TITLE

COATING SOLUTION FOR FORMATION OF COATING AND USE THEREOF

FIELD OF THE INVENTION

The present invention relates to a coating solution capable of forming a coating having excellent antireflection and antistatic performances, a process for producing the same, and a monolayer or laminate coated substrate having a coating formed from one or two types of the coating solutions on a substrate. More particularly, the present invention is concerned with one or two types of coating solutions capable of forming a coating containing a particulate inorganic compound in monodisperse condition, a process for producing the same, and a coated substrate having the above coating formed on a substrate. Further, the present invention is concerned with a coating solution capable of forming a transparent conductive coating being excellent not only in adhesion with a substrate and smoothness of the surface of the coating but also in durability inclusive of water and alkali resistances, a coated substrate having the above coating formed on the surface thereof, and a display unit.

BACKGROUND OF THE INVENTION

Conventionally, a coating solution for formation of a coating comprising a particulate inorganic compound and a

matrix is used to form a coating on the surface of a substrate, such as plates of glass and plastics, in order to impart thereto various functions, for example, antireflection and antistatic properties.

For example, a method for forming a transparent coating having antireflection and antistatic properties on the surface of a display panel of a cathode-ray tube, a fluorescent character display tube, a plasma display unit, a liquid crystal display unit and the like, in order to prevent reflection of external light and electrostatic charge thereon, and a coating solution for use in the formation of the above transparent coating, have been proposed (see Japanese Laid-Open Publication Nos. 154445/1989, 298301/1989 and 78946/1991).

Japanese Laid-Open Publication No. 193971/1988 discloses a coating solution for formation of a conductive coating, which comprises conductive particles, such as tin oxide and indium oxide, and a vehicle (matrix) composed of an organosilicon compound, such as an alkoxysilane.

In Japanese Laid-Open Publication No. 54613/1989 and International Publication Nos. WO89/03114 and WO90/02157, the present applicant has proposed a coating solution for formation of a conductive coating, which comprises a conductive material and a matrix composed of a partial hydrolysate of an alkoxysilane and an acetylacetonato chelate, such as bis(acetylacetonato)dialkoxyzirconium, in the form of a mixture with a mixed solvent composed of

water and an organic solvent, and has also proposed a substrate having on its surface a conductive coating obtained from the above coating solution.

However, in the formation of a coating on a substrate by the use of the above conventional coating solution for formation of a coating containing a particulate inorganic compound, even if the particulate inorganic compound is present in monodisperse condition in the coating solution, it has occurred that part of the particulate inorganic compound is aggregated during the step of forming a coating, so that a desirable coating in which the particulate inorganic compound is present in monodisperse condition cannot be obtained.

The coating having part of a particulate inorganic compound aggregated has drawbacks in that not only are the antireflection and antistatic properties and the mechanical properties, such as scratch resistance, thereof poor but also part of aggregated particles are viewed as points, that is, a point defect is likely to be caused, and further in that it is likely for the coating to suffer from staining with fingerprints or the like, as compared with the coating in which the particulate inorganic compound is present in monodisperse condition.

In the above situation, the inventors have made extensive and intensive studies with a view toward providing a coating solution for formation of a coating, which is free from aggregation of inorganic compound

particles likely to occur in a coating solution comprising a particulate inorganic compound and also free from aggregation of inorganic compound particles likely to occur during the step of forming a coating from the coating solution. Further, the inventors have made extensive and intensive studies with a view toward providing a substrate having a coating in which a particulate inorganic compound is present in monodisperse condition. As a result, they have found that small amounts of cations and anions present in the coating solution act as an important factor for aggregating the particulate inorganic compound both in the coating solution and during the step of forming a coating.

Illustratively stated, the inventors' analysis of conventional coating solutions has shown that some of them generally contain ions, such as Na^+ ion, in a dispersion of a particulate inorganic compound because an alkali metal in usually added to a dispersion of a particulate inorganic compound, such as a colloidal solution of an inorganic compound, to stabilize the particles. Further, because an acid or aqueous ammonia is used in producing a partial hydrolysate of an acetylacetonato chelate, an alkoxysilane or a metal alkoxide to be used as a matrix in a coating solution for formation of a coating, cations, such as alkali metal, ammonium and various polyvalent metal ions, inorganic anions, such as halogen, sulfuric acid, nitric acid and phosphoric acid, and/or organic anions, such as formic and acetic acids, are present in the resultant

solution containing the matrix. Therefore, most of the coating solutions prepared from a dispersion of a particulate inorganic compound and/or a solution of a matrix have ion concentrations exceeding several tens of millimoles per 100 g of all solid contents contained in the coating solution. The dispersion condition of a particulate inorganic compound in a coating solution having such a high ion concentration is not necessarily good, and particulate inorganic compounds being in monodisperse condition in the respective coating solutions just after the preparation thereof are likely to gradually aggregate. Further, aggregates of part of a particulate inorganic compound are observed in the coating formed on a substrate by applying thereto the conventional coating solution having such a high ion concentration. This coating prepared from the above coating solution may suffer from an unevenness in the film thickness and a haze due to the aggregation of the particulate inorganic compound.

The inventors have found that, if the concentration of the above cations and anions present in the coating solution for formation of a coating is limited to a specific level or lower, the dispersion condition of the particulate inorganic compound in the coating solution becomes good as well as the monodisperse condition of the particulate inorganic compound is maintained favorably in the coating obtained from the coating solution. Based on this finding, the present invention has been completed.

OBJECT OF THE INVENTION

The present invention has been made to overcome the above drawbacks of the prior art, and thus it is an object of the present invention to provide a coating solution which is capable for forming a coating containing a particulate inorganic compound in monodisperse condition on a substrate, such as those of glass, plastics, metals and ceramics. It is another object of the present invention to provide a process for producing the above coating solution.

It is a further object of the present invention to provide a coated substrate having the above coating on a substrate, especially a coated substrate having excellent antireflection and antistatic performances.

It is still a further object of the present invention to provide a coating solution comprising conductive particles having a specific particle size distribution and a partial hydrolysate of an alkoxysilane having a specific molecular weight distribution; a coated substrate obtained by applying the above coating solution on a transparent substrate, such as those of glass and plastics, to form a coating being excellent in adhesion with the substrate, smoothness of the surface of the coating and durability; processes for producing the same; and a display unit including the above coating.

SUMMARY OF THE INVENTION

The coating solution for formation of a coating according to the present invention comprises a particulate inorganic compound and at least one matrix selected from the group consisting of a partial hydrolysate of an acetylacetonato chelate, a partial hydrolysate of an alkoxysilane and a partial hydrolysate of a metal alkoxide in the form of a dispersion or solution in water and/or an organic solvent,

wherein the coating solution has an ion concentration of 10 mmol or less per 100 g of all solid contents contained in the coating solution.

With respect to the coating solution for formation of a coating according to the present invention, it is preferred that the particulate inorganic compound is in the form of conductive particles:

(a) having an average particle size of 50 nm or less,

(b) comprising particles each having a particle size of 60 nm or less in an amount of 60 % by weight or greater,

(c) comprising particles each having a particle size of 10 nm or less in an amount of 5 % by weight or greater, and

(d) comprising particles each having a particle size of 100 nm or greater in an amount of 15 % by weight or less, and

that the matrix is the a partial hydrolysate of an alkoxysilane:

(1) having an average molecular weight of 1,500 to 10,000,

(2) comprising a polymer having a molecular weight of 3,000 or less in an amount of 50 % by weight or less, and

(3) comprising a polymer having a molecular weight of 10,000 or greater in an amount of 20 % by weight or less.

The above coating solution is produced by a process comprising subjecting any one of a dispersion of a particulate inorganic compound, a solution of a matrix and a coating solution prepared by mixing thereof to treatment for removing cations and/or anions so that the ion concentration of the obtained coating solution is 10 mmol or less per 100 g of all solid contents contained in the coating solution.

The coated substrate according to another aspect of the present invention comprises a substrate and, a monolayer or laminated coating formed thereon by applying the above coating solution.

The above coated substrate may be produced by a process comprising coating the above coating solution for formation of a coating on a surface of a substrate to form an uncured coating on the surface of the substrate and heating the uncured coating to effect curing.

The display unit according to a further aspect of the present invention comprises a display panel having on its

outer surface a transparent conductive coating formed by applying the above coating solution for formation of a coating.

The above display unit and coated substrate, such as that having the coating formed on a transparent substrate, e.g., a lens, are excellent not only in antireflection and antistatic performances but also in adhesion with the substrate and durability.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates a bar chart for use in measurement of a resolving power; and

Fig. 2 illustrates an apparatus for measuring a resolving power.

