nonlinear resistors having a uniform particle size of 5 to 10 µm.

To the voltage nonlinear resistors, 50% by weight of a glass powder, 5% by weight of a binder (ethyl cellulose), and 40% by weight of solvent were added to provide a paste. The paste was printed on a substrate, and the printed substrate was then heat treated at 450° C to prepare a voltage nonlinear device.

The voltage-current characteristic of this voltage nonlinear device was the same as that shown in curve A in Fig. 2. When the element area was 1 mm^2 and the distance between electrodes was 30 µm, the voltage nonlinear index α was 26, which is large in the low current region. Further, the varistor voltage at a current of 10^{-6} A was 28 ± 3 V at the number of the elements of 50, and was satisfactorily stable.

Examples 9 to 14

In Examples 9 to 14, the same procedures as in Example 8 were performed, except that the insulating films were formed by mixing MnO, NiO, and Al_2O_3 in the composition as shown in Table 2.

Table 2 gives of a summary of the production conditions of the voltage nonlinear resistors and the electrical characteristics of the resultant resistor devices from the same.

Table 2

Item / Example No.	Metal oxides comprising insulating film layer: Type	Amount (mol%) (*)	Voltage nonlinear index α
8	MnO NiO Al_2O_3	0.5 0.5 0.005	26
9	MnO NiO Al_2O_3	0.5 1.0 0.002	20
10	MnO NiO Al_2O_3	0.5 5.0 0.002	15
11	MnO NiO Al_2O_3	0.5 0.1 0.005	22
12	MnO NiO AlO_3	0.1 0.5 0.005	16
13	MnO NiO Al_2O_3	1.0 0.5 0.005	23
14	MnO NiO Al_2O_3	5.0 0.5 0.005	18

Note: (*) ... Molar% of metal oxides based on the molar amount of semiconductor particulates.

spherical particulates having a particle size of 2 to 20 µm, an average particle size of 5 to 10 µm, and a major axis/minor axis ratio (l_1/l_2) in the range of 1 to 1.5.

The zinc oxide particulates were mixed with 0.5 mol% each of $MnCO_3$ and Co_2O_3 powder and 0.005 mol% of an $Al(NO_3)_3 \cdot nH_2O$ solution based on the weight of the zinc oxide particulates were added and mixed. The mixture was fired at 1200° C for 1 hour, then lightly pulverized and classified to provide voltage nonlinear resistors having substantially spherical shape, and a particle size of 5 to 10 µm. The resistors were uniform in the size. The particles of the voltage nonlinear resistors had a substantially spherical particle form as shown in Fig. 1A.

The above-mentioned voltage nonlinear resistors were mixed with 50% by weight each of a glass powder, 5% by weight of a binder (ethyl cellulose), and 40% by weight of a solvent to provide a paste. The paste was printed on a substrate, and the resultant printed substrate was subjected to a heat treatment at 450°C to prepare voltage nonlinear elements.

The voltage-current characteristic of this voltage nonlinear elements was extremely close to that shown in curve A of Fig. 2. When the element area was 1 mm^2 and the distance between electrodes was 30 μm, the voltage nonlinear index α was 25, as listed in Table 3, which was a large value in the low current region. The varistor voltage at a current of 10^{-4} A was 28 ± 3 V at the number of the elements of 50, and was very even.

Table 3 shows the process conditions in the procedures in Example 15.

Examples 16 to 21

In each of Examples 16 to 21, the same procedures as in Example 15 were performed, except that in the formation of the insulating film, a mixture of MnO, Co_2O_3, and Al_2O_3 in the composition shown in Table 3 was used.

The production conditions of the voltage nonlinear resistors and the electrical characteristics of the resultant voltage nonlinear resistor elements from the same are shown in Table 3.

Comparative Example 2

The same procedures as in Comparative Example 1 were carried out except that, as shown in Table 3, instead of Bi_2O_3, 0.5 mol% of MnO, 0.5 mol% of Co_2O_3, and 0.005 mol% of Al_2O_3 were used in the same way as in Example 1. When the element area was 1 mm^2 and the distance between electrodes was 30 μm, the voltage nonlinear index a was 15 as shown in Table 3, and was small in the low current region. The varistor voltage at a current of 10^{-6} A was 27 ± 5 V at the number of the elements of 50, and had a relatively large fluctuation.

