



(86) Date de dépôt PCT/PCT Filing Date: 2007/09/26
(87) Date publication PCT/PCT Publication Date: 2008/04/17
(45) Date de délivrance/Issue Date: 2014/01/28
(85) Entrée phase nationale/National Entry: 2009/03/31
(86) N° demande PCT/PCT Application No.: JP 2007/068678
(87) N° publication PCT/PCT Publication No.: 2008/044469
(30) Priorité/Priority: 2006/10/06 (JP2006-275654)

(51) Cl.Int./Int.Cl. *C01G 9/02* (2006.01),
B32B 17/10 (2006.01), *C08K 3/22* (2006.01),
C08L 101/00 (2006.01), *C09D 7/12* (2006.01)

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(54) Titre : PARTICULES ULTRAFINES D'OXYDE DE ZINC ET PROCEDE DE PRODUCTION DE CELLE-CI
(54) Title: ULTRA-FINE ZINC OXIDE PARTICLE AND METHOD FOR PRODUCTION THEREOF

(57) **Abrégé/Abstract:**

The object of the present invention is to provide an ultrafine zinc oxide having a sufficient visible light transmittance in addition to an infrared ray shielding ability and conductivity, and also to provide a production method thereof. The ultrafine zinc oxide contains an element having a valence number of 3 or more, bears a metal compound on the surface, and has an average primary particle diameter of 0.1 μm or smaller.



ABSTRACT

The object of the present invention is to provide an ultrafine zinc oxide having a sufficient visible light transmittance in addition to an infrared ray shielding ability and conductivity, and also to provide a production method thereof. The ultrafine zinc oxide contains an element having a valence number of 3 or more, bears a metal compound on the surface, and has an average primary particle diameter of 0.1 μm or smaller.

DESCRIPTION

ULTRA-FINE ZINC OXIDE PARTICLE AND METHOD FOR PRODUCING THEREOF

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TECHNICAL FIELD

The present invention relates to an ultrafine zinc oxide and a method for producing the same.

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BACKGROUND ART

Recently, environmental issues have increasingly drawn attention. Especially, in order to prevent global warming, energy saving, for example, by reducing electric consumption in air conditioning, has been studied. As one of positive methods to promote the energy saving, shielding of heat ray in sunlight has been studied to suppress the temperature increase in a space such as a house or a vehicular interior.

About 50% of total energy of sunlight is the energy from infrared rays. The energy of infrared ray itself is as low as one tenth of that of ultraviolet ray. However, infrared rays bring high thermal effect in the entire sunlight energy. Therefore, shielding infrared ray is required to accomplish the above-mentioned purpose. Particularly, windows of building, vehicular windows, telephone boxes, and the like are required to shield infrared rays coming in the inside spaces through transparent materials such as glass. To shield infrared rays, it is necessary either to absorb and thermally diffuse infrared ray or to reflect infrared ray.

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However, if shielding material for infrared ray simultaneously shields even visible light, interior spaces may become dark and visibility in the spaces may be deteriorated. Therefore, a material for shielding infrared ray should be transparent to visible light. For such a reason, a material which can transmits visible light but reflects or absorbs

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infrared rays has been demanded. Additionally, such a material is desirably a particle-dispersion type material since it is widely applicable for various purposes and is advantageous in view of the production equipment and cost.

5 On another hand, demands for a conductive metal oxide material having conductivity have been increased in recent years. The material may be further required to have transparent to visible light depending on its the uses. Thus, a material which transmits visible light but reflects or absorbs infrared
10 rays has been demanded. The conductive metal oxide material shields infrared ray. Thus, if the material having a transparent characteristic to visible light is produced, the material satisfies both demands for infrared shielding and for visible-light transmitting.

15 Previously proposed heat ray shielding materials and conductive materials include metal-evaporated films, organic additives, or inorganic (semi)conductors. However, the metal-evaporated films has drawbacks such as less transparency of visible light, poor durability, and high cost of apparatuses
20 for producing the film (See Patent Documents 1 to 5). Organic additives have also a drawback in low weather resistance. Further, the organic additives takes advantage of absorption attributed to vibration movement of molecules for shielding infrared ray. Thus, heat radiation as heat energy is caused
25 again after the absorption (See Patent documents 6 and 7). Further, carbonate salts of various kinds of metals are also employed based on utilization of the heat ray absorption by thermal stretching and vibration of carbonyl groups. However, the carbonate salts also have an essential drawback of the
30 narrow absorption wavelength range.

 As inorganic (semi)conductive materials, tin-doped indium oxide (ITO) and antimony-doped tin oxide (ATO) have been mainly studied in these years. Particularly, ITO is a promising material as a transparent heat ray shielding material, and has
35 actually been utilized. Until now, a number of studies on ITO

as a transparent conductive film have been actively made. As a result, ITO has been utilized in various fields of electronic materials such as FPD (Flat Panel Display) materials and touch panel materials. It has been known that ITO has optical characteristics such as infrared ray shielding ability together with such electric characteristics. The optical characteristics are regarded as byproducts of the electric characteristics and vice versa. When ITO has electric conductivity, it simultaneously has the heat ray shielding property. However, since indium is expensive, a substitute material has been demanded. With respect to ATO, the toxicity of antimony may cause a problem.

On another hand, methods of shielding near infrared ray by resin coatings containing metal-doped zinc oxide, ITO, or ATO have also been studied (See Patent documents 8 to 11). Such methods are advantageous in that inexpensive materials are applicable and treatment is simple. Zinc oxide also has absorbability to ultraviolet ray and accordingly has an advantage that it can absorb both ultraviolet and infrared rays. However, visible light transparency is required for applying to a transparent substrate such as windows of buildings, vehicular windows, telephone boxes, and the like. To establish transparency of zinc oxide particles, zinc oxide particles should be an ultrafine zinc oxide with an average primary particle diameter of about 0.1 μm or smaller. However, zinc oxide particles generally have large particles, because such zinc oxide particles aggregate in a higher-temperature sintering process. Higher-temperature sintering process is necessary to produce zinc oxide particles having high carrier concentration and high crystallinity for performing excellent heat shielding ability and conductivity (See Non-patent document 1). To solve the problem, metal fine particles with improved dispersibility have been studied (see Patent documents 12 and 13). However, it is very difficult to satisfy all characteristics of an average primary particle diameter fine

enough to establish transparency, sufficient infrared ray shielding ability and sufficient conductivity. Moreover, zinc oxide is intrinsically inferior in environmental durability. Therefore, zinc oxide has not yet been practically used for
5 infrared ray shielding.

- Patent document 1: JP-A-57-59748
Patent document 2: JP-A-57-59749
Patent document 3: JP-B-03-72011
10 Patent document 4: JP-B-04-929
Patent document 5: JP-B-05-6766
Patent document 6: JP-A-04-160037
Patent document 7: JP-A-05-126650
Patent document 8: JP-A-07-291680
15 Patent document 9: JP-A-10-310759
Patent document 10: JP-A-08-281860
Patent document 11: JP-A-2000-186237
Patent document 12: JP-A-2004-124033
Patent document 13: JP-A-05-319808
20 Non-Patent document 1: Shangfeng Du, "Calcination Effects on the Properties of Gallium-Doped Zinc Oxide Powders", J. Am. Ceram. Soc., 89[8]2440-2443 (2006)

DISCLOSURE OF THE INVENTION

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PROBLEMS TO BE SOLVED BY THE INVENTION

In view of the above state of the art, it is an object of the present invention to provide an ultrafine zinc oxide having sufficient infrared ray shielding ability and
30 conductivity, and further having sufficient visible light transparency, and a method for producing such an ultrafine zinc oxide.

MEANS FOR SOLVING THE PROBLEM

35 One aspect of the present invention provides an ultrafine

zinc oxide, comprising an element having a valence number of 3 or more, the zinc oxide bearing a metal compound on the surface thereof, and having an average primary particle diameter of 0.1 μm or smaller.

5 The element having a valence number of 3 or more is preferably at least one element selected from the group consisting of Sc, Y, In, Ga, Al, Ti, B, and lanthanides.

 The metal compound is preferably a compound of at least one element selected from the group consisting of Si, Zr, Sn,
10 Mg, Hf, Ge, Mo, W, V, Nb, Ta, Ca, Sr, and Ba.