DETAILED DESCRIPTION OF THE INVENTION

The coating solution for formation of a coating, the process for producing the same and the coated substrate according to the present invention will now be described in detail.

Coating Solution for Formation of Coating

First, the coating solution of the present invention will be described.

The coating solution of the present invention comprises a particulate inorganic compound and a matrix in the form of a dispersion or solution in water and/or an organic solvent.

Examples of particulate inorganic compounds dispersed in the coating solution of the present invention include particulate inorganic oxides, such as particulate silica, titania (inclusive of partially reduced titania), zirconia, alumina, ceria, iron oxide, tungsten oxide, tin oxide and antimony oxide, and particulate fluorides, such as particulate magnesium fluoride, potassium fluoride and calcium silicofluoride.

Further, the particulate inorganic compound for use in the present invention may be particles of a composite composed of a plurality of the above inorganic compounds or a mixture of the above particles.

In the present invention, the size and type of the particulate inorganic compound to be dispersed in the coating solution are selected and one or more types of particulate inorganic compounds are added to the coating solution, depending on the functions to be imparted to the surface of the substrate.

For example, by applying a coating solution comprising a particulate silica as the particulate inorganic compound, a finely uneven coating can be formed on the surface of a substrate, so that reflection on the surface of the substrate can be reduced due to the fine unevenness. On the other hand, a conductive coating can be formed on the substrate by applying a coating solution comprising a conductive particulate inorganic oxide selected from tin oxide doped with antimony, fluorine or the like, indium

oxide doped with tin (ITO) and antimony oxide as the particulate inorganic compound.

The refractive index of the coating formed on the substrate can be regulated by selecting the type of the particulate inorganic compound contained in the coating solution or the combination of a plurality of particulate inorganic compounds. For example, a coating having high refractive index and transparency can be obtained by employing titania, ceria, iron oxide or the like as the particulate inorganic compound. On the other hand, a coating having low refractive index and surface reflectance can be obtained by employing magnesium fluoride, calcium fluoride or the like as the particulate inorganic compound.

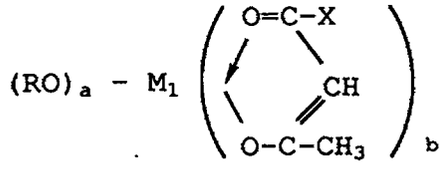
A coating having low surface reflectance can also be obtained by employing, as the particulate inorganic compound, a porous particulate compound oxide prepared by treating a particulate compound oxide as disclosed in Japanese Patent Application No. 91650/1992 previously filed by the present applicant with an acid to leach away part of non-silica metal elements.

The particulate inorganic compound for use in the present invention preferably has an average particle size of 3 to 300 nm. When the coating must have smoothness and strength and when the particulate inorganic compound is a crystalline or amorphous particulate conductive inorganic oxide, it is especially preferred that the average particle size of the particles be in the range of 3 to 100 nm. When

the particulate inorganic compound is used to impart antireflection properties to the surface of the substrate, it is preferred that the average particle size of the particles be in the range of 40 to 300 nm. With respect to the particulate inorganic compound, further, it is desired that the sizes of particles be as uniform as possible, and that the coefficient of variation of particle sizes [(standard deviation/average particle size) x 100] be 30 % or lower, preferably 20 % or lower, still preferably 10 % or lower.

The coating solution of the present invention comprises at least one matrix selected from partial hydrolysates of an acetylacetonato chelate, an alkoxysilane and a metal alkoxide.

The above partial hydrolysate of an acetylacetonato chelate for use as the matrix in the present invention is a chelate having acetylacetone ligands, which is a condensate of a compound represented by the following formula 1:



... (1)

wherein a + b is 2 to 4; a is 0 to 3; b is 1 to 4; R represents $-C_nH_{2n+1}$ (in which n is 3 or 4); X represents $-CH_3$, $-OCH_3$, $-C_2H_5$ or $-OC_2H_5$; and M_1 represents an element selected from the elements of Groups IB, IIA and B, IIIA

and B, IVA and B, VA and B, VIA, VIIA and VIIIA of the periodic table or a vanadyl (VO). Preferred combinations of these elements and vanadyl, a and b are as shown in the following Table 1.

Table 1

a	0 - 1	0 - 2	0 - 3
b	1 - 2	1 - 3	1 - 4
a+b	2	3	4
M_1	Co, Cu, Mg Mn, Pb, Ni Zn, Sn, Ba Be, VO	Al, Cr, Fe V, Co, In Ta, Y, B	Ti, Zr, Hf Sb

Examples of acetylacetonato chelates include dibutoxybis(acetylacetonato)zirconium, tributoxymono(acetylacetonato)zirconium, bis(acetylacetonato)lead, tris(acetylacetonato)iron, dibutoxybis(acetylacetonato)hafnium and mono(acetylacetonato)tributoxyhafnium.

The partial hydrolysate of an alkoxysilane may be obtained from any alkoxysilanes exhibiting hydrolyzability. In the present invention, however, a preferred partial hydrolysate is obtained from an alkoxysilane represented by the formula:

$$R^1_nSi(OR^2)_{4-n}$$

wherein each of R^1 and R^2 independently represents a group selected from an aryl group, an acrylic group, a

vinyl group, an alkyl group having 1 to 8 carbon atoms and $-C_2H_4OC_mH_{2m+1}$ in which m is an integer of 1 to 4; and n is an integer of 0 to 3.

Examples of alkoxysilanes represented by the above formula include tetramethoxysilane, tetraethoxysilane, tetraisopropoxysilane, tetrabutoxysilane, tetraoctoxysilane, methyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, methyltriisopropoxysilane, dimethyldimethoxysilane, methyltributoxysilane, octyltriethoxysilane, phenyltrimethoxysilane and vinyltrimethoxysilane.

The partial hydrolysate of a metal alkoxide may be used as the matrix. The partial hydrolysate of a metal alkoxide is a condensate of a compound represented by the formula:

$$M^2(OR)_n$$

wherein M^2 represents a metal atom; R represents an alkyl group or $-C_mH_{2m}O_2$ in which m is an integer of 3 to 10; and n is an integer equal to the valence of M^2. Condensates selected from these may be used singly or in combination. In the formula, M^2 is not particularly limited as long as it is a metal atom. Preferably, however, it is selected from the group consisting of Be, Al, Sc, Ti, V, Cr, Fe, Ni, Zn, Ga, Ge, As, Se, Y, Zr, Nb, In, Sn, Sb, Te, Hf, Ta, W, Pb, Bi, Ce and Cu.

Examples of metal alkoxides exhibiting hydrolyzability include tetrabutoxyzirconium, tetraoctyloxytitanium and diisopropoxy-dioctyloxytitanium.

Partial hydrolysates of the acetylacetonato chelate, the alkoxysilane and the metal alkoxide can be obtained by conventional methods, for example, by mixing at least one compound selected from acetylacetonato chelates, alkoxysilanes and metal alkoxides each having hydrolyzability with an alcohol, such as methanol or ethanol, and adding water and an acid or alkali to the mixture. In the preparation of a partial hydrolysate as described above, it is preferred that the average molecular weight of the partial hydrolysate be regulated to about 1,500 - 10,000, preferably 2,000 - 7,000 (in terms of polystyrene), from the viewpoint that a coating having an even thickness can be obtained.

The appropriate mixing ratio of particulate inorganic compound (F) to matrix (M) mixed together to obtain the coating solution of the present invention depends on the properties and conditions which must be exhibited by the coating obtained from the coating solution, and is not particularly limited. However, it is preferred that the ratio of F/M (by weight) in terms of an oxide of each of the ingredients be in the range of 0.05 to 7.

In particular, the coating formed from a coating solution comprising a particulate inorganic compound (F), such as particulate silica, having an average particle size

of 40 to 300 nm, preferably 80 to 200 nm and a matrix (M) at a ratio of F/M of 1 to 5 (by weight), exhibits excellent antireflection performance, low haze and marked scratch resistance. A color cathode-ray tube free of color shade on display image can be obtained by forming the above coating, as an antireflecting film, on the surface of a face plate of the color cathode-ray tube.

Further, a coating which is excellent in both conductivity and antireflection performance, can be formed from a coating solution comprising the above particulate silica and a particulate conductive inorganic oxide together with a matrix. The above coating which is excellent in both conductivity and antireflection performance, can also be formed on a substrate by first applying a coating solution comprising a particulate conductive inorganic oxide and a matrix to form a conductive coating on the substrate and subsequently applying a coating solution comprising a particulate silica and a matrix to form an antireflecting film on the conductive coating.