Table 3

Ex. No. (Item)	Metal oxide comprising insulating film layer: Type	Amt (mol%) (*)	Primary firing temp. (°C)	Secondary firing temp. (°C)	Voltage nonlinear index α of resister device
15	MnO	0.5	1200	1150	25
	Co_2O_3	0.5			
	Al_2O_3	0.005			
16	MnO	0.1	1200	1200	12
	Co_2O_3	0.1			
	Al_2O_3	0.001			
17	MnO	0.5	1200	1250	24
	Co_2O_3	1.0			
	Al_2O_3	0.005			
18	MnO	0.5	1200	1180	19
	Co_2O_3	5.0			
	Al_2O_3	0.005			
19	MnO	0.1	1200	1200	15
	Co_2O_3	0.5			
	Al_2O_3	0.005			
20	MnO	1.0	1200	1230	20
	Co_2O_3	0.5			
	Al_2O_3	0.005			
21	MnO	5.0	1200	1150	18
	Co_2O_3	0.5			
	Al_2O_3	0.005			
Comp. Ex. 2	MnO	0.5	1200	None	15
	Co_2O_3	0.5			
	Al_2O_3	0.005			

Note: (*) ... Molar% of metal oxides based on the weight of the semiconductor particulates.

Example 22

A zinc oxide powder having a particle size of 0.05 to 1 μm was shaped into pellets, and the pellets were then fired at 1200 °C for 2 hours. This fired product was pulverized and classified to provide semiconductor particulates having a particle size of 5 to 10 μm.

Next, MnO, Co_2O_3, La_2O_3, and Al_2O_3 were added to and mixed in the amounts shown in Table 4 with the zinc oxide particulates. The mixture was fired at 1200 °C for 1 hour, then the fired product was lightly pulverized and classified to provide voltage nonlinear resistors with an average particle size of 5 to 10 μm, and a ratio $1_1/1_2$ of the major axis to the minor/axis of the particles of 1:1.5.

The voltage nonlinear resistors were added with 50% by weight of a glass powder, 5% by weight of a binder (ethyl cellulose), and 40% by weight of solvent, based on the weight of the resistors to provide a paste. A substrate was printed with the paste and then heat treated at 450 °C to produce voltage nonlinear elements.

The voltage-current characteristic of the voltage nonlinear elements was extremely close to that shown by curve A of Fig. 2. The voltage nonlinear index α at an element area of 1 mm^2 and at a distance between electrodes of 30 μm was 25 which was a large value in the low current region. Further, the varistor voltage at a current of 10^{-5} A was 28 ± 3 V at the number of the elements of 50, was satisfactorily stable.

A pulse with a pulse width of 1 ms and a pulse voltage of 30 V was applied 100,000 times to the elements, then the change in the varistor voltage was investigated, whereupon it was found to be +0.6%, i.e., almost no fluctuation was observed.

For comparison, the change in the varistor voltage in application of 100,000 pulses to the elements of Comparative Example 1 in the same way as above was determined. As a result, it was found that the change was +2.8%, and was relatively large.

Examples 23 to 28

In each of Examples 23 to 28, the same procedures as in Example 22 were carried out except that the insulating films were formed from a mixtures of MnO, Co_2O_3, La_2O_3, and Al_2O_3 in the composition shown in Table 4.

A summary of the production conditions of the voltage nonlinear resistors and the electrical characteristics of the resultant resistor devices obtained from the same are shown in Table 4.

Comparative Example 3

The same procedures as in Example 22 were performed, except that the insulating film layer was formed from MnO and Co_2O_3 in the composition shown in Table 4. The voltage-current characteristic of the resultant voltage nonlinear device obtained from the resistors was substantially the same as that shown in curve B of Fig. 2. In the same way as in Example 22, the voltage nonlinear index α at an element area of 1 mm^2 and at a distance between electrodes of 30 μm was 12 which was relatively small in the low current region. The varistor voltage at a current of 10^{-5} A was 27 ± 6 V at the number of the elements of 50, and had a relatively large fluctuation.

The change in the varistor voltage after application of pulses was +2.5%, and relatively large.