 It is preferable that the amount of the element having a valence number of 3 or more is within the range of 0.001 to 0.2 mol per mole of zinc oxide.

 It is preferable that the amount of the metal oxide is
15 within the range of 0.5 to 20 mass% of surface-treated zinc oxide.

 Another aspect of the present invention provides a method for producing the above-mentioned ultrafine zinc oxide, comprising:

20 - coating the surface of zinc oxide containing an element having a valence number of 3 or more or a precursor compound to be converted into zinc oxide containing an element having a valence number of 3 or more by firing with a sintering-preventing component; and

25 - firing the zinc oxide or the precursor compound at 600 to 850°C.

 In the above, the sintering-preventing component is preferably silica.

 In the above method, it is preferable that the amount of
30 the element having a valence number of 3 or more is within the range of 0.001 to 0.2 mol per mol of zinc oxide. It is also preferable that the amount of silica is within the range of 0.5 to 20 mass% as the mass proportion of SiO_2 in a surface-treated zinc oxide.

35 Still another aspect of the present invention provides

coating composition containing the above-mentioned ultrafine zinc oxide.

Further still another aspect of the present invention provides a thermoplastic resin composition containing the above-mentioned ultrafine zinc oxide.

Further still another aspect of the present invention provides an ink composition containing the above-mentioned ultrafine zinc oxide.

Further still another aspect of the present invention provides a laminated article comprising a glass substrate layer and an infrared ray shielding layer, wherein the infrared ray shielding layer comprising the above-mentioned ultrafine zinc oxide and a binder resin.

Further still another aspect of the present invention provides a ultrafine zinc oxide, comprising an element having a valence number of 3 or more, the zinc oxide bearing a Si compound on the surface thereof, and having an average primary particle diameter of 0.1 μm or smaller, wherein the element having a valence number of 3 or more is Ga, wherein the amount of Ga is within the range of 0.001 to 0.2 mol per mol of zinc oxide, and the amount of the Si compound is within the range of 0.5 to 20 mass% of surface-treated zinc oxide to zinc oxide subjected to coating treatment.

The present invention will be described below in detail.

The present invention provides an ultrafine zinc oxide, comprising an element having a valence number of 3 or more. The zinc oxide bears a metal compound on its surface, and has an average primary particle diameter of 0.1 μm or smaller. The ultrafine zinc oxide has excellent infrared ray shielding property and conductivity because of the presence of an element having a valence number of 3 or more. The ultrafine zinc oxide also has sufficient transparency because of its

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visible light transparency. The sufficient visible light transparency in addition to the infrared ray shielding ability and conductivity of the ultrafine zinc oxide has not been known at the time of completion of the present invention and have newly found by the inventors of the present invention.

The element having a valence number of 3 or more is not particularly limited and may be any of elements having a valence number of 3 or more with the infrared ray shielding ability and conductivity. Preferable element is, however, at least one of the elements selected from the group consisting of Sc, Y, In, Ga, Al, Ti, B, and lanthanides. More preferable elements are elements belonging to Group XIII in the periodic table, and

still more preferable elements are In, Ga, and Al.

In the present invention, the amount of the element having a valence number of 3 or more is preferably within the range of 0.001 to 0.2 mol per mol of zinc oxide. The amount is more preferably 0.01 to 0.1 mol and particularly preferably 0.02 to 0.1 mol per mol of zinc oxide. If the amount is lower than 0.001 mol, the infrared ray shielding property may become insufficient and therefore it is not preferable. On the contrary, if it exceeds 0.2 mol, the effect may become saturated, which results in economical disadvantage, and thus, it is not preferable. Furthermore, surplus elements are not sufficiently diffused in zinc oxide crystal and are deposited on grain boundaries in the form of compounds. As a result, the deposited elements scatter visible light and the infrared ray shielding property and conductivity may undesirably be lowered.

The metal compound is derived from a sintering-preventing component, which will be described later. It is preferably a compound of at least one element selected from the group consisting of Si, Zr, Sn, Mg, Hf, Ge, Mo, W, V, Nb, Ta, Ca, Sr, and Ba and more preferably a compound of Si, Zr, Sn, Mg, or Hf and even more preferably a compound of Si or Sn. The metal compound is coated on the ultrafine zinc oxide of the present invention in the form of an oxide, hydroxide, carbonate, or sulfate of the above-mentioned metal elements.

The amount of the metal compound is preferably within the range of 0.5 to 20 mass% of the coated zinc oxide, as the amount of oxides. It is more preferably 0.5 to 15 mass%, still more preferably 1 to 10 mass%, and particularly preferably 1 to 5 mass%. If the amount of the above-mentioned metal compound is less than 0.5 mass%, the sintering preventing may become insufficient. In addition, the particles may become coarse, which leads to deterioration of transparency. Thus, it is not preferable. If it exceeds 20 mass%, the proportion of zinc oxide is relatively decreased to result in decrease of the heat ray shielding ability. Furthermore, the conductivity may be

decreased because of insulation by the excess sintering-preventing component. Thus, it is not preferable, either.

The average primary particle diameter of the ultrafine zinc oxide of the present invention is preferably 0.1 μm or smaller. The ultrafine zinc oxide having average primary particle diameter within such a range can suppress scattering of the visible light and is excellent in transparency. In this invention, the average primary particle diameter can be calculated from the relation for determining of BET specific surface area. Assuming that the particle shape is spherical, the average primary particle diameter of the sphere can be calculated from the relation:

$$\begin{aligned} & (\text{BET specific surface area}) \\ 15 \quad & = (\text{The spherical surface area of the sphere}) / \\ & [(\text{The volume of the sphere}) \times (\text{Specific gravity of the material})]. \end{aligned}$$

The average primary particle diameter is more preferably 0.07 μm or smaller.

20 The BET specific surface area of the ultrafine zinc oxide of the present invention is preferably 10 to 100 m^2/g . If the BET specific surface area exceeds 100 m^2/g , cohesion between the ultrafine zinc oxides becomes so strong that separating treatment of the coagulated particles, which requires much energy and time, may be needed. Furthermore, property deterioration may be progressed with the lapse of time. On the contrary, if it is less than 10 m^2/g , highly transparent product may not be obtained. The BET specific surface area is more preferably 10 to 70 m^2/g .

30 The optical transmittance of 550-nm light through the ultrafine zinc oxide of the present invention is preferably 75% or higher and more preferably 80% or higher for the purpose for establishing excellent visible light transparency. The optical transmittance of 1900-nm light through the ultrafine zinc oxide of the present invention is preferably 80% or lower

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and more preferably 70% or lower for the purpose for establishing excellent infrared ray transparency.

The volume resistivity value of the ultrafine zinc oxide of the present invention is preferably 10,000 Ωcm or lower, more preferably 2,000 Ωcm or lower, and still more preferably 1,000 Ωcm or lower for the purpose for establishing excellent conductivity.

Methods for the ultrafine zinc oxide of the present invention are not particularly limited. An example of the method will be explained in detail in the followings. The production method of the ultrafine zinc oxide described below is one aspect of the present invention, but the ultrafine zinc oxide of another aspect of the present invention is not limited to those produced by the below.

The ultrafine zinc oxide of the present invention can be produced by:

- coating the surface of zinc oxide containing an element having a valence number of 3 or more or a precursor compound to be zinc oxide containing an element having a valence number of 3 or more by firing with a sintering-preventing component on and

- firing the zinc oxide or the precursor compound at 600 to 850°C.

The method provides an ultrafine particle having the surface layer containing the sintering-preventing component which prevents the particles from aggregating by sintering. The product ultrafine particles are kept maintained as ultrafine particles even after firing at a high temperature enough to efficiently form solid solution, because of the element having a valence number of 3 or more. Consequently, the method can provides ultrafine particles having sufficient transparency, infrared ray shielding ability and conductivity.

The amount of the sintering-preventing component is preferably within the range of 0.5 to 20 mass% of surface-treated zinc oxide as the amount of oxides in the

sintering-preventing component. It is more preferably 0.5 to 15 mass%, furthermore preferably 1 to 10 mass%, and particularly preferably 1 to 5 mass%. If it is less than 0.5 mass%, prevention of sintering may be insufficient and no ultrafine particles may be produced. On the contrary, if it exceeds 20 mass%, the proportion of zinc oxide is relatively smaller and infrared ray shielding effect may be insufficient.