In the present invention, a coating which is excellent not only in conductivity but also in adhesion with a substrate and durability, can be obtained by applying a coating solution in which the particulate inorganic compound is in the form of transparent conductive particles with a particle size distribution:

(a) having an average particle size of 50 nm or less, preferably 5 to 30nm,

(b) comprising particles each having a particle size of 60 nm or less in an amount of 60 % by weight or greater, preferably 80 % by weight or greater,

(c) comprising particles each having a particle size of 10 nm or less in an amount of 5 % by weight or greater, preferably 20 % by weight or greater, and

(d) comprising particles each having a particle size of 100 nm or greater in an amount of 15 % by weight or less, preferably 5 % by weight or less, and

the matrix is a partial hydrolysate of an alkoxysilane:

(1) having an average molecular weight of 1,500 to 10,000, preferably 2,500 to 7,500,

(2) comprising a polymer having a molecular weight of 3,000 or less in an amount of 50 % by weight or less, preferably 20 % by weight or less, and

(3) comprising a polymer having a molecular weight of 10,000 or greater in an amount of 20 % by weight or less, preferably 10 % by weight or less.

In the formation of the above coating, it is preferred that the ratio of F [particulate inorganic compound (conductive particles)] / M (matrix) by weight be in the range of 0.5 to 5.

In the coating solution of the present invention, water and/or an organic solvent are used as a dispersion medium.

The organic solvent is selected from those capable of stisfactorily dissolving or dispersing the particulate inorganic compound and the matrix. Examples of such organic solvents include alcohols, such as methanol, ethanol, propanol and butanol; ethylene glycol ethers, such as methyl cellosolve and ethyl cellosolve; glycols, such as ethylene glycol and propylene glycol; esters, such as methyl acetate, ethyl acetate and methyl lactate; ketones, such as acetone and methyl ethyl ketone; and ethers, such as butyl ether and tetrahydrofuran.

In the coating solution of the present invention, it is desired that the concentration of the total of the particulate inorganic compound and the matrix is in the range of 0.1 to 30 % by weight, especially 0.5 to 20 % by weight.

Further, in the coating solution of the present invention, it is requisite for the total of concentrations of cations, such as alkali metal ion, ammonium ion and polyvalent metal ion, inorganic anions, such as mineral acids, and organic anions, such as formic acid and acetic acid, contained in the coating solution to be 10 mmol or less per 100 g of all solid contents contained in the coating solution. When the ion concentration of the coating solution is reduced to 10 mmol or less per 100 g of

all solid contents contained in the coating solution, the dispersion condition of the particulate inorganic compound contained in the coating solution is excellent, and a coating solution in which substantially no particle aggregates are present can be obtained. A monodisperse condition of the particulate inorganic compound in this coating solution is maintained during the step of forming a coating. As a result, a coating containing the particulate inorganic compound in monodisperse condition can be formed on the surface of a substrate. That is, no particle aggregates are observed in the coating obtained by applying a coating solution having an ion concentration of 10 mmol or less per 100 g of all solid contents contained in the coating solution to a substrate, and, hence, a coating free of point defect and uneven film thickness attributable to aggregation of inorganic compound particles can be formed on the substrate.

The reason for the maintenance of the monodisperse condition of the particulate inorganic compound in the coating solution of the present invention is presumed that the extremely low concentration of ions in the coating solution increases Debye length of the surface of particles to. thereby increase the mutual repulsion of the particles, so that the particles can maintain a desirable dispersion condition.

The terminology "ion concentration of the coating solution of the present invention" used herein means the

total of concentrations of cations, such as ammonium, alkali metal and polyvalent metal ions, inorganic anions, such as halogen and mineral acids, and organic anions, such as formic and acetic acids, which are present in the coating solution. The terminology "ions which are present in the coating solution" used herein means not only ions present in isolated form in the solvent of the coating solution but also ions adsorbed or adhered to the particulate inorganic compound, the matrix, etc.

In the present invention, the ion concentration is measured and calculated as follows.

First, the coating solution is dried at about 100 to 110 °C, and the resultant solid contents are weighed.

Thus, the weight of all solid contents contained in the coating solution is obtained.

The solid contents are entirely dissolved in an acid, etc. The amount of alkali metal and alkaline earth metal ions contained in the solution is measured by atomic absorption spectrometry, and the amount of other metal ions is measured by emission spectral analysis (ICP).

Separately, the coating solution is directly analyzed by potentiometric titration to determine the amount of ammonium ion and anions.

From the thus determined amount of solid contents and total amount of ions, the ion concentration is calculated per 100 g of solid contents.

Process for Producing Coating Solution for Formation of Coating

The process for producing a coating solution according to the present invention will now be described.

A preliminary solution for the coating solution of the present invention is generally produced by dispersing or dissolving predetermined amounts of the particulate inorganic compound and the matrix in pure water, an organic solvent such as alcohol and a solvent composed of a mixture thereof. In this process, the preliminary solution may be produced by mixing the particulate inorganic compound with a hydrolyzable compound as a precursor for the matrix in a solvent and then partially hydrolyzing the hydrolyzable compound.

Deionization is performed after the production of the preliminary solution or at an appropriate stage of the process for producing the same so that the ion concentration of the resultant coating solution becomes 10 mmol or less per 100 g of all solid contents contained in the coating solution.

The particulate inorganic compound to be added to the coating solution may be either powdery or in the form of a sol having been dispersed in a solvent, such as water.

When the powder is to be dispersed, the particulate inorganic compound is mixed with the matrix, and uniformly dispersed by means of a sand mill, etc. Alternatively, the coating solution may be obtained by uniformly dispersing

the particulate inorganic compound in a dispersion medium, such as water, and then mixing the dispersion with the matrix. In this case, both of the dispersion of the particulate inorganic compound and the matrix may be previously deionized.

The above-mentioned conductive particles having specific average particle size and particle size distribution may be obtained by pulverizing and/or classifying the conventional conductive particles by appropriate means until the average particle size and particle size distribution thereof fall within the above specific ranges.

The pulverization and/or classification for controlling the average particle size and particle size distribution of the conductive particles may be conducted for the powder or the sol thereof. The above pulverization and/or classification may be performed either before or after the preparation of a coating solution for formation of a coating.

The above partial hydrolysate of an alkoxysilane having specific average molecular weight and molecular weight distribution may be obtained by a method comprising hydrolyzing the alkoxysilane in, for example, a solvent composed of a mixture of water and an alcohol in the presence of an acid, such as nitric acid, hydrochloric acid or acetic acid.

The above hydrolysis of the alkoxysilane is preferably performed under the conditions such that:

Acid/SiO_2 = 0.0001 to 0.05 (wt./wt.), and

water/SiO_2 = 4 to 16 (mol/mol),

wherein SiO_2 indicates the amount of the alkoxysilane in terms of SiO_2.

With respect to the coating solution prepared from the matrix solution and the sol of particulate inorganic compound having been deionized until the ion concentration becomes 10 mmol or less per 100 g of all solid contents, generally, no further deionization of the resultant coating solution is required.

However, in the event that the ion concentration of the prepared coating solution exceeds 10 mmol per 100 g of all solid contents contained in the coating solution, deionization of the coating solution is performed to reduce the ion concentration to 10 mmol or less per 100 g of all solid contents.

The method for deionization is not particularly limited as long as, finally, the ion concentration of the coating solution for formation of a coating is 10 mmol or less per 100 g of all solid contents contained in the coating solution. However, as preferred deionization methods, there can be mentioned one in which either the dispersion of the particulate inorganic compound and/or the solution of the matrix as precursors for the coating solution or the coating solution produced therefrom is

contacted with cation exchange resin and/or anion exchange resin, and another in which either the dispersion and/or the solution or the coating solution is purified with an ultrafilter membrane.

The above contact with the cation and/or anion exchange resin may be performed by passing either the dispersion and/or the solution or the coating solution through a column packed with the cation or anion exchange resin or a mixture thereof at least once. Alternatively, it may be performed by adding the cation and/or anion exchange resin to either the dispersion and/or the solution or the coating solution, followed by agitation for an appropriate period of time.

Coated Substrate

The coated substrate of the present invention will now be described in detail.

The coated substrate of the present invention comprises a substrate, such as a plate and a film, composed of glass, a plastic, a metal, a ceramic or the like and, superimposed thereon, a coating formed from the above coating solution.

The above coating may be either a monolayer coating formed from a coating solution comprising at least one particulate inorganic compound and a matrix, or a laminated coatings comprising the above monolayer coating and, superimposed thereon, another coating formed from a coating

solution comprising a particulate inorganic compound capable of imparting functions different from those imparted by the above particulate inorganic compound and a matrix. These coatings may each have a protective coating with various functions formed thereon.