Table 4

Ex. No. / Item	Composition of metal oxide comprising insulating film layer: Type	Amount (mol%) (%)	Voltage nonlinear index α	Change in varistor voltage
22	MnO	0.25	27	+0.6%
	Co_2O_3	0.5		
	La_2O_3	0.25		
	Al_2O_3	0.005		
23	MnO	0.1	22	+0.8%
	Co_2O_3	0.5		
	La_2O_3	0.25		
	Al_2O_3	0.005		
24	MnO	0.5	23	+1.0%
	Co_2O_3	0.5		
	La_2O_3	0.5		
	Al_2O_3	0.005		
25	MnO	0.1	15	+1.2%
	Co_2O_3	0.1		
	La_2O_3	0.25		
	Al_2O_3	0.005		
26	MnO	1.0	20	+0.7%
	Co_2O_3	0.5		
	La_2O_3	0.5		
	Al_2O_3	0.002		

Table 4 (Continued)

Ex. No. (Item)	Composition of metal oxide comprising insulating film layer: Type	Amount (mol%) (*)	Voltage nonlinear index α	Change in varistor voltage
27	MnO	1.0	21	+0.9%
	Co_2O_3	1.0		
	La_2O_3	1.0		
	Al_2O_3	0.005		
28	MnO	1.0	19	+1.0%
	Co_2O_3	0.5		
	La_2O_3	5.0		
	Al_2O_3	0.005		
Comp. Ex. 1	Bi_2O_3	0.5	6	+2.8%
3	MnO	0.5	12	+2.5%
	Co_2O_3	0.5		

Note: (*) ... Molar% of metal oxides based on the molar amount of semiconductor particulates.

Example 29

10 g of the voltage nonlinear resistor particles (varistor) prepared in Example 22, 5 g of a glass powder, 1 g of ethyl cellulose, and 5 ml of ethyl carbitol were mixed well altogether to provide a paste. A first glass substrate which was patterned in advance, by a usual method with ITO, etc., for predetermined picture element electrodes (5 mm x 5 mm) and signal electrodes (distance between the picture element electrode and signal electrode: 50 μm), was printed with the above-mentioned paste through a screen having a predetermined pattern. The printed first glass substrate was heat-treated at 300 to 500 °C to prepare a base plate on which the pixel picture element electrodes were connected to the signal electrodes through the varistor films.

Separately, an emulsion prepared from 20 g of a 10% aqueous solution of PVA and 6 g of a liquid crystal (trademark: E-44, Merck Co.) containing 150 mg of a dichromatic dye dissolved therein was coated by a doctor blade on a second glass substrate which was patterned in advance for a predetermined scanning electrode by ITO. This was dried to provide a polymer dispersion type liquid crystal (having a thickness of 15 μm). The two substrates were joined together and the surroundings of the resultant composite body were sealed to prepare a liquid crystal display panel. The sectional explanatory view of the panel is given in Fig. 3.

As shown in Fig. 3, a plurality of picture element electrodes 11a are arranged on the surface of the first transparent glass substrate 12a in accordance with a predetermined pattern. Further, a plurality of signal electrodes 13 are arranged adjacent to the picture element electrodes 11a so that electrical signals can be applied to the picture element electrodes 11a. Further, a plurality of varistor films 14 (nonlinear resistors) were arranged between the picture element electrodes 11a and the adjoining signal electrodes 13 to connect the same with each other. Further, a second transparent glass substrate 12b was arranged in parallel to and at a distance from the first glass substrate 12a to form a space between the two. A transparent scanning electrode 11b was fixed at the bottom of the second glass substrate 12b.

In the space between the first glass substrate 12a and the second glass substrate 12b, a polymer dispersion type liquid crystal layer 15 including the above-mentioned liquid crystal was formed.

The positional relationships between the signal electrodes 13, the varistor films 14, and the picture element electrode 11a are shown in Fig. 4A, Fig. 4B, and Fig. 4C.

As shown in Fig. 4A, the plurality of picture element electrodes 11a were connected independently from each other to the signal electrodes 13 through the varistor films 14. As shown in Fig. 4B and Fig. 4C, the picture element electrodes 11a and the signal electrodes 13 were fixed to the first glass substrate 12a and were mutually connected through the varistor films 14 comprised of the plurality of varistor particles 14a.