More specifically, the method of the present invention for producing an ultrafine zinc oxide can be performed, for example, in the following manner. The method for producing the ultrafine zinc oxide described below involves steps of (1) preparing a solid state pre-mixture of zinc oxide or a precursor compound to be converted into zinc oxide by firing and an element having a valence number of 3 or more; (2) mixing the pre-mixture of the step (1) with a sintering-preventing component; and (3) firing the mixture obtained in the step (2) at a temperature within the range of 600 to 850°C.

In the step (1), zinc oxide or a precursor compound to be converted into zinc oxide by firing is used. The precursor compound is not particularly limited and examples of the precursor compound include zinc hydroxide, zinc carbonate, basic zinc carbonate, zinc sulfate, and zinc nitrate.

In the above step (1), a solid state pre-mixture of zinc oxide or a precursor compound to be converted into zinc oxide by firing (hereinafter zinc oxide and the precursor compound are sometimes referred to as "a zinc compound or zinc compounds", collectively) with an element having a valence number of 3 or more in a solid state is prepared. The solid state pre-mixture may be prepared by:

- dry-mixing of zinc oxide or a precursor compound to be converted into zinc oxide by firing with a prescribed amount of a compound of an element having a valence number of 3 or more using a ball mill;

- a method for depositing an insoluble salt of the compound of the element having a valence number of 3 or more

evenly on the zinc oxide surface, comprising adding a prescribed amount of a water-soluble salt of the compound of an element having a valence number of 3 or more to an aqueous dispersion of zinc oxide with adjusting pH to be neutral using an acidic or alkaline agent (so-called, "simultaneous neutralization"), to deposit the insoluble salt; or

- a method for simultaneously and evenly depositing insoluble salts of zinc and the element having a valence number of 3 or more, comprising using an aqueous mixed solution of a water soluble salt of zinc and a water soluble salt of the compound of the element having a valence number of 3 or more and an acidic or alkaline agent, (so-called, "a simultaneous depositing method").

An element having a valence number of 3 or more to be used in the above step (1) is not particularly limited and may be single substances or their compounds. Examples of the compound of the element having a valence number of 3 or more include boron compounds such as boric acid, lithium borate and sodium borate; aluminum compounds such as sodium aluminate, aluminum sulfate, aluminum chloride, aluminum nitrate, and aluminum tripropoxide; gallium compounds such as gallium oxide, gallium nitrate, and gallium chloride; and indium compounds such as indium oxide and indium chloride.

Examples of the compound also include scandium compounds such as scandium acetate, scandium carbonate, scandium chloride, scandium fluoride, scandium iodide, scandium nitrate, scandium oxide, scandium trifluoromethanesulfonate, and scandium tris(dodecyl sulfate).

Examples of the compound further include yttrium compounds such as yttrium acetate, yttrium oxide, yttrium bromide, yttrium carbonate, yttrium chloride, yttrium fluoride, yttrium iodide, yttrium isopropoxide, yttrium naphthenate, yttrium naphthate, yttrium neodecanate, yttrium nitrate, yttrium 2-ethylhexanoate, hexafluoroacetylacetonate yttrium, yttrium oxalate, yttrium peroxyacid salt, yttrium sulfate,

yttrium sulfide, and yttrium
tris(2,2,6,6-tetramethyl-3,5-heptanedioate).

Examples of the compound also include titanium compounds
such as titanium tetrachloride, titanyl sulfate, titanium
5 tetraisopropoxide, and sodium titanate.

Examples of the compound also include lanthanide
compounds such as acetates, bromides, carbonates, chlorides,
fluorides, iodides, nitrates, oxalates, oxides, phosphates,
stearates, and sulfates of lanthanides.

10 In the step (2), which is to be carried out successively,
a sintering-preventing component having a sintering preventing
effect is added to the pre-mixture of a zinc compound and an
element having a valence number of 3 or more obtained in the
step (1). Addition of the sintering-preventing component as
15 a sintering-preventing agent suppresses extreme grain growth,
enables to perform firing at a high temperature, and makes it
easier to diffuse the element having a valence number of 3 or
more in the zinc oxide crystal. Accordingly, while keeping the
particle diameter small, infrared ray shielding ability and
20 conductivity are produced. That is, excellent infrared ray
shielding ability and conductivity are produced while
maintaining fine particle shape.

The sintering-preventing component is a component
capable of preventing particles from sintering therebetween at
25 the time of firing zinc oxide. The sintering-preventing
component also prevents the particle diameter from enlarging
by coagulation of the particles. The sintering-preventing
component used in the present invention has substantially no
adverse effect on the infrared ray shielding ability and
30 conductivity. Sintering temperature of the
sintering-preventing component is higher than that of zinc
oxide, and the refractive index of the sintering-preventing
component is not too high after firing. Furthermore, the
sintering-preventing component has substantially no effect on
35 the conductivity of the ultrafine zinc oxide.

The above-mentioned sintering-preventing component is not particularly limited as long as it meets the above-mentioned physical properties. The same metal compounds as the mentioned above or those which are converted into the above-mentioned metal compounds by drying or firing may be used. Examples of those having the above-mentioned physical properties specifically include compounds of at least one element selected from the group consisting of Si, Zr, Sn, Mg, Hf, Ge, Mo, W, V, Nb, Ta, Ca, Sr, and Ba, and more specifically include their halides such as chlorides, oxides, hydroxides, nitrates, carbonates, and sulfates. Two or more of these components may be used in combination. Preferred as the sintering-preventing component are Si, Zr, Sn, Mg, Hf, or their compounds because of excellent physical properties and more preferred are Si, Sn or their compounds. Addition of the sintering-preventing component simultaneously improves environmental durability of zinc oxide.

If the above-mentioned sintering-preventing component has a higher sintering temperature than zinc oxide, the component can prevent zinc oxide particles from aggregation in sintering the particles since the sintering-preventing component is hard to be sintered compared with zinc oxide when zinc oxide is fired at a sintering temperature or higher. As a result, the average particle diameter of the ultrafine zinc oxide will be kept within the above-mentioned range. The refractive index not so much high after firing leads to provide a sintering-preventing component having excellent visible light transparency without deteriorating transparency of the product ultrafine zinc oxide. In sintering process, the above-mentioned sintering-preventing component may be incorporated in the zinc oxide crystal. Even in such a case, sintering-preventing component is required to have no effect on the conductivity. From this viewpoint, the compounds of the above-mentioned elements are preferable.

Specific examples of the above-mentioned

sintering-preventing component include silica, zirconium chloride, tin chloride, magnesium nitrate, hafnium chloride, germanium chloride, molybdenum oxide, tungsten oxide, vanadium oxide, niobium oxide, tantalum oxide, calcium hydroxide, strontium carbonate, and barium sulfate.

As the sintering-preventing component to be used in the step (2), any form of the component can be applied as long as the component covers the zinc oxide surface. Examples of the sintering-preventing component include precipitates from colloids or solutions. A method for adding the sintering-preventing component to the pre-mixture is not particularly limited and may be:

- dry-mixing of a mixture of a zinc compound and an element having a valence number of 3 or more with a powdery sintering-preventing component using a ball mill;

- a method comprising simultaneously neutralizing a basic compound containing a sintering-preventing component (for example, such a basic compound may be sodium silicate, ammonium tungstate, and the like) in an aqueous dispersion of a mixture of a zinc compound and an element having a valence number of 3 or more, to deposit an oxide on the surface of the mixture, followed by drying or firing the deposition to give the sintering-preventing component; and

- a method comprising gradually adding a metal alkylate compound (e.g. alkyl silicate such as ethyl silicate) to an aqueous dispersion of a mixture of a zinc compound and an element having a valence number of 3 or more, followed by drying or firing the mixture.

A method to carry out the above-mentioned step (2) may be any of the above-mentioned methods. However, a method which produces the most excellent effect is the method comprising adding a basic compound such as sodium silicate in an aqueous dispersion of a mixture of zinc compound and an element having a valence number of 3 or more and then simultaneously neutralizing the mixture with an acid, to allow deposition over

such a sufficient time that hydrated silicon oxide in form of a dense coating on the surface of the mixture should be formed.