The final coating has properties, such as conductivity, high or low refractive index and antireflection performance, dependent on the type of the particulate inorganic compound contained in the coating, and the ratio of the particulate inorganic compound to the matrix.

As apparent from the above, the coated substrates of the present invention comprehend a substrate provided with a conductive coating, a coated substrate having a desirable reflectance, a substrate provided with an antireflection coating and a coated substrate being excellent in both conductivity and antireflection performance.

Of these, the substrate provided with a conductive coating preferably has a surface resistivity of 10^3 to 10^{10} $\Omega/\square$, and preferred examples thereof include a face plate of a cathode-ray tube having a transparent conductive coating on its outer surface and a platen glass of a copier having a transparent conductive coating on its surface which is brought into contact with an original.

With respect to the substrate provided with an antireflection coating, it is feasible to produce one having a reflectance of not higher than 1 %, and preferred

examples thereof include a transparent substrate, such as a lens or a face plate of a cathode-ray tube, having a transparent antireflection coating formed on its surface or outer surface.

Examples of such antireflection coatings include a coating having a finely uneven surface, a coating composed of a transparent matrix and, contained therein, particles having a refractive index lower than that of the matrix, and a coating laminate composed of a coating with a high refractive index and, arranged thereon to form a surface, a coating with a low refractive index.

The coated substrate of the present invention comprehends a laminate comprising the conventional functional coating-applied substrate such as glass having an NESA film formed thereon and, superimposed on the coating thereof, the coating formed from the coating solution of the present invention.

The coating of the coated substrate of the present invention may contain a small amount of a dye or a pigment. In this coated substrate, the coating absorbs rays with specific wavelengths, depending on the dye or pigment contained in the coating, so that, for example, the image contrast can be improved on a cathode-ray tube comprising the coated substrate.

In the present invention, the transparent conductive coating produced from the above coating solution comprising conductive particles having specific average particle size

and particle size distribution as the particulate inorganic compound and a matrix having specific average molecular weight and molecular weight distribution, is a smooth and dense film free of unevenness and voids (pores or minute cracks) attributed to particle aggregates.

The terminology "smoothness" used herein refers to not only freedom from unevenness and little surface roughness but also void free denseness.

Accordingly, the above substrate provided with a transparent conductive coating is not only excellent in both of optical characteristics, such as transparency and low haze, and surface hardness, but also exhibits improved durability in an acid or alkali atmosphere or a highly hot and humid atmosphere and improved adhesion between the coating and the substrate, further having excellent stain resistance. The terminology "stain resistance" used herein means properties of the coating such that it is less likely for the surface of the coating to suffer from stains, and that, if it is stained, the staining matter can easily be removed.

A transparent conductive coated substrate having any desired surface resistivity of between 10^3 and 10^{10} $\Omega/\square$, and a haze of 1 % or less can be obtained by forming the above transparent conductive coating on the surface of a substrate and, optionally, further forming a transparent protective film on the transparent conductive coating .

Moreover, by performing a nonglare treatment described later during the step of forming a coating, a transparent conductive substrate exhibiting a glossiness of 40 to 90 % while having a surface resistivity as exhibited when the nonglare treatment is not conducted, can be obtained.

It is preferred that the coating of the thus obtained coated substrate according to the present invention have a thickness of 0.05 to 0.7 μm.

The coated substrate of the present invention can be obtained by first applying the above coating solution to the surface of a substrate, such as glass or a plastic, by dipping, spinner, spray, roll coater, flexographic printing and other methods, subsequently drying the layer of the coating solution formed on the surface of the substrate at room temperature to 90 °C, and thereafter heating the dried layer at 100 °C or higher to effect curing thereof.

In the present invention, further, a coated substrate having the above effects of the present invention more markedly exhibited can be produced by the procedure described below.

Illustratively stated, after the above solution-coating or drying step, or during the drying step, the coating in the uncured state is either irradiated with an electromagnetic wave having a wavelength smaller than that of visible light, or exposed to a gas atmosphere capable of expediting curing reaction.

Examples of electromagnetic waves for use in the irradiation of the uncured coating before heating include ultraviolet radiation, electron beam, X-rays and gamma-rays. In practice, ultraviolet radiation is preferred. For example, the coating in the uncured state is irradiated with an ultraviolet radiation with an energy flux of 100 mJ/cm^2 or greater, preferably 1000 mJ/cm^2 or greater emitted from a mercury lamp, as an ultraviolet radiation source, having luminous intensity maximums at about 250 nm and 360 nm and having a luminous intensity of 10 mW/cm^2 or higher, preferably 100 mW/cm^2 or higher.

Examples of gases capable of expediting curing reaction in the uncured coating before heating include ammonia and ozone.

For example, the treatment for expediting the curing of the coating may be carried out by exposing the coating in the uncured state to an active gas atmosphere, as indicated above, having a gas concentration of 100 to 10,000 ppm, preferably 1000 to 10,000 ppm for a period of 1 to 60 min.

The above treatment for expediting the curing accelerate not only the polymerization of the matrix but also the evaporation of the water and solvent remaining in the coating. As a result, the thermal curing conditions, such as heating temperature and time, to be applied in the subsequent heating step, can be relieved.

In the present invention, a nonglaring transparent coated substrate provided with a coating having on its surface a vast plurality of fine ringlike protrusions and recesses can be obtained by preheating the surface of a substrate, such as glass or a plastic, to about 40 - 90 °C, then spraying the coating solution onto the preheated surface while maintaining the temperature, and thereafter heating the coating to effect curing. When the transparent coated substrate is produced by the above procedure, the apparent surface smoothness of the coating is slightly lost but the coated substrate does not suffer from any performance lowering in stain resistance and durability.

The above treatment for expediting the curing can be performed prior to this thermal curing.

The transparent protective coating which may be formed on the coating produced by the above process, can be formed by successively carrying out the same application, drying and heating as in the process for producing the coating. The above treatment for expediting the curing and/or the treatment for rendering the surface of the coating nonglaring may be performed during the step of forming the transparent protective coating.

The coating solution for use in forming the transparent protective coating preferably comprises either the above matrix for use in the present invention only or the matrix together with the particulate inorganic compound

suitable for imparting desired functions to the coated substrate.

It is preferred that the above transparent protective coating have a thickness of about 0.5 μm or less.

Display Unit Equipped with Transparent Conductive Coated Substrate

The display unit of the present invention is an apparatus capable of electrically displaying images, such as a cathode-ray tube (CRT), a fluorescent character display tube (FIP), a plasma display (PDP) and a liquid crystal display (LCD), comprising a display panel having the transparent conductive coating formed on its outer surface. That is, the display unit of the present invention is equipped with a display panel provided with a transparent conductive coating as a transparent conductive coated substrate.

This transparent conductive coating is formed by applying the above coating solution for formation of a transparent conductive coating among the various forms of the coating solution of the present invention.

The thus formed display panel provided with a transparent conductive coating is excellent in all of conductivity, smoothness, durability, adhesion between the coating and the substrate and stain resistance. The resolving power of a display image viewed through this

display panel provided with a transparent conductive coating, can be maintained at a high level.

Incidentally, every display panel provided with a transparent conductive coating for use in the present invention has a surface resistivity of between 10^3 and 10^{10} Ω/□. When the treatment for rendering the coating nonglaring is not conducted, it exhibits a haze of 1 % or less and a resolving power of 70 bars/cm or higher. On the other hand, when the above treatment is conducted, it exhibits a glossiness of 40 to 90 % and a resolving power of 60 bars/cm or higher.

Herein, the resolving power is determined by the following method.

As shown in Fig. 1, a bar chart 1 having printed a given number per 1 cm of bars 2 is applied to one side of a test display panel on which no coating is formed, and said panel is placed in a test device 4 shown in Fig. 2 so that the side of said panel to which the bar chart has been applied is positioned inside the test device 4. In the test device 4 having a white inner wall 2 pieces of fluorescent lamps (20W) are placed laterally at an interval of 30 cm at a distance of 50 cm from the position of the test display panel. In this case, the bar chart used is changed successively from one having a small number of bars per 1 cm to the other having a larger number of bars per 1 cm, and the maximal number of bars per 1 cm in the bar

chart that can be confirmed by visual observation is taken as the resolving power.