A drive circuit was connected to the signal electrodes and scanning electrode of the above-mentioned liquid crystal display panel apparatus. When this apparatus was driven at ±100 V and at a duty ratio of 1/64, a clear display could be carried out with a contrast ratio of 15 or more, without crosstalk.

Examples 30 to 36

In each of Examples 30 to 36, the same procedures as in Example 22 were performed, except that the insulating film layers were formed from MnO, HfO_2, and Al_2O_3 in the compositions shown in Table 5.

The voltage nonlinear indexes α of the resultant resistor devices are shown in Table 5.

Table 5

Ex. No. (Item)	Composition of metal oxides comprising insulating film layer: Type	Amount (mol%) (*)	Voltage nonlinear index α
30	MnO	0.5	25
	HfO_2	0.5	
	Al_2O_3	0.005	
31	MnO	0.5	21
	HfO_2	1.0	
	Al_2O_3	0.002	
32	MnO	0.5	18
	HfO_2	5.0	
	Al_2O_3	0.002	
33	MnO	0.5	22
	HfO_2	0.1	
	Al_2O_3	0.005	
34	MnO	0.1	14
	HfO_2	0.5	
	Al_2O_3	0.005	
35	MnO	1.0	21
	HfO_2	0.5	
	Al_2O_3	0.005	
36	MnO	5.0	18
	HfO_2	0.5	
	Al_2O_3	0.005	

Note: (*) ... mol% of metal oxides based on the molar amount of semiconductor particulates.

Examples 37 to 43

In each of Examples 37 to 43, the same procedures as in Example 22 were carried out, except that the insulating film layer was formed from MnO, Dy_2O_3, and Al_2O_3 in the compositions shown in Table 6.

The voltage nonlinear indexes α of the resultant resistor devices are shown in Table 6.

Table 6

Ex. No.	Item: Composition of metal oxides comprising insulating film layer — Type	Amount (mol%) (*)	Voltage nonlinear index α
37	MnO	0.5	25
	Dy_2O_3	0.5	
	Al_2O_3	0.005	
38	MnO	0.5	22
	Dy_2O_3	1.0	
	Al_2O_3	0.002	
39	MnO	0.5	16
	Dy_2O_3	5.0	
	Al_2O_3	0.002	
40	MnO	0.5	20
	Dy_2O_3	0.1	
	Al_2O_3	0.005	
41	MnO	0.1	17
	Dy_2O_3	0.5	
	Al_2O_3	0.005	
42	MnO	1.0	24
	Dy_2O_3	0.5	
	Al_2O_3	0.005	
43	MnO	5.0	20
	Dy_2O_3	0.5	
	Al_2O_3	0.005	

Note: (*) ... mol% of metal oxides based on the molar amount of semiconductor particulates.

CAPABILITY OF EXPLOITATION IN INDUSTRY

The voltage nonlinear resistor of the present invention is comprised of substantially spherical particulates of an inorganic semiconductor on the surfaces of which particulates insulating films comprised of oxides of metallic elements of groups IIIA, IIIB, IVA, IVB, VA, VIIB, and VIII of the Periodic Table are coated. When a voltage nonlinear resistor element is prepared from these resistors, an undesirable fuse-adhesion of these resistors and scattering of the components are prevented, and thus there is little fluctuation in the number of the resistor elements located between electrodes, and fluctuation in contact area in the direction of orientation of the voltage nonlinear resistor particulates forming the resistor elements was not substantially occur. Therefore, there is no fluctuation in the parallel static capacitance and the contact among particulates becomes mainly a point contact, and thus, the parallel static capacitance becomes smaller. Further, there is little variation in the varistor voltages among elements and the voltage-current characteristics are excellent.

Therefore, the voltage nonlinear resistors of the present invention are useful for apparatuses for absorbing abnormally high voltages and apparatuses for voltage stabilization. In particular, they are suitable as switching elements of matrix drive type liquid crystal display devices.

Claims

1. A voltage nonlinear resistor comprising inorganic semiconductor particulates and an inorganic insulating film layer covering the surface of the particulates,
   said insulating film layer consisting essentially of at least one member selected from the group consisting of oxides of metallic elements of group IIIA, group IIIB, group IVA, group IVB, group VA, group VIIB, and group VIII of the Periodic Table.