Next, the step (the step (3)) of firing the mixture containing the zinc compound and a compound of an element having
5 a valence number of 3 or more containing the sintering-preventing component obtained in the above-mentioned step (2) is performed. The step (3) gives the ultrafine zinc oxide of the present invention.

The firing conditions of the step (3) are not particularly
10 limited. Preferred are conditions in which the zinc compound changes to zinc oxide and the element having a valence number of 3 or more is sufficiently diffused in a substrate composed of the zinc oxide. In the above-mentioned viewpoint, the firing temperature is preferably 600 to 850°C. When the temperature
15 is 600°C or higher the crystallinity of zinc oxide can be increased and the element having a valence number of 3 or more can easily be diffused. When the temperature is 850°C or lower, the sintering preventing effect of the sintering-preventing component can affect effectively to give the ultrafine zinc
20 oxide with an average primary particle diameter of 0.1 μm or smaller. The above-mentioned firing temperature is preferably 650 to 850°C and more preferably 700 to 800°C.

To improve the semiconductive property of zinc oxide, the firing ambient atmosphere is preferably inert gas atmosphere
25 or reducing atmosphere. Reducing atmosphere is more preferable. The apparatus to be used for firing is not particularly limited as long as the apparatus can heat zinc oxide while keeping the atmosphere. Examples of the apparatus include a rotary kiln and an electric furnace.

30 The reducing atmosphere may be mixed gas atmosphere containing hydrogen and nitrogen and mixed gas atmosphere containing carbon monoxide and nitrogen. In terms of safety and cost, the mixed gas atmosphere containing hydrogen and nitrogen is preferable. In the mixed gas atmosphere containing
35 hydrogen and nitrogen, the amount of hydrogen is preferably 1%

by volume or more, and more preferably 5% by volume or more. The inert gas component may further include helium and argon in addition to nitrogen. They may be used alone or some of them may be used in combination.

5 The gas flow rate in the above-mentioned step (3) is not particularly limited and, for example, it is sufficient to add the amount equal to 1/10% by volume or more of the space volume to be heated in the apparatuses necessary for firing per minute. The addition timing of the ambient gas in the firing is
10 preferably at the beginning for firing in the reducing atmosphere, for example, in the case of the mixed gas of hydrogen and nitrogen. Alternatively, hydrogen may be added after the temperature reaches the highest temperature.

 The firing step may be conducted only once, or may be
15 repeated in a plurality of times. In the case of repeating firing steps in a plurality of times, the firing condition steps may be altered at each step. In the case where the last firing step is carried out in oxidizing atmosphere in the step (3), it is preferable to select a condition so that the properties
20 of the product ultrafine zinc oxide are not deteriorated. Grinding and classifying treatment may be optionally carried out before or after the above-mentioned step (3).

 The grinder to be used for the above grinding is not particularly limited, but includes dry type grinders such as
25 a hammer mill, a vapor phase energy fluid mill, an edge runner, and a pin mill, and wet type grinders such as an aqua mill, a sand mill, and a colloid mill.

 Inorganic or organic surface treatment may be optionally carried out for the ultrafine zinc oxide obtained in the step
30 (3). The way of surface treatment is not particularly limited and may be a surface treatment with hydrated aluminum oxide to improve the coating suitability; a silane coupling treatment for improving the dispersibility to a thermoplastic resin; and the like. These surface treatment agents and surface treatment
35 methods may be properly selected in a conventional manner.

The ultrafine zinc oxide of the present invention is remarkably excellent in transparency and may be preferably added as an excellent transparent and heat ray shielding agent having an absorption band in a wavelength range longer than 1500 nm, as a transparent conductive material with a volume resistivity of 1000 Ωcm or lower for coating compositions, thermoplastic resin compositions, and ink compositions. The ultrafine zinc oxide is also an excellent in both ultraviolet ray shielding ability and heat ray shielding ability since the ultrafine zinc oxide has ultraviolet absorbability derived from an intrinsic characteristic of zinc oxide. A coating composition, a thermoplastic resin composition, and an ink composition containing the zinc oxide are also other aspects of the present invention.

The coating composition of the present invention can provide a glass substrate with excellent heat ray shielding ability and conductivity by applying the composition to the substrate. The thermoplastic resin composition of the present invention can provide excellent heat ray shielding ability to a glass substrate by forming a film in a conventionally known film-forming method such as extrusion molding and then laminating the film on the glass substrate by a conventionally known laminating method. A glass substrate layer produced in this manner and a laminate comprising an infrared ray shielding or conductive layer containing the ultrafine zinc oxide as a heat ray shielding agent or a conductive material and a binder resin are also other aspects of the present invention.

The ultrafine zinc oxide of the present invention can be used as a transparent antistatic film and a transparent coating composition for imparting electric antistatic characteristics taking advantage of its excellent conductivity. For example, the ultrafine zinc oxide can be used preferably as an antistatic material for applying the ultrafine zinc oxide or laminating a film containing the ultrafine zinc oxide on the surface of screens of liquid crystal and plasma displays for which high

visible light transmittance and dust-proof property are required. Further, it can be suitably used to apply to wrapping materials of electronic materials, or used as wrapping materials in form of films, which are considerably affected by static electricity. Alternatively, it can be used preferably for preventing the static electricity of insulating substances from charging. Such insulating substances include topcoats on coating faces for which static charge has to be prevented while the design property of the materials is maintained and plastics.

EFFECT OF THE INVENTION

The ultrafine zinc oxide of the present invention can shield infrared ray with wavelength of 1500 nm or longer and has a volume resistivity value of 1000 Ωcm or lower and transparency. Such ultrafine zinc oxide can be used preferably for a resin composition, glass composition and the like. Further, the method for producing the ultrafine zinc oxide of the present invention is a method capable of preferably producing the above-mentioned ultrafine zinc oxide.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a light transmitting spectrum obtained in Evaluation Example B-1.

Fig. 2 is a scanning electron microscopic photograph of Example B-5 obtained in Evaluation Example B-3. In this photograph, particles have a fine shape.

Fig. 3 is a scanning electron microscopic photograph of Comparative Example 3 obtained in Evaluation Example B-3. In this photograph, particles are coarsened.

Fig. 4 is a schematic drawing of an apparatus employed in Evaluation Example B-4.

Fig. 5 is the results of temperature measurement with lapse of time in Evaluation Example B-4.

Explanation of Symbols

1. Incandescent lamp
2. Films to be evaluated
3. Thermocouple

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BEST MODE FOR CARRYING OUT THE INVENTION

Hereinafter, the present invention will be described more in detail referring to the following non-limiting Examples.

10

(Example A-1)

An aqueous zinc chloride solution was prepared by completely dissolving 100 g of zinc oxide (Grade 1 zinc oxide, Sakai Chemical Industry Co., Ltd., Sakai, Japan) in an aqueous hydrochloric acid solution containing 250 g of 35-mass% hydrochloric acid (Extra pure grade) and 350 g of purified water. To the prepared aqueous zinc chloride solution, 14.7 g of gallium nitrate octahydrate was added, and mixed the mixture until gallium nitrate octahydrate was completely dissolved to form a transparent solution. Separately, prepare an aqueous ammonium bicarbonate solution was prepared by dissolving 230 g of ammonium bicarbonate (Extra pure grade) in 1500 g of purified water. The above-mentioned aqueous zinc chloride solution in which gallium nitrate was dissolved was added to the aqueous ammonium bicarbonate solution over 120 minutes to produce precipitate. Next, 150 ml of an aqueous solution containing 23.5 g (corresponding to 5 g as SiO_2) of sodium metasilicate nonahydrate (Extra pure grade), and 10-mass% sulfuric acid were simultaneously added while the flow rates were adjusted so as to keep pH within the range of 7 to 9 over 90 minutes. Then, the obtained precipitate was sufficiently washed, separated from the liquid phase, and dried at 130°C over 5 hours. Next, the dried powder was pulverized by an agate mortar to give a precursor to be fired. The precursor to be fired was put in an alumina boat and heated to 700°C at the

heating rate of 200°C/hour using a tubular furnace while a mixed gas of 0.21 L/minute of nitrogen gas and 0.09 L/minute of hydrogen gas was circulated. After being kept as it was for 2 hours, the substance was cooled to room temperature to give
5 ultrafine zinc oxide A-A. The average primary particle diameter of the ultrafine zinc oxide A-A was 0.025 µm.