In the display unit of the present invention, the light reflectance of the display panel can be reduced to 1 % or less by forming a transparent conductive coating containing not only conductive particles but also a particulate compound, such as particles of oxide of titanium and oxide of zirconium, for regulating refractive index on an outer surface of the display panel and further forming a protective film or a protective film containing a particulate compound, such as particles of MgF_2 and CaF_2, for regulating refractive index on the surface of the transparent conductive coating. That is, the light reflection on the surface of a display screen can be reduced, so that it becomes easier to view the image displayed on the display panel.

Thus, in the display unit of the present invention, various improvements, such as reduction of light reflection on the display screen, can be made, for example, by forming a special protective film on a transparent conductive coating superimposed on the outer surface of the display panel.

EFFECT OF THE INVENTION

A coating containing a particulate inorganic compound in monodisperse condition can be formed on a substrate of glass, a plastic, a metal, a ceramic, etc. by applying the

coating solution for formation of a coating, comprising a particulate inorganic compound and a matrix, according to the present invention. Further, various functions, such as conductivity and/or antireflection property and desirable refractive index, can be imparted to the coating as well as the haze of the coating can be reduced and the transparency, scratch resistance and adhesion with substrates of the coating can be improved, by changing the type of the particulate inorganic compound contained in the coating solution and the ratio of the particulate inorganic compound to the matrix charged. Still further, the particulate inorganic compound can be monodispersed in the coating, so that, by applying the coating solution for formation of a coating according to the present invention, it is feasible not only to obtain a flat coating with even thickness but also to form a coating exhibiting performances, such as conductivity and antireflection performances, comparable to those of the coating from the conventional coating solution, even if the amount of particulate inorganic compound contained in the coating solution is decreased.

Furthermore, every coating formed on a substrate in the above manner is almost or entirely free of void and pin hole, thereby being extremely dense, so that it has excellent chemical and boiling resistances and is also excellent in stain resistance, ensuring extremely less amounts of stains from the hand, etc.

The above coating solution capable of forming a coating having excellent properties can simply and surely be produced by the process for producing a coating solution according to the present invention.

In the process for producing a coated substrate according to the present invention, the thermal curing conditions can be relieved by implementing treatments for expediting curing, such as irradiating the coating before heating and in the uncured state with an electromagnetic wave having a wavelength smaller than that of visible light, or exposing the same to a specific gas atmosphere.

The coated substrate of the present invention is suitable for use as a display panel of a cathode-ray tube, a liquid crystal display unit or the like, a lens of a camera, etc. due to the formation of the above coating having excellent properties on the substrate.

The display unit of the present invention can retain antistatic and electromagnetic shielding effects on the display screen for a prolonged period of time under a severe circumstance, due to the provision of the above display panel having a transparent conductive coating having excellent properties formed on the surface thereof. Accordingly, it is less likely for dirt and dust to deposit on the display screen, and the conditions in which IC breakage and malfunctioning are rare can be maintained for a prolonged period of time.

Still further, the resolving power of a display image viewed through the above display panel provided with a transparent conductive coating is kept at a high level, so that the display unit of the present invention ensures a clear image.

Hereinbelow, the present invention will be described in greater detail with reference to the following Examples, which should not be construed as limiting the scope of the invention.

EXAMPLES

Examples 1 to 8 and Comparative Example 1

A. Preparation of Matrix Solutions M1 to M5

As indicated in Table 2, matrix solutions M1 to M5 having various average molecular weights, solid contents and ion concentrations were prepared by hydrolyzing ethyl silicate 28 (SiO2: 28 % by weight), ethyl silicate 40 (SiO_2: 40 % by weight), dibutoxybis(acetylacetonato)zirconium ($Zr(AA)_2(OBu)_2$; ZrO_2: 10 % by weight) and titanium tetraisopropoxide ($Ti(OC_3H_7)_4$; TiO_2: 10 % by weight) as precursor in solvents composed of pure water, ethanol and 35 % hydrochloric acid as indicated in Table 2, optionally followed by deionization treatment.

The deionization treatment was carried out by a process comprising mixing each of the matrix solutions with an amphoteric ion exchange resin (Diaion SMNUPB produced by Mitsubishi Chemical Industries, Ltd.), agitating the

mixture, and removing the ion exchange resin from the matrix solution.

Table 2

Matrix Solution	Precursor		Mixed solution: Pure water (g)	Ethanol (g)	35% hydrochloric acid (g)	Hydrolysis temperature (°C)	Deionization treatment	Average molecular weight	* (% by weight)	Ion concentration **
		Weight (g)								
M1	Ethyl silicate 28	100	34	146	0.3	100	Not applied.	4500	10	10.0
M2	Ethyl silicate 40	100	96	600	4	50	Applied.	2000	5	1.0
M3	Ethyl silicate 28	90	30	132	0.1	150	Not applied.	7000	10	3.2
	$Zr(AA)_2(OBu)_2$	10								
M4	Ethyl silicate 40	100	96	600	4	50	Applied.	1500	5	9.6
M5	$Ti(OC_3H_7)_4$	100	9	91	0.1	100	Applied.	1000	5	0.1

* : Concentration of solid contents

** : (mmol/100 g solid contents)

B. Preparation of Inorganic Compound Sols F1 to F8

(1) Preparation of Conductive Antimony-Doped Tin Oxide Sol (F1)

333 Grams of potassium stannate and 69.5 g of tartar emetic were dissolved in 1,019 g of pure water to obtain an aqueous solution of potassium stannate and tartar emetic.

The whole of this aqueous solution of potassium stannate and tartar emetic was added to 1,876 g of pure water heated at 50 °C over a period of 12 hr while adjusting the pH of the mixture to 10 by the addition of concentrated nitric acid. Thus, an antimony-containing tin oxide hydrate was obtained.

This antimony-containing tin oxide hydrate was ultrafiltered from the reaction mixture. The resultant filter cake was washed with pure water, and fired in the air at 550 °C for 3 hr to thereby obtain powder of a conductive antimony-doped tin oxide.

400 Grams of the obtained powder of a conductive antimony-doped tin oxide was added to 1,600 g of an aqueous solution containing 40 g of potassium hydroxide, and milled at 30 °C for 5 hr in a sand mill to obtain a conductive antimony-doped tin oxide sol.

This sol was deionized in the same manner as in the above deionization of the matrix solution, thereby obtaining a conductive antimony-doped tin oxide sol (F1) having the average particle size, solid content and ion concentration indicated in Table 3.

(2) Preparation of Silica Sol (F2)

Silica sol (SI-200P produced by Catalysts & Chemicals Industries, Co., Ltd.) was heated at 200 °C for 3 hr in an autoclave, and treated with an amphoteric ion exchange resin (Diaion SMNUPB produced by Mitsubishi Chemical Industries, Ltd.). Thus, a silica sol (F2) having the average particle size, solid content and ion concentration indicated in Table 3 was obtained.

(3) Preparation of Titania Sol (F3)

Titania sol (PW-1010 produced by Catalysts & Chemicals Industries, Co., Ltd.) was treated with the above amphoteric ion exchange resin. Thus, a titania sol (F3) having the average particle size, solid content and ion concentration indicated in Table 3 was obtained.

(4) Preparation of Magnesium Fluoride Sol (F4)

An aqueous solution obtained by dissolving 508.3 g of magnesium chloride hexahydrate in 12,500 g of pure water and an aqueous solution obtained by dissolving 470.7 g of potassium fluoride dihydrate in 12,500 g of pure water were simultaneously added to 25,000 g of pure water over a period of 6 hr. Thus, a magnesium fluoride sol was obtained.

This magnesium fluoride sol was aged at 90 °C for 2 hr, and treated with the above amphoteric ion exchange resin. Thus, a magnesium fluoride sol (F4) having the average particle size, solid content and ion concentration indicated in Table 3 was obtained.

(5) Preparation of Silica Sol (F5)

Silica sol (SI-45P produced by Catalysts & Chemicals Industries Co., Ltd.) was treated with a cation exchange resin (Diaion SK-1B produced by Mitsubishi Chemical Industries, Ltd.). Thus, a silica sol (F5) having the average particle size, solid content and ion concentration indicated in Table 3 was obtained.

(6) Preparation of Silica-Alumina Sol (F6)

A mixture (pH: 10.5) of 20 g of a silica sol having an average particle size of 5 nm and an SiO_2 concentration of 20 % by weight and 380 g of pure water was heated to 80 °C. Subsequently, 1,800 g of an aqueous sodium silicate solution having a concentration, in terms of SiO_2, of 1.5 % by weight and 1,800 g of an aqueous sodium aluminate solution having a concentration, in terms of Al_2O_3, of 0.5 % by weight were simultaneously added to the mixture. The temperature of the reaction mixture was kept at 80 °C while adding the above aqueous solutions. After the completion of the addition, the reaction mixture was cooled to room temperature, thereby obtaining a sol of a silica·alumina compound oxide having an average particle size of 20 nm and an SiO_2/Al_2O_3 molar ratio of 5.1.