2. A resistor according to claim 1, wherein said semiconductor particulates comprises as a main component, at least one member selected from the group of zinc oxide, barium titanate, and silicon carbide.

3. A resistor according to claim 1, wherein said semiconductor particulates have an average particle size of 0.1 to 20 μm.

4. A resistor according to claim 1, wherein said semiconductor particulates are substantially spherical and the ratio of the length 1_1 of the major axis and the length 1_2 of the minor axis is from 1:1 to 1:3.

5. A resistor according to claim 1, wherein the said insulating film layer is in an amount of 10^{-4} to 30 mol% based on the molar amount of the said semiconductor particulates.

6. A resistor according to claim 1, wherein the thickness of the said insulating film layer is 0.001 to 5 μm.

7. A resistor according to claim 1, wherein the said insulating film layer consists essentially of at least one member of oxides of Al, Ga, In, La, Dy, Si, Ge, Sn, Ti, Zr, Hf, Sb, Bi, Mn, Co, Rh, Ir, Fe, Ru, Ni, Pd, and Pt.

8. A resistor according to claim 7, wherein the said insulating film layer consists essentially of oxides of Mn, Ni, and Al.

9. A resistor according to claim 8, wherein said insulating film layer includes 0.1 to 10 mol% of MnO, 0.1 to 10 mol% of NiO, and 10^{-4} to 1 mol% of Al_2O_3, based on the molar amount of the semiconductor particulates.

10. A resistor according to claim 7, wherein said insulating film layer consists essentially of oxides of Mn, Co, and Al.

11. A resistor according to claim 10, wherein said insulating film layer includes 0.1 to 10 mol% of MnO, 0.1 to 10 mol% of Co_2O_3, and 10^{-4} to 1 mol% of Al_2O_3, based on the molar amount of the semiconductor particulates.

12. A resistor according to claim 7, wherein said insulating film layer consists essentially of oxides of Mn, Co, La, and Al.

13. A resistor according to claim 12, wherein said insulating film layer includes 0.1 to 10 mol% of MnO, 0.1 to 10 mol% of Co_2O_3 , 0.1 to 10 mol% of La_2O_3, and 10^{-4} to 1 mol% of Al_2O_3, based on the molar amount of the semiconductor particulates.

14. A resistor according to claim 7, wherein said insulating film layer consists essentially of oxides of Mn, Hf, and Al.

15. A resistor according to claim 14, wherein said insulating film layer includes 0.1 to 10 mol% of MnO, 0.1 to 10 mol% of HfO_2, and 10^{-4} to 1 mol% of Al_2O_3, based on the molar amount of the semiconductor particulates.

16. A resistor according to claim 7, wherein said insulating film layer consists essentially of oxides of Mn, Dy, and Al.

17. A resistor according to claim 16, wherein said insulating film layer includes 0.1 to 10 mol% of MnO, 0.1 to 10 mol% of Dy_2O_3, and 10^{-4} to 1 mol% of Al_2O_3 based on the molar amount of the semiconductor particulates.

18. A process for production of a voltage nonlinear resistors comprising applying at least one step of firing at a temperature of 1000° C or more, and at least one pulverizing step after at least one said firing step to a material for producing an inorganic semiconductor therefrom to provide inorganic semiconductor particulates;

mixing the above-mentioned semiconductor particulates with a material compound including at least one member selected from oxides of metallic elements of group IIIA, group IIIB, group IVA, group IVB, group VA, group VIIB, and group VIII of the Periodic Table, and capable of producing inorganic oxides thereof; and

firing the mixture at a temperature of 1000° C or more, to form insulating film layers consisting essentially of at least one member selected from inorganic oxides of the metallic elements on the surfaces of the above-mentioned semiconductor particulates.

19. A process according to claim 18, wherein before the step of forming the insulating film, a classifying operation is applied to the pulverized semiconductor particulates.

20. A process according to claim 18, wherein a primary firing operation is applied to the semiconductor-producing material at a temperature of 1000 to 1400° C, at least one pulverizing operation is applied to the fired product, and a secondary firing operation is applied to the pulverized product at a temperature of 1000 to 1400° C.