(Example A-2)

Ultrafine zinc oxide A-B was obtained in the same manner
10 as Example A-1, except that the amount of sodium metasilicate nonahydrate (Extra pure grade) was set to be 4.7 g (corresponding to 1 g as SiO₂). The average primary particle diameter of the ultrafine zinc oxide A-B was 0.034 µm.

15 (Example A-3)

Ultrafine zinc oxide A-C was obtained in the same manner as Example A-1, except that the amount of sodium metasilicate nonahydrate (Extra pure grade) was set to be 47.0 g (corresponding to 10 g as SiO₂). The average primary particle
20 diameter of the ultrafine zinc oxide A-C was 0.018 µm.

(Example A-4)

Ultrafine zinc oxide A-D was obtained in the same manner as Example A-1, except that 14.7 g of gallium nitrate
25 octahydrate was replaced with 14.8 g of aluminum chloride hexahydrate. The average primary particle diameter of the ultrafine zinc oxide A-D was 0.030 µm.

(Example A-5)

30 Ultrafine zinc oxide A-E was obtained in the same manner as Example A-1, except that 14.7 g of gallium nitrate octahydrate was replaced with 10.8 g of indium chloride tetrahydrate. The average primary particle diameter of the ultrafine zinc oxide A-E was 0.035 µm.

(Example A-6)

Ultrafine zinc oxide A-F was obtained in the same manner as Example A-1, except that 14.7 g of gallium nitrate octahydrate was replaced with 34.3 g of gallium nitrate octahydrate. The average primary particle diameter of the ultrafine zinc oxide A-F was 0.016 μm .

(Example A-7)

Ultrafine zinc oxide A-G was obtained in the same manner as Example A-1, except that the firing temperature was set to 800°C in lieu of 700°C. The average primary particle diameter of the ultrafine zinc oxide A-G was 0.031 μm .

(Comparative Example A-1)

An aqueous zinc chloride solution was prepared by completely dissolving 100 g of zinc oxide (Grade 1 zinc oxide, Sakai Chemical Industry Co., Ltd., Sakai, Japan) in an aqueous hydrochloric acid solution containing 250 g of 35-mass% hydrochloric acid (Extra pure grade) and 350 g of purified water. To the prepared aqueous zinc chloride solution, 14.7 g of gallium nitrate octahydrate was added, and mixed the mixture until gallium nitrate octahydrate was completely dissolved to form a transparent solution. Separately, an aqueous ammonium bicarbonate solution was prepared by dissolving 230 g of ammonium bicarbonate (Extra pure grade) in 1500 g of purified water. The aqueous zinc chloride solution in which gallium nitrate was dissolved was added to the aqueous ammonium bicarbonate solution over 120 minutes to produce precipitate. Then, the obtained precipitate was sufficiently washed, separated from the liquid phase, and dried at 130°C over 5 hours. Next, the dried powder was pulverized by an agate mortar to give a precursor to be fired. The precursor to be fired was put in an alumina boat and heated to 700°C at 200°C/hour while circulating a mixed gas of 0.21 L/minute of nitrogen gas and 0.09 L/minute of hydrogen gas using a tubular furnace. After

being kept as it was for 2 hours, the substance was cooled to room temperature to give silica-free ultrafine zinc oxide A-H. The average primary particle diameter of the ultrafine zinc oxide A-H was 0.13 μm .

5

(Comparative Example A-2)

Silica-free ultrafine zinc oxide A-I was obtained in the same manner as Comparative Example A-1, except that 14.7 g of gallium nitrate octahydrate was replaced with 14.8 g of aluminum chloride hexahydrate. The average primary particle diameter of the ultrafine zinc oxide A-I was 0.35 μm .

10

(Comparative Example A-3)

Silica-free ultrafine zinc oxide A-J was obtained in the same manner as Comparative Example A-1, except that 14.7 g of gallium nitrate octahydrate was replaced with 10.8 g of indium chloride tetrahydrate. The average primary particle diameter of the ultrafine zinc oxide A-J was 0.53 μm .

15

20 (Comparative Example A-4)

Ultrafine zinc oxide A-K was obtained in the same manner as Example A-1, except that the firing temperature was set to 900°C in lieu of 700°C. The average primary particle diameter of the ultrafine zinc oxide A-K was 0.21 μm .

25

The synthesis conditions and BET specific surface area of the ultrafine zinc oxides obtained in the above-mentioned Examples A-1 to A-7 and Comparative Examples A-1 to A-4 are illustrated in Table 1.

30

Table 1

		Ultrafine zinc oxide	Preparation condition				Analysis of prepared substance		Evaluation example
			Element having a valence number of three or more	Added amount per mol of zinc oxide (mol)	Silica amount (g/100 g of ZnO)	Firing temperature (°C)	Element having a valence number of three or more	Metal compound	
Examples	A-1	A-A	Ga	0.03	5	700	Content mol/mol of ZnO	mass % of silica	BET specific surface area (m ² /g)
	A-2	A-B	Ga	0.03	1	700	0.028	0.8	31
	A-3	A-C	Ga	0.03	10	700	0.028	7.9	60
	A-4	A-D	Al	0.05	5	700	0.049	4.2	35
	A-5	A-E	In	0.03	5	700	0.028	4.1	30
	A-6	A-F	Ga	0.07	5	700	0.070	3.9	65
	A-7	A-G	Ga	0.03	5	800	0.029	4.1	34
Comparative Examples	A-1	A-H	Ga	0.03	—	700	0.030	—	8
	A-2	A-I	Al	0.03	—	700	0.028	—	3
	A-3	A-J	In	0.03	—	700	0.028	—	2
	A-4	A-K	Ga	0.03	5	900	0.029	4.1	5

(Analysis method A)

The composition of the ultrafine zinc oxides obtained in Examples A-1 to A-7 and Comparative Examples A-1 to A-4 was analyzed.

In 50 ml of pure water, each 0.2 g sample of the ultrafine zinc oxide was added. Then, hydrochloric acid (for analysis use) was further added thereto, and mixed the mixture until it became a completely transparent solution. The obtained aqueous solution was transferred to a 100 ml measuring flask, and pure water was added in the flask to adjust the total volume to be 100 ml.

The obtained aqueous solution was analyzed by ICP emission spectrophotometer (SPS 1700 HVR modelTM, Seiko Instruments Inc., Chiba, Japan). Using a previously produced analytical curve, the amount of the element having a valence number of 3 or more and the amount of silica were determined. Then the determined amounts of the element or silica were converted by calculation to the amount relative to the amount of zinc oxide.

Table 1 illustrates the amounts of the element having a valence number of 3 or more represented by mol amount per mol of ZnO. The amounts of silica are represented by mass% in the prepared substance.

(Evaluation Example A) - Evaluation of heat ray shielding ability in the form of thin film

Heat ray shielding abilities of the ultrafine zinc oxides obtained in the Examples A-1 to A-7 and Comparative Examples A-1 to A-4 were tested as follows.

Each ultrafine zinc oxide-dispersed coating material was prepared by mixing 2.36 g of each ultrafine zinc oxide, 5.5 g of alkyd resin varnish (Beckosol J-524TM, Dainippon Ink and Chemicals, Inc., Tokyo, Japan), 2.8 g of melamine resin varnish (Super Beckamine J-820TM, Dainippon Ink and Chemicals, Inc.) and 5.7 g of xylene (Extra pure grade) and dispersing them together

with 30 g of 1.5 mm ϕ glass beads using a paint conditioner over 180 minutes. Next, a small amount of the dispersion coating material was sampled on a glass plate and formed into a film using a No. 12 bar coater and successively baked at 130°C over 30 minutes to give each film for evaluation. The optical transmittance of the film for evaluation was measured by UV-VIS-NIR spectrophotometers (V-570TM type spectrophotometer and ILN 471TM type integration apparatus, JASCO Corp., Tokyo, Japan). The transmittances at 550 nm and 1900 nm are illustrated in Table 2.