This sol was treated with a cation exchange resin, and the pH of the sol was adjusted to 8. 10 Liters of a 0.1 % by weight aqueous acetic acid solution was gradually added to 2 kg of the above sol to partially leach Al from silica-alumina compound oxide particles. Pure water was added to

the resultant sol, and ultrafiltered to separate the Al dissolved in the sol. Thus, a sol of a silica·alumina compound oxide having an SiO_2/Al_2O_3 molar ratio of 50 was obtained.

This sol was heated at 200 °C for 3 hr in an autoclave, and deionized in the same manner as in the above deionization of the matrix solution, thereby obtaining a silica-alumina sol (F6) having the average particle size, solid content and ion concentration indicated in Table 3.

(7) Preparation of Silica-Alumina Sol (F7)

1,800 Grams of an aqueous sodium silicate solution having a concentration, in terms of SiO_2, of 0.5 % by weight and 1,800 g of an aqueous sodium aluminate solution having a concentration, in terms of Al_2O_3, of 1.4 % by weight were simultaneously added to 400 g of a 0.1 % by weight aqueous sodium hydroxide solution heated to 80 °C. The temperature of the reaction mixture was kept at 80 °C while adding the above aqueous solutions. After the completion of the addition, the reaction mixture was cooled to room temperature, thereby obtaining a sol of a silica·alumina compound oxide having an average particle size of 80 nm and an SiO_2/Al_2O_3 molar ratio of 0.6.

This sol was treated with a cation exchange resin, and the pH of the sol was adjusted to 10.5. 300 Grams of a silicic acid solution having a SiO_2 concentration of 2 % by weight was added to 1.5 kg of the above sol over a period of 6 hr to effect a surface treatment of the silica-alumina

compound oxide particles contained in the sol while maintaining the temperature of the sol at 80 °C. Then, 30 liters of a 0.01 N aqueous hydrochloric acid solution was gradually added to the above sol to partially leach Al from the silica-alumina compound oxide particles. Pure water was added to the resultant sol, and ultrafiltered to separate the Al dissolved in the sol. Thus, a sol of a silica·alumina compound oxide having an SiO_2/Al_2O_3 molar ratio of 30 was obtained.

This sol was treated at 200 °C for 3 hr in an autoclave, thereafter deionized in the same manner as in the above deionization of the matrix solution, thereby obtaining a silica-alumina sol (F7) having the average particle size, solid content and ion concentration indicated in Table 3.

(8) Preparation of Pigment-Dispersed Sol (F8)

A dispersion obtained by dispersing 100 g of titanium black (produced by Ishihara Sangyo Co., Ltd.) and 30 g of silica sol (SI-30 produced by Catalysts & Chemicals Industries, Co., Ltd.) in 300 g of pure water, was milled in a sand mill for 3 hr. The resultant dispersion was diluted with pure water to a solid content of 5 % by weight, treated with an amphoteric ion exchange resin (Diaion SMNUPB produced by Mitsubishi Chemical Industries, Ltd.), and concentrated with an ultrafilter membrane. Thus, a pigment-dispersed sol (F8) having the average

particle size, solid content and ion concentration indicated in Table 3 was obtained.

C. Production of Coating Solution for Formation of Coating

The above matrix solutions M1 to M5 and inorganic compound sols F1 to F8 were mixed together at varied ratios, and diluted with varied diluents to thereby obtain the coating solutions for formation of coatings having varied solid contents, F/M ratios and ion concentrations, as indicated in Table 4.

Table 3

Sol of inorganic compound	Particulate Inorganic Compound		Sol	
		Particle size (nm)	Concentration of solid contents (% by weight)	Ion concentration (mmol/100 g solid contents)
F1	Conductive antimony-doped tin oxide	10	20	1.1
F2	Silica	200	30	0.05
F3	Titania	10	10	1.6
F4	Magnesium fluoride	200	10	4.8
F5	Silica	80	20	25.2
F6	Silica-Alumina	20	20	0.2
F7	Silica-Alumina	80	20	0.3
F8	Titania and Silica	50	20	2.0

Table 4

	Matrix Solution [Weight (g)]	Sol of Inorganic Compound [Weight (g)]	Diluent [Weight (g)]	Coating Solution		
				Concentration of solid contents (% by weight)	Ratio of F/M	Ion Concentration (mmol/100g solid contents)
Ex. 1	M1 (100)	F1 (100)	Ethanol (1800)	1.5	2	4.5
Ex. 2	M2 (100)	F2 (66.7)	Ethanol (633.3) Diacetone alcohol (33.3)	3.0	4	0.2
Ex. 3	M1 (100)	F1 (200) F3 (100)	Ethanol (3600)	1.5	5	7.5
Ex. 4	M3 (100)	F1 (200)	Ethanol (3003)	1.5	4	5.4
Ex. 5	M2 (100)	F4 (50)	Ethanol (850)	1.0	1	3.1
Ex. 6	M2 (100)	F6 (50)	Ethanol (600)	2.0	2	3.8
Ex. 7	M2 (100)	F7 (75)	Ethanol (492)	3.0	3	2.9
Ex. 8	M5 (100)	F8 (125)	Ethanol (1575) Diacetone alcohol (200)	1.5	5	1.8
Com. Ex. 1	M4 (100)	F5 (66.7)	Ethanol (633.3) Diacetone alcohol (33.3)	3.0	4	18.5

Examples 9 to 16 and Comparative Example 2

I. Production of Coated Substrate

As indicated in Table 5, coated substrates were produced by forming a single or double transparent coating layer on the surface of a glass plate as a substrate, using the coating solutions obtained in Examples 1 to 8 and Comparative Example 1.

The formation of the coating layers was conducted as follows.

(1) Coating method: spinner

1st layer (on substrate)	100 rpm, 60 sec
2nd layer (top layer)	200 rpm, 60 sec

provided that the rotational frequency of the spinner in the formation of the 2nd coating layer in Example 13 was 100 rpm.

(2) Coating temperature: room temperature

(3) Heating conditions: 160 °C, 30 min

II. Evaluation of Coated Substrate

The following evaluations were made with respect to each of the thus obtained coated substrates.

(a) Unevenness of Film Thickness, Point Defect

With respect to each of the coated substrates, unevenness of film thickness and point defect were visually checked while illuminating the surface thereof by means of an illuminator for visual check (WA-LSH manufactured by Olympus Optical Co., Ltd.).

(b) Haze

The haze of the surface of the coating of each of the coated substrates was measured by the use of a haze computer (manufactured by Suga Shikenki K.K.).

(c) Reflectance

The 5° specular reflectance of a light with a wavelength of 550 nm on the surface of the coating of each of the coated substrates was measured by means of a spectrophotometer for ultraviolet and visible region (manufactured by Nippon Denshi K.K.).

(d) Surface Resistivity

The surface resistivity of the coating of each of the coated substrates was measured by a surface resistivity meter (HIRESTA or LORESTA manufactured by Mitsubishi Petrochemical Co., Ltd.).

(e) Film Strength

An office eraser (No. 50-50 produced by LION) was placed on the coating of each of the coated substrates, and given 200 reciprocating slidings under a load of 1 kg. Thereafter, whether or not the coating peeled was visually checked.

(f) Boiling Resistance

Each of the coated substrates was immersed in boiling water for 30 min, and then whether or not the coating peeled was visually checked.

Examples 17 and 18

Coated substrates were produced and evaluated in the same manner as in Example 9, except that a panel for a 14

inch cathode-ray tube was used as a substrate, and that the conditions for forming coatings were changed as follows.

(1) Coating method: spinner

200 rpm, 60 sec

(2) Coating temperature: room temperature

(3) Heating conditions: 160 °C, 30 min

Results are shown in Table 5.

Table 5

	Type of Coating Solution		Appearance (visual check)	
	1st layer	2nd layer	Thickness of Film	Point Defect
Example 9	Example 1	Example 2	Even.	Not observed.
Example 10	Example 2	-	Even.	Not observed.
Example 11	Example 1	Example 5	Even.	Not observed.
Example 12	Example 3	Example 2	Even.	Not observed.
Example 13	Example 4	Example 2	Even.	Not observed.
Example 14	Example 5	-	Even.	Not observed.
Example 15	Example 4	Example 5	Even.	Not observed.
Example 16	Example 12	*	Even.	Not observed.
Example 17	Example 6	-	Even.	Not observed.
Example 18	Example 7	-	Even.	Not observed.
Comparative Example 2	Comparative Example 1	-	Uneven.	Observed.