21. A process according to claim 18, wherein said operation for forming the insulating film layer is carried out at a temperature of 1000 to 1400° C.

Fig.1A

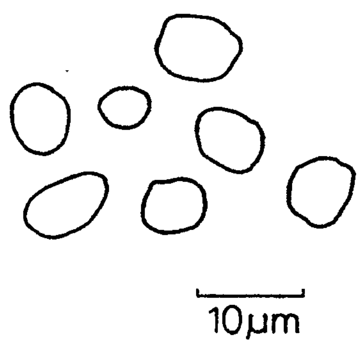


Fig.1B

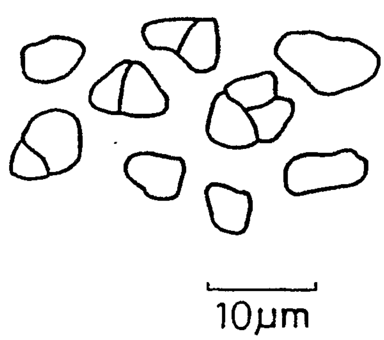


Fig. 2

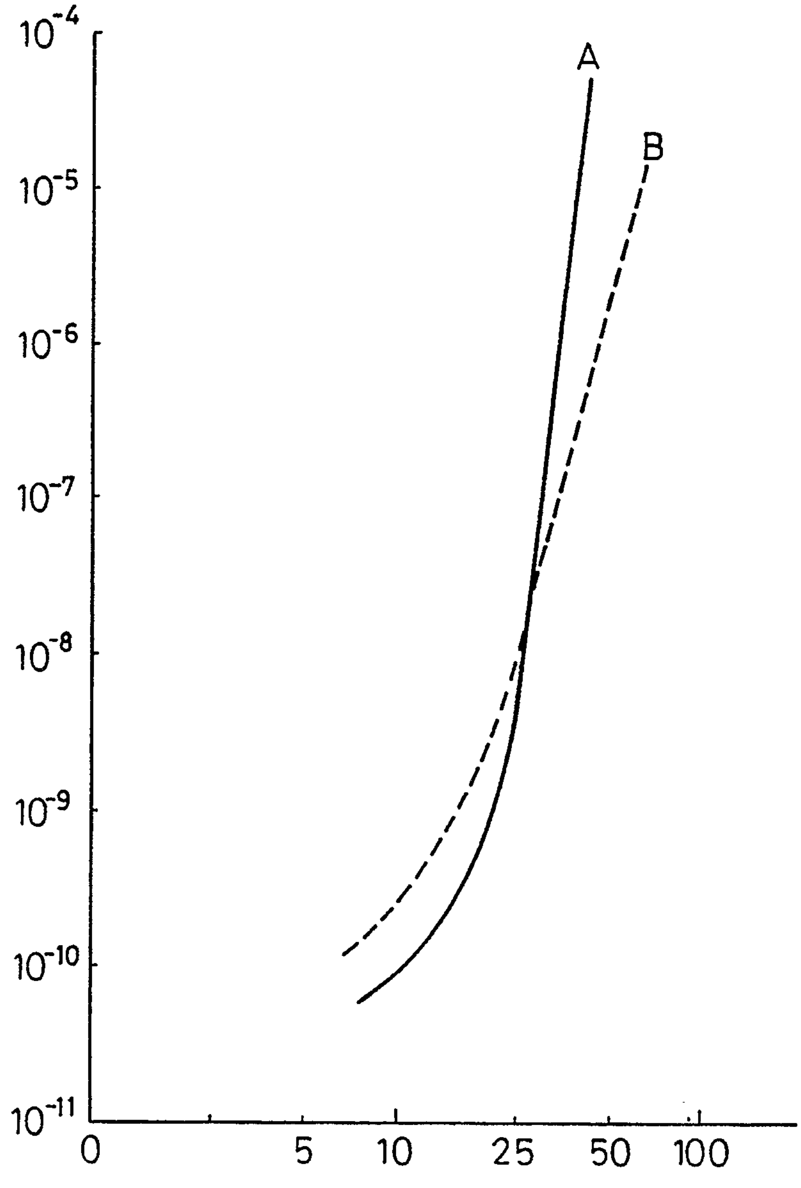


Fig. 3

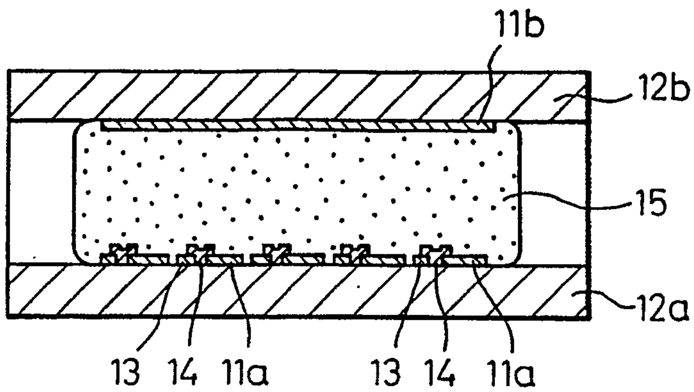


Fig. 4A

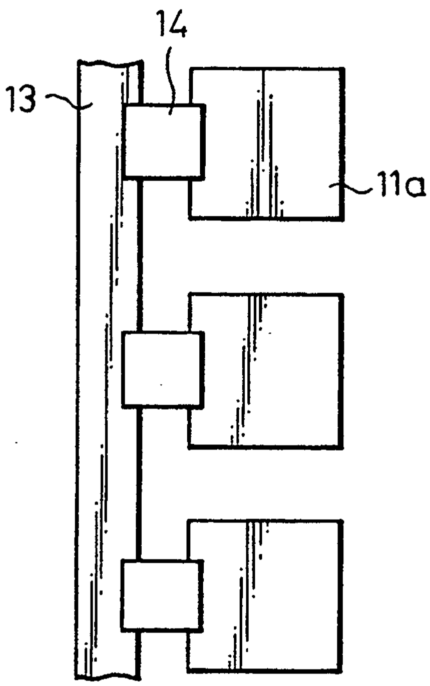


Fig. 4B

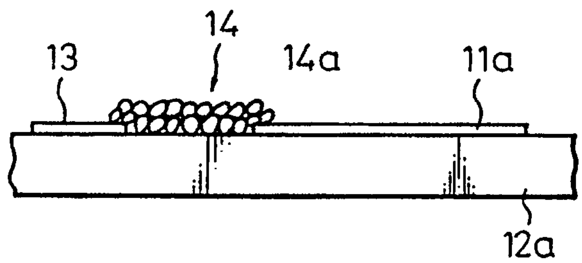
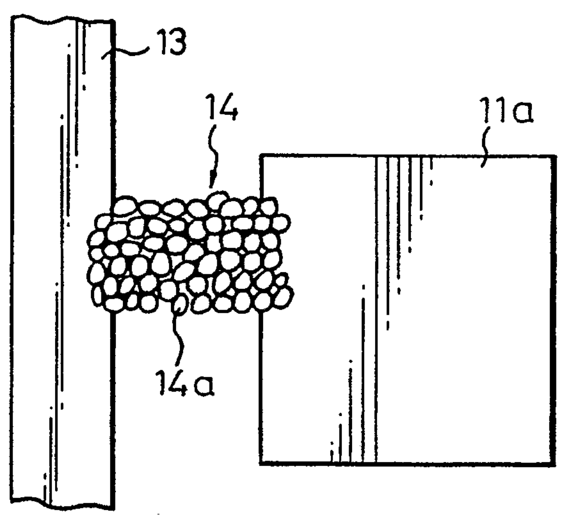


Fig. 4C



INTERNATIONAL SEARCH REPORT

International Application No PCT/JP89/01154

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl^5 H01C7/10

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	H01C7/10

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

Jitsuyo Shinan Koho	1926 - 1989
Kokai Jitsuyo Shinan Koho	1971 - 1989

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	JP, B2, 60-28121 (Matsushita Electric Ind. Co., Ltd.), 3 July 1985 (03. 07. 85), (Family: none)	1 - 21

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
January 12, 1990 (12. 01. 90)	January 29, 1990 (29. 01. 90)
International Searching Authority	**Signature of Authorized Officer**
Japanese Patent Office	