Table 2

		Ultrafine zinc oxide	550 nm	1900 nm
Examples	A-1	A-A	82	2
	A-2	A-B	83	5
	A-3	A-C	85	3
	A-4	A-D	80	60
	A-5	A-E	71	67
	A-6	A-F	86	6
	A-7	A-G	83	2
Comparative Examples	A-1	A-H	55	6
	A-2	A-I	66	65
	A-3	A-J	52	71
	A-4	A-K	65	2

Table 2 shows that the zinc oxide containing Ga of Examples A-1 to A-3, A-6 and A-7 became desirable zinc oxide fine particles having high visible light transmittance at 550 nm and significantly low near infrared ray transmittance at 1900 nm. The results of zinc oxide of Comparative Examples A-1 and A-4, show that the specific surface area was considerably decreased and transparency was lost since the zinc oxide of Comparative Example A-1 did not contain silica as the sintering-preventing agent, and the zinc oxide of Comparative

Example A-4 was fired at temperature as high as 900°C. On the other hand, the results of the zinc oxides of Examples A-4 and A-5, which contained Al and In respectively, showed that the zinc oxides had excellent properties such as high visible light transmittance at 550 nm and low near infrared ray transmittance at 1900 nm as compared with the silica-free zinc oxide of Comparative Examples A-2 and A-3.

(Example B-1)

10 An aqueous zinc chloride solution was prepared by completely dissolving 100 g of zinc oxide (Grade 1 zinc oxide) in an aqueous hydrochloric acid solution containing 250 g of 35-mass% hydrochloric acid (Extra pure grade) and 350 g of purified water. To the prepared aqueous zinc oxide solution, 15 15.9 g of scandium chloride hexahydrate (reagent) was added and mixed the mixture to dissolve zinc oxide until the solution became transparent. Separately, an aqueous sodium carbonate solution was prepared by 154.6 g of sodium carbonate (Extra pure grade) was dissolved in 1546 g of purified water. The aqueous 20 zinc oxide solution in which scandium chloride was dissolved was added to the aqueous sodium carbonate solution over 120 minutes to produce precipitate. Then, the precipitate was sufficiently washed, separated from liquid phase, and dried at 130°C over 5 hours. Next, the dried powder was pulverized in 25 an agate mortar to give a precursor compound. The precursor compound was set in a magnetic crucible and fired at 400°C for 1 hour using a muffle furnace to give a mixed oxide of scandium and zinc. Under stirring condition, the mixed oxide was put in 1000 g of purified water and successively, 90 ml of an aqueous 30 solution containing 14.2 g (corresponding to 3 g as SiO₂) of sodium metasilicate nonahydrate (Extra pure grade) and 10-mass% sulfuric acid (reagent) were simultaneously added while the flow rates were adjusted as to keep pH within the range of 7 to 9 over 90 minutes. Then, the obtained precipitate was 35 sufficiently washed, separated from the liquid phase and dried

at 130°C over 5 hours.

The dried powder was subsequently pulverized by an agate mortar to give a precursor to be fired. The precursor to be fired was put in an alumina boat and heated to 700°C at the heating rate of 200°C/hour using a tubular furnace while a mixed gas of 0.285 L/minute of nitrogen gas and 0.015 L/minute of hydrogen gas was circulated. After being kept as it was for 2 hours, the substance was cooled to room temperature to give ultrafine zinc oxide B-A. The average primary particle diameter of the ultrafine zinc oxide B-A was 0.021 μm and the volume resistivity value of the ultrafine zinc oxide B-A was 521 Ωcm .

(Example B-2)

Ultrafine zinc oxide B-B was obtained in the same manner as Example B-1, except that 15.9 g of scandium chloride hexahydrate (reagent) was replaced with 23.5 g of yttrium nitrate hexahydrate (reagent). The average primary particle diameter of the ultrafine zinc oxide B-B was 0.031 μm and the volume resistivity value of the ultrafine zinc oxide B-B was 665 Ωcm .

(Example B-3)

Ultrafine zinc oxide B-C was obtained in the same manner as Example B-1, except that 15.9 g of scandium chloride hexahydrate (reagent) was replaced with 18.0 g of indium chloride tetrahydrate (for chemical use). The average primary particle diameter of the ultrafine zinc oxide B-C was 0.041 μm and the volume resistivity value of the ultrafine zinc oxide B-C was 459 Ωcm .

(Example B-4)

Ultrafine zinc oxide B-D was obtained in the same manner as Example B-1, except that 15.9 g of scandium chloride hexahydrate (reagent) was replaced with 23.4 g of gallium

nitrate octahydrate (reagent). The average primary particle diameter of the ultrafine zinc oxide B-D was 0.024 μm and the volume resistivity value of the ultrafine zinc oxide B-D was 333 Ωcm .

5

(Example B-5)

Ultrafine zinc oxide B-E was obtained in the same manner as Example B-1, except that 15.9 g of scandium chloride hexahydrate (reagent) was replaced with 23.0 g of aluminum
10 nitrate nonahydrate (JIS Extra pure grade). The average primary particle diameter of the ultrafine zinc oxide B-E was 0.022 μm and the volume resistivity value of the ultrafine zinc oxide B-E was 474 Ωcm .

15 (Example B-6)

Ultrafine zinc oxide B-F was obtained in the same manner as Example B-1, except that 15.9 g of scandium chloride hexahydrate (reagent) was replaced with 11.6 g of titanium (IV) chloride (reagent). The average primary particle diameter of
20 the ultrafine zinc oxide B-F was 0.024 μm and the volume resistivity value of the ultrafine zinc oxide B-F was 514 Ωcm .

(Example B-7)

An aqueous zinc chloride solution was prepared by
25 completely dissolving 100 g of zinc oxide (Grade 1 zinc oxide) in an aqueous hydrochloric acid solution containing 250 g of 35 mass% hydrochloric acid (Extra pure grade) and 350 g of purified water. Separately, an aqueous sodium carbonate solution was prepared by dissolving 154.6 g of sodium carbonate
30 (Extra pure grade) in 1546 g of purified water. The aqueous zinc oxide solution was added to the aqueous sodium carbonate solution over 120 minutes to produce precipitate. Then, the precipitate was sufficiently washed, mixed with 3.8 g of boric acid (Extra pure grade) and stirred for 20 minutes. Next, the
35 obtained slurry was evaporated and dried at 130°C and the

obtained dried powder was pulverized in an agate mortar to give a precursor compound. The precursor compound was set in a magnetic crucible and fired at 400°C for 1 hour using a muffle furnace to obtain a mixed oxide of boron and zinc. The mixed
5 oxide was put in 1000 g of purified water with stirring, and successively, 90 ml of an aqueous solution containing 14.2 g (corresponding to 3 g as SiO₂) of sodium metasilicate nonahydrate (Extra pure grade) and 10-mass% sulfuric acid (reagent) were simultaneously added while the flow rates were
10 adjusted as to keep pH within the range of 7 to 9 over 90 minutes. Then, the obtained precipitate was sufficiently washed, separated from the liquid phase and dried at 130°C over 5 hours.

Next, the dried powder was pulverized by an agate mortar to given a precursor to be fired. The precursor to be fired
15 was put in an alumina boat and heated to 700°C at the heating rate of 200°C/hour using a tubular furnace while a mixed gas of 0.285 L/minute of nitrogen gas and 0.015 L/minute of hydrogen gas was circulated. After being kept as it was for 2 hours, the substance was cooled to room temperature to give ultrafine
20 zinc oxide B-G. The average primary particle diameter of the ultrafine zinc oxide B-G was 0.021 μm and the volume resistivity value of the ultrafine zinc oxide B-G was 536 Ωcm.

(Example B-8)

25 Ultrafine zinc oxide B-H was obtained in the same manner as Example B-1, except that 15.9 g of scandium chloride hexahydrate (reagent) was replaced with 26.7 g of cerium nitrate hexahydrate (Extra pure grade). The average primary particle diameter of the ultrafine zinc oxide B-H was 0.019 μm and the
30 volume resistivity value of the ultrafine zinc oxide B-H was 543 Ωcm.