* Coating solution for formation of a protective coating, composed of a dilution of 100 g of Matrix M1 in 900 g of ethanol.

Table 5 (continued)

	Haze (%)	Reflectance (550 nm) (%)	Surface Resistivity (Ω/□)	Film Strength	Boiling Resistance
Example 9	0.1	-	2×10^7	No peeling.	No peeling.
Example 10	0.8	0.8	-	No peeling.	No peeling.
Example 11	0.6	0.4	4×10^7	No peeling.	No peeling.
Example 12	0.8	0.2	1×10^7	No peeling.	No peeling.
Example 13	0.7	0.2	5×10^6	No peeling.	No peeling.
Example 14	0.0	1.3	-	No peeling.	No peeling.
Example 15	0.0	0.6	7×10^6	No peeling.	No peeling.
Example 16	0.1	0.2	5×10^8	No peeling.	No peeling.
Example 17	0.2	0.9	-	No peeling.	No peeling.
Example 18	0.9	0.4	-	No peeling.	No peeling.
Comparative Example 2	2.5	0.5	-	Peeled.	Peeled.

Examples 19 to 26 and Comparative Examples 3 and 4

D. Preparation of Matrix Solutions M6 to M12

Ethyl silicate 28 (concentration of SiO_2: 28 % by weight) or ethyl silicate 40 (concentration of SiO_2: 40 % by weight) was added to a solvent composed of an organic solvent, pure water and an acid, and hydrolyzed under the conditions as indicated in Table 6, thereby obtaining a matrix. Thus, matrix solutions M6 to M12 were prepared. Deionization was conducted in the same manner as in the preparation of matrix solutions M1 to M5.

E. Preparation of Conductive Antimony-Doped Tin Oxide Sols F9 to F13

(1) Conductive antimony-doped tin oxide sol F9 is the same as the above-mentioned conductive antimony-doped tin oxide sol F1, which were prepared in the same manner as described above and had the average particle size and particle size distribution indicated in Table 7.

(2) Conductive antimony-doped tin oxide sol F10 was obtained in the same manner as in item (1) above, except that the pH at the formation of the tin oxide hydrate was adjusted to 8.5.

(3) Conductive antimony-doped tin oxide sol F11 was obtained by a process comprising ultrafiltering of the dispersion of tin oxide hydrate obtained in the same manner as in item (2) above, washing, addition of 300 g of a 5 % by weight aqueous H_2O_2 solution, heating at 100 °C for 30

min, transfer to an autoclave and heating at 300 °C for 2 hr.

(4) Conductive antimony-doped tin oxide sol F12 was obtained in the same manner as in item (1) above, except that there was conducted the milling in the sand mill for 3 hr, and followed by centrifuging (5000 rpm, 1hr).

(5) Conductive antimony-doped tin oxide sol F13 was obtained in the same manner as in item (1) above, except that the aqueous solution of KOH at the milling in the sand mill contained 10 g of KOH.

F. Production of Coating Solution for Formation of Transparent Conductive Coating

The above matrix solutions M6 to M12, the above conductive antimony-doped tin oxide sols F9 to F13 and diluents each composed of an organic solvent and/or pure water were mixed together, followed by addition of an acid to adjust pH, thereby obtain coating solutions for formation of transparent conductive coatings as indicated in Table 8.

Table 6

Type of Matrix	Alkoxysilane (g)		Organic Solvent (g)		Pure Water (g)	Acid (g)	
M6	Ethyl silicate -28	100	Ethanol	782.9	50.4	61% HNO_3	0.14
M7	Ethyl silicate -40	100	Ethanol	604.0	96.0	35% HCl	0.50
M8	Ethyl silicate -28	100	Isopropanol	53.0	33.6	35% HCl	0.50
M9	Ethyl silicate -40	100	Ethanol	604.0	96.0	61% HNO_3	0.02
M10	Ethyl silicate -40	100	Ethanol Methanol n-Butanol	31 18 18	96.0	61% HNO_3	4.0
M11 (Comp.)	Ethyl silicate -40	100	Ethanol	508.0	192.0	61% HNO_3	0.01
M12 (Comp.)	Ethyl silicate -40	100	Ethanol	648.0	48.0	61% HNO_3	0.06

Comp.: Comparative Example

Table 6 (continued)

Reaction Conditions		Average Molecular Weight	Molecular Weight			Ion Concentration (mmol/100 g)
Temp. (°C)	Time (Hr)		1000 or less (%)	3000 or less (%)	10000 or greater (%)	
120	1	2800	5	50	5	0.1
100	0.5	2300	10	40	0	0.4
40	48	4200	≦1	20	10	0.3
100	0.5	7500	≦1	10	10	1.2
25	45 min	1600	0	50	0	0.8
100	0.5	12000	≦1	10	30	0.5
100	0.5	900	70	90	0	2.9

Table 7

Sol No.	Average Particle Size (Å)	Particle Size Distribution (%)			Concentration of Solid Contents (% by weight)	Ion Concentration
		100 Å or less	600 Å or less	1000 Å or greater		
F9	100	80	80	0	20	1.1
F10	400	10	60	10	20	2.5
F11	200	40	90	0	20	0.9
F12	300	5	100	0	20	2.0
F13 (Comp.)	900	2	10	30	20	31.0

Comp.: Comparative Example

Table 8

(Coating Solution for Formation of Transparent Conductive Coating)

	Conductive Sol (g)		Matrix (g)		Diluent (g)		pH	Concentration of Solid Contents (% by weight)	Other Additive	Ion Concentration
Ex. 19	F10	30	M6	120	Ethanol	170	3.0	3.0		1.6
Ex. 20	F9	30	M7	67	Water Ethanol	33 337	2.5	2.0		0.9
Ex. 21	F11	30	M8	10	Isopropanol Ethanol	30 30	2.0	7.5		0.8
Ex. 22	F11	30	M7	60	DAA Ethanol	45 315	3.0	2.0	Dye *	5.2
Ex. 23	F11	30	M7	40	DAA Ethanol	45 325	3.0	2.5	**	1.8
Ex. 24	F9	30	M6	67	Water Ethanol	107 107	3.0	2.5		1.2
Ex. 25	F12	30	M9	60	Ethanol	360	2.0	2.0		2.5
Ex. 26	F9	30	M10	32	n-Butanol Methanol	149 149	1.5	1.5		1.7
Comp. Ex. 3	F11	30	M11	80	Water Ethanol	60 163	3.0	3.0		1.1
Comp. Ex. 4	F13	30	M7	60	DAA Ethanol	45 405	3.0	3.0		22.3
Comp. Ex. 5	F9	30	M12	60	Ethanol	360	2.0	2.0		2.6

DAA: Diacetone alcohol

* : (Rhodamine 6G) (0.06% by weight)

** : Dibutoxybis(acetylacetonato)zirconium (10 g)

Examples 27 to 34 and Comparative Examples 6 to 8

Production of Transparent Conductive Coated Display Panel

Each of the coating solutions obtained in Examples 19 to 26 and Comparative Examples 3 to 5 as indicated in Table 8 was applied to a display panel (14 inch) for a cathode-ray tube, either preheated to a predetermined temperature or not, under the conditions indicated in Table 9, thereby obtaining transparent conductive coated display panels.

The coating conditions and conditions for treatment for expediting curing were as follows.

Spraying: sprayer manufactured by Spraying System Co.
1A nozzle, air pressure of 1.5 kg/cm^2,
feeding rate of 20 ml/min, feeding for 1 min

Spinner: 100 rpm, 30 sec

Ultraviolet radiation: mercury lamp, 500 mW/cm^2
6000 mj

Treatment with ammonia: 5 min in 10,000 ppm NH_3 vapor atmosphere

Evaluation of Transparent Conductive Coated Display Panel

The following evaluations were made with respect to the thus obtained transparent conductive coated display panels. Results are shown in Table 10.

Haze: measured in the same manner as in Examples 9 to 18.