(Example B-9)

Ultrafine zinc oxide B-I was obtained in the same manner
35 as Example B-1, except that 15.9 g of scandium chloride

hexahydrate (reagent) was replaced with 27.4 g of europium nitrate hexahydrate (reagent). The average primary particle diameter of the ultrafine zinc oxide B-I was 0.022 μm and the volume resistivity value of the ultrafine zinc oxide B-I was
5 540 Ωcm .

(Example B-10)

Ultrafine zinc oxide B-J was obtained in the same manner as Example B-1, except that 15.9 g of scandium chloride
10 hexahydrate (reagent) was replaced with 23.8 g of ytterbium chloride hexahydrate (reagent). The average primary particle diameter of the ultrafine zinc oxide B-J was 0.025 μm and the volume resistivity value of the ultrafine zinc oxide B-J was
15 692 Ωcm .

(Example B-11)

Ultrafine zinc oxide B-K was obtained in the same manner as Example B-1, except that 15.9 g of scandium chloride hexahydrate (reagent) was replaced with 3.7 g of aluminum
20 nitrate nonahydrate (JIS Extra pure grade). The average primary particle diameter of the ultrafine zinc oxide B-K was 0.026 μm and the volume resistivity value of the ultrafine zinc oxide B-K was 547 Ωcm .

25 (Example B-12)

Ultrafine zinc oxide B-L was obtained in the same manner as Example B-1, except that 15.9 g of scandium chloride hexahydrate (reagent) was replaced with 69.1 g of aluminum
30 nitrate nonahydrate (JIS Extra pure grade). The average primary particle diameter of the ultrafine zinc oxide B-L was 0.035 μm and the volume resistivity value of the ultrafine zinc oxide B-K was 481 Ωcm .

(Example B-13)

35 Ultrafine zinc oxide B-M was obtained in the same manner

as Example B-5, except that 90 ml of the aqueous solution containing 14.2 g (corresponding to 3 g as SiO_2) of sodium metasilicate nonahydrate (Extra pure grade) and 10-mass% sulfuric acid (reagent) were replaced with 90 ml of an aqueous solution containing 5.7 g (corresponding to 3 g as ZrO_2) of zirconium chloride (reagent) and 10-mass% sodium hydroxide aqueous solution (reagent). The average primary particle diameter of the ultrafine zinc oxide B-M was 0.026 μm and the volume resistivity value of the ultrafine zinc oxide B-M was 450 Ωcm .

(Example B-14)

Ultrafine zinc oxide B-N was obtained in the same manner as Example B-5, except that 90 ml of the aqueous solution containing 14.2 g (corresponding to 3 g as SiO_2) of sodium metasilicate nonahydrate (Extra pure grade) and 10-mass% sulfuric acid (reagent) were replaced with 90 ml of an aqueous solution containing 7.0 g (corresponding to 3 g as SnO_2) of tin(IV) chloride pentahydrate (Extra pure grade) and 10-mass% sodium hydroxide aqueous solution (reagent). The average primary particle diameter of the ultrafine zinc oxide B-N was 0.027 μm and the volume resistivity value of the ultrafine zinc oxide B-N was 593 Ωcm .

(Example B-15)

Ultrafine zinc oxide B-O was obtained in the same manner as Example B-5, except that 90 ml of the aqueous solution containing 14.2 g (corresponding to 3 g as SiO_2) of sodium metasilicate nonahydrate (Extra pure grade) and 10-mass% sulfuric acid (reagent) were replaced with 90 ml of an aqueous solution containing 19.1 g (corresponding to 3 g as MgO) of magnesium nitrate hexahydrate (Extra pure grade) and 10-mass% sodium hydroxide aqueous solution (reagent). The average primary particle diameter of the ultrafine zinc oxide B-O was 0.028 μm and the volume resistivity value of the ultrafine zinc

oxide B-O was 608 Ωcm .

(Example B-16)

Ultrafine zinc oxide B-P was obtained in the same manner
5 as Example B-5, except that 90 ml of the aqueous solution
containing 14.2 g (corresponding to 3 g as SiO_2) of sodium
metasilicate nonahydrate (Extra pure grade) and 10-mass%
sulfuric acid (reagent) were replaced with 90 ml of an aqueous
solution containing 4.6 g (corresponding to 3 g as HfO_2) of
10 hafnium chloride (reagent) and an aqueous solution of 10-mass%
sodium hydroxide (reagent). The average primary particle
diameter of the ultrafine zinc oxide B-P was 0.020 μm and the
volume resistivity value of the ultrafine zinc oxide B-P was
632 Ωcm .

15

(Example B-17)

Ultrafine zinc oxide B-Q was obtained in the same manner
as Example B-5, except that 14.2 g (corresponding to 3 g as SiO_2)
of sodium metasilicate nonahydrate (Extra pure grade) was
20 replaced with 3.8 g (corresponding to 0.8 g as SiO_2) of sodium
metasilicate nonahydrate (Extra pure grade). The average
primary particle diameter of the ultrafine zinc oxide B-Q was
0.054 μm and the volume resistivity value of the ultrafine zinc
oxide B-Q was 893 Ωcm .

25

(Example B-18)

Ultrafine zinc oxide B-R was obtained in the same manner
as Example B-5, except that 14.2 g (corresponding to 3 g as SiO_2)
of sodium metasilicate nonahydrate (Extra pure grade) was
30 replaced with 71.1 g (corresponding to 15 g as SiO_2) of sodium
metasilicate nonahydrate (Extra pure grade). The average
primary particle diameter of the ultrafine zinc oxide B-R was
0.012 μm and the volume resistivity value of the ultrafine zinc
oxide B-R was 352 Ωcm .

35

(Example B-19)

Ultrafine zinc oxide B-S was obtained in the same manner as Example B-5, except that reducing firing temperature was set to 600°C in lieu of 700°C. The average primary particle
5 diameter of the ultrafine zinc oxide B-S was 0.017 μm and the volume resistivity value of the ultrafine zinc oxide B-S was 647 Ωcm .

(Example B-20)

10 Ultrafine zinc oxide B-T was obtained in the same manner as Example B-5, except that reducing firing temperature was set to 850°C in lieu of 700°C. The average primary particle diameter of the ultrafine zinc oxide B-T was 0.051 μm and the volume resistivity value of the ultrafine zinc oxide B-T was
15 145 Ωcm .

(Comparative Example B-1)

An aqueous zinc chloride solution was prepared by completely dissolving 100 g of zinc oxide (Grade 1 zinc oxide,
20 Sakai Chemical Industry Co., Ltd.) in an aqueous hydrochloric acid solution containing 250 g of 35-mass% hydrochloric acid (Extra pure grade) and 350 g of purified water. To the prepared aqueous zinc oxide solution, 0.46 g of aluminum nitrate nonahydroxide (JIS Extra pure grade) was further added and mixed
25 the mixture until aluminum nitrate nonahydroxide was completely dissolved to form a transparent solution. Separately, an aqueous sodium carbonate solution was prepared by dissolving 154.6 g of sodium carbonate (Extra pure grade) in 1546 g of purified water. The above-mentioned aqueous zinc oxide
30 solution in which aluminum nitrate nonahydrate was dissolved was added to the aqueous sodium carbonate solution over 120 minutes to produce precipitate. Then, the precipitate was sufficiently washed, separated from liquid phase, and dried at 130°C over 5 hours. The dried powder was subsequently
35 pulverized in an agate mortar to give a precursor compound.

The precursor compound was set in a magnetic crucible and fired at 400°C for 1 hour using a muffle furnace to give a mixed oxide of aluminum and zinc. Under stirring condition, the mixed oxide was put in 1,000 g of purified water and successively, 5 90 ml of an aqueous solution containing 14.2 g (corresponding to 3 g as SiO₂) of sodium metasilicate nonahydrate (Extra pure grade) and 10-mass% sulfuric acid (reagent) were simultaneously added while the flow rates were adjusted as to keep pH within the range of 7 to 9 over 90 minutes. Then, the obtained 10 precipitate was sufficiently washed, was separated from the liquid phase, and dried at 130°C over 5 hours.