Table 9

(Transparent Conductive Coated Display Panel)

	Coating Solution	Conductive Coating			Protective Coating				Treatment for Expediting Curing
		Pre-heating Temperature	Coating Method	(Drying) Heating Conditions	Coating solution	Pre-heating Temperature	Coating Method	Heating Conditions	
Ex. 27	Ex. 19	60°C	Spray	180°C/30min	-	-	-	-	-
Ex. 28	Ex. 20	60°C	Spray	(90°C/1min)	Matrix M6	60°C	Spray	180°C/30min	-
Ex. 29	Ex. 21	Room temp.	Spinner	(90°C/1min)	Matrix M6	Room temp.	Spinner	250°C/30min	-
Ex. 30	Ex. 22	40°C	Spinner	(90°C/1min) 180°C/30min	-	-	-	-	-
Ex. 31	Ex. 23	40°C	Spinner	(90°C/1min)	Matrix M6	60°C	Spray	150°C/30min	*
Ex. 32	Ex. 24	40°C	Spray	(90°C/1min) 180°C/30min	-	-	-	-	-
Ex. 33	Ex. 25	Room temp.	Spinner	(90°C/1min) 160°C/30min	-	-	-	-	**
Ex. 34	Ex. 26	60°C	Spray	180°C/30min	-	-	-	-	-
Comp. Ex. 6	Comp. Ex. 3	60°C	Spray	180°C/30min	-	-	-	-	-
Comp. Ex. 7	Comp. Ex. 4	40°C	Spinner	180°C/30min	-	-	-	-	-
Comp. Ex. 8	Comp. Ex. 5	Room temp.	Spinner	(90°C/1min) 180°C/30min	-	-	-	-	-

* : UV treatment after drying and after application of a protective solution

** : Treatment with NH_3 vapor after drying

Table 10

	Glossiness G (%)	Haze H (%)	Surface Resistivity Rs Ω/□	Film Strength		Boiling Resistance				Stain Resistance	Resolving Power (bars/cm)
						30 min		60 min			
				ΔG	Rm/Rs	ΔG	Rm/Rs	ΔG	Rm/Rs		
Ex. 27	58	7.9	5×10^9	7.8	1.5	-0.9	0.9	-1.5	1.2	2H	65
Ex. 28	50	6.3	5×10^8	3.1	0.9	-1.0	1.0	-2.0	1.1	9H	75
Ex. 29	89	0.0	1×10^6	0.0	1.1	0.0	1.0	0.0	1.0	9H	85
Ex. 30	96	0.2	7×10^7	4.7	2.1	-1.1	0.8	-2.5	0.6	7H	80
Ex. 31	78	0.0	1×10^8	1.2	1.1	0.0	1.1	-0.3	1.1	9H	80
Ex. 32	92	0.8	8×10^8	3.3	2.8	-1.8	1.5	-4.0	2.5	2H	80
Ex. 33	96	0.5	2×10^7	1.8	0.9	-0.1	1.0	-1.3	1.0	4H	80
Ex. 34	59	8.0	2×10^9	8.0	1.3	-2.0	0.9	-4.0	0.8	2H	65
Comp. Ex. 6	54	10.5	3×10^9	13.4	3.0	-6.6	2.3	-45.0	1000	B	50
Comp. Ex. 7	89	1.8	2×10^8	35.2	25.8	-20.6	5.0	Peeled.		2H	80
Comp. Ex. 8	92	0.3	5×10^{11}	4.9	1.5	-1.5	3.0	4.0	4.1	3H	85

Glossiness: measured in accordance with Japanese Industrial Standard K7105-81 (measuring angle: 60 °)

Surface Resistivity: measured in the same manner as in Examples 9 to 18.

Film Strength: An office eraser (equivalent to No. 50-50 produced by LION) was placed on the coating, and given 200 reciprocating slidings under a load of 1 kg. A difference between glossiness before slidings and that after slidings (ΔG) and a ratio of surface resistivity before slidings (Rs) and that after slidings (Rm) were determined.

Boiling Resistance: Glossiness and surface resistivity of the coated panel after immersion in boiling water for 30 or 60 min were compared with those before the immersion.

Stain Resistance: A line was drawn on the coating by a pencil having a pencil hardness of between 6B and 9H under a load of 1 kg. The line trace was lightly wiped with a gauge soaked with ethanol. 10 Wipings were made, and the pencil hardness with which the trace was still viewable upon the 10 wipings was determined as an

indication of the stain resistance.

Resolving Power: evaluated by the method described hereinbefore.

As apparent from Table 10, the transparent conductive coatings formed from the coating solutions of the present invention exhibit little or only a slight change in glossiness and surface resistivity when subjected to film strength and boiling resistance tests. Further, they are also excellent in stain resistance. On the other hand, the display panel provided with the coating formed from the coating solution of Comparative Example 3 in which a matrix having a small average molecular weight was employed, had a surface resistivity as high as 5×10^{11} $\Omega/\square$. The reason would be formation of an insulating layer around at least part of conductive particles due to the phenomenon of coupling of low molecular weight components of the matrix, on the surface of the conductive particles. However, in the present invention, such phenomenon does not occur, so that a coating exhibiting stable surface resistivity can be obtained.

What is claimed is:

1. A coating solution for formation of a coating, comprising a particulate inorganic compound and at least one matrix selected from the group consisting of a partial hydrolysate of an acetylacetonato chelate, a partial hydrolysate of an alkoxysilane and a partial hydrolysate of a metal alkoxide, in the form of a dispersion or solution in water and/or an organic solvent,

wherein the coating solution has an ion concentration of 10 mmol or less per 100 g of all solid contents contained in the coating solution.

2. The coating solution as claimed in claim 1, wherein the particulate inorganic compound is in the form of conductive particles:

(a) having an average particle size of 50 nm or less,

(b) comprising particles each having a particle size of 60 nm or less in an amount of 60 % by weight or greater,

(c) comprising particles each having a particle size of 10 nm or less in an amount of 5 % by weight or greater, and

(d) comprising particles each having a particle size of 100 nm or greater in an amount of 15 % by weight or less, and

the matrix is the partial hydrolysate of an alkoxysilane:

(1) having an average molecular weight of 1,500 to

10,000,

(2) comprising a polymer having a molecular weight of 3,000 or less in an amount of 50 % by weight or less, and

(3) comprising a polymer having a molecular weight of 10,000 or greater in an amount of 20 % by weight or less.

3. A process for producing the coating solution for formation of a coating as claimed in claim 1 or 2, which comprises subjecting the dispersion of the particulate inorganic compound, the solution of the matrix or the coating solution prepared by mixing thereof to treatment for removing cations and/or anions so that the ion concentration of the obtained coating solution is 10 mmol or less per 100 g of all solid contents contained in the coating solution.

4. A coated substrate comprising a substrate and, a coating formed thereon from the coating solution as claimed in claim 1 or 2.

5. A process for producing a coated substrate, comprising coating the coating solution as claimed in claim 1 or 2 on a surface of a substrate to form an uncured coating and heating the uncured coating formed from the surface of the substrate to form the coated substrate, wherein the coating in the state of being uncured is irradiated with an electromagnetic wave having a wavelength smaller than that of visible light.

6. A process for producing a coated substrate, comprising coating the coating solution as claimed in claim 1 or 2 on a surface of a substrate to form an uncured coating and heating the uncured coating formed on the surface of the substrate to form the coated substrate, wherein the coating in the state of being uncured is exposed to a gas atmosphere capable of expediting curing reaction.

7. A display unit comprising a display panel having on its outer surface a transparent conductive coating formed from the coating solution as claimed in claim 1 or 2.

8. The display unit as claimed in claim 7, comprising a display panel having a transparent protective coating formed on the surface of the transparent conductive coating.

9. The display unit as claimed in claim 7 or 8, wherein the display panel comprising the transparent conductive coating has a surface resistivity of 10^3 to 10^{10} $\Omega/\square$, a haze of 1 % or less and a resolving power of 70 bars/cm or higher.

10. The display unit as claimed in claim 7 or 8, wherein the display panel comprising the transparent conductive coating has a surface resistivity of 10^3 to 10^{10} $\Omega/\square$, a glossiness of 40 to 90 % and a resolving power of 60 bars/cm or higher.

11. The display unit as claimed in claim 8, wherein the display panel comprising the transparent conductive coating and the transparent protective coating has a surface resistivity of 10^3 to 10^{10} Ω/□, a glossiness of 40 to 90%, a surface reflectance of 1% or less and a resolving power of 60 bars/cm or higher.

12. A coating solution as herein described.

13. A coating solution as herein described with particular reference to any one of the Examples.

14. A process for preparing a coating solution as herein described.

15. A process for preparing a coating solution as herein described with particular reference to any one of the Examples.

16. A coated substrate as herein described.

17. A coated substrate as herein described with particular reference to any one of the Examples.

18. A process for producing a coated substrate as herein described.

19. A process for producing a coated substrate as herein described with particular reference to any one of the Examples.

20. A display unit as herein described.

21. A display unit as herein described with particular reference to any one of the Examples.

* C L M S *

22. A coating solution as claimed in claim 1 or claim 2 when prepared by a process as claimed in claim 3.

23. A coated substrate as claimed in claim 4 when prepared by a process as claimed in claim 5 or claim 6.