The dried powder was subsequently pulverized by an agate mortar to obtain a precursor to be fired. The precursor to be fired was put in an alumina boat and heated to 700°C at the 15 heating rate of 200°C/hour using a tubular furnace while a mixed gas of 0.285 L/minute of nitrogen gas and 0.015 L/minute of hydrogen gas was circulated. After being kept as it was for 2 hours, the substance was cooled to room temperature to obtain ultrafine zinc oxide B-U. The average primary particle 20 diameter of the ultrafine zinc oxide B-U was 0.027 μm and the volume resistivity value of the ultrafine zinc oxide B-U was 35,000 Ωcm.

(Comparative Example B-2)

25 Ultrafine zinc oxide B-V was obtained in the same manner as Comparative Example B-1, except that 0.46 g of aluminum nitrate nonahydrate (JIS Extra pure grade) was replaced with 115.2 g of aluminum nitrate nonahydrate (JIS Extra pure grade). The average primary particle diameter of the ultrafine zinc 30 oxide B-V was 0.045 μm and the volume resistivity value of the ultrafine zinc oxide B-V was 581 Ωcm.

(Comparative Example B-3)

35 Ultrafine zinc oxide B-W was obtained in the same manner as Comparative Example B-1, except that 0.46 g of aluminum

nitrate nonahydrate (JIS Extra pure grade) was replaced with 23.0 g of aluminum nitrate nonahydrate (JIS Extra pure grade), and 14.2 g (corresponding to 3 g as SiO₂) of sodium metasilicate nonahydrate (Extra pure grade) was replaced with 0.95 g (corresponding to 0.2 g as SiO₂) of sodium metasilicate nonahydrate (Extra pure grade). The average primary particle diameter of the ultrafine zinc oxide B-W was 0.153 μm and the volume resistivity value of the ultrafine zinc oxide B-W was 376 Ωcm.

10

(Comparative Example B-4)

Ultrafine zinc oxide B-X was obtained in the same manner as Comparative Example B-3, except that 14.21 g (corresponding to 3 g as SiO₂) of sodium metasilicate nonahydrate (Extra pure grade) was replaced with 142.0 g (corresponding to 30 g as SiO₂) of sodium metasilicate nonahydrate (Extra pure grade). The average primary particle diameter of the ultrafine zinc oxide B-X was 0.007 μm and the volume resistivity value of the ultrafine zinc oxide B-X was 1,276 Ωcm.

15
20

(Comparative Example B-5)

Ultrafine zinc oxide B-Y was obtained in the same manner as Example B-5, except that reducing firing temperature of 700°C was replaced with 500°C. The average primary particle diameter of the ultrafine zinc oxide B-Y was 0.014 μm and the volume resistivity value of the ultrafine zinc oxide B-Y was 950 Ωcm.

25

(Comparative Example B-6)

Ultrafine zinc oxide B-Z was obtained in the same manner as Example B-5, except that reducing firing temperature was set to 1,000°C in lieu of 700°C. The average primary particle diameter of the ultrafine zinc oxide B-Z was 0.536 μm and the volume resistivity value of the ultrafine zinc oxide B-Z was 30 Ωcm.

30
35

(Comparative Example B-7)

Ultrafine zinc oxide (FINEX-50TM, manufactured by Sakai Chemical Industry Co., Ltd.) was used as ultrafine zinc oxide B- α . The average primary particle diameter of the ultrafine zinc oxide B- α was 0.021 μm and the volume resistivity value of the ultrafine zinc oxide B- α was 22,870,000 Ωcm .

Table 3-A

Example No.	Ultrafine zinc oxide	Preparation condition				
		Element having a valence number of three or more		Coating agent		Firing temperature
		Type	Amount per mol of zinc oxide (mol)	Type	Silica amount per 100 g of ZnO (g)	
B-1	B-A	Sc	0.05	Si	3	700
B-2	B-B	Y	0.05	Si	3	700
B-3	B-C	In	0.05	Si	3	700
B-4	B-D	Ga	0.05	Si	3	700
B-5	B-E	Al	0.05	Si	3	700
B-6	B-F	Ti	0.05	Si	3	700
B-7	B-G	B	0.05	Si	3	700
B-8	B-H	Ce	0.05	Si	3	700
B-9	B-I	Eu	0.05	Si	3	700
B-10	B-J	Yb	0.05	Si	3	700
B-11	B-K	Al	0.008	Si	3	700
B-12	B-L	Al	0.15	Si	3	700
B-13	B-M	Al	0.05	Zr	3	700
B-14	B-N	Al	0.05	Sn	3	700
B-15	B-O	Al	0.05	Mg	3	700
B-16	B-P	Al	0.05	Hf	3	700
B-17	B-Q	Al	0.05	Si	0.8	700
B-18	B-R	Al	0.05	Si	15	700
B-19	B-S	Al	0.05	Si	3	600
B-20	B-T	Al	0.05	Si	3	850

Table 3-B

Comparative Example No.	Ultrafine zinc oxide	Preparation condition					
		Element having a valence number of three or more		Coating agent		Firing temperature	
		Type	Amount per mol of zinc oxide (mol)	Type	Silica amount per 100 g of ZnO (g)		
B-1	B-U	Al	0.001	Si	3	700	
B-2	B-V	Al	0.25	Si	3	700	
B-3	B-W	Al	0.05	Si	0.2	700	
B-4	B-X	Al	0.05	Si	30	700	
B-5	B-Y	Al	0.05	Si	3	500	
B-6	B-Z	Al	0.05	Si	3	1000	
B-7	B- α	—	—	—	—	—	

Table 3-C

Example No.	Ultrafine zinc oxide	Analysis of prepared substance				Evaluation				
		Element having a valence number of three or more		Metal compound		Physical property		Optical transmittance		Electric resistivity
		Element	Content mol/mol of ZnO	Element	mass % as oxide	Average primary particle diameter (μm)	BET specific surface area (m ² /g)	At 550 nm (%)	At 1900 nm (%)	Volume resistivity value (Ω cm)
B-1	B-A	Sc	0.049	Si	2.5	0.021	51	87	41	521
B-2	B-B	Y	0.049	Si	2.5	0.031	35	88	46	665
B-3	B-C	In	0.049	Si	2.4	0.041	26	76	44	459
B-4	B-D	Ga	0.049	Si	2.5	0.024	44	86	4	333
B-5	B-E	Al	0.050	Si	2.5	0.022	49	82	50	474
B-6	B-F	Ti	0.049	Si	2.5	0.024	44	83	58	514
B-7	B-G	B	0.048	Si	2.6	0.021	52	88	59	536
B-8	B-H	Ce	0.048	Si	2.4	0.019	56	86	63	543
B-9	B-I	Eu	0.048	Si	2.4	0.022	48	86	67	540
B-10	B-J	Yb	0.047	Si	2.3	0.025	43	84	59	692
B-11	B-K	Al	0.008	Si	2.6	0.026	41	86	53	547
B-12	B-L	Al	0.148	Si	2.4	0.035	31	82	46	481
B-13	B-M	Al	0.050	Zr	2.5	0.026	42	81	42	450
B-14	B-N	Al	0.049	Sn	2.5	0.027	40	81	45	593
B-15	B-O	Al	0.049	Mg	2.5	0.028	38	80	48	608
B-16	B-P	Al	0.050	Hf	2.5	0.020	53	83	50	632
B-17	B-Q	Al	0.049	Si	0.7	0.054	20	80	30	893
B-18	B-R	Al	0.050	Si	11.4	0.012	93	89	68	352
B-19	B-S	Al	0.050	Si	2.5	0.017	62	89	55	647
B-20	B-T	Al	0.050	Si	2.5	0.051	21	75	22	145

Table 3-D

Comparative Example No.	Ultrafine zinc oxide	Analysis of prepared substance				Evaluation				
		Element having a valence number of three or more		Metal compound		Physical property		Optical transmittance		Electric resistivity
		Element	Content mol/mol of ZnO	Element	mass % as oxide	Average primary particle diameter (μ m)	BET specific surface area (m^2/g)	At 550 nm (%)	At 1900 nm (%)	Volume resistivity value (Ω cm)
B-1	B-U	Al	0.0008	Si	2.6	0.027	40	83	82	35000
B-2	B-V	Al	0.248	Si	2.3	0.045	24	59	57	581
B-3	B-W	Al	0.050	Si	0.2	0.153	7	54	58	376
B-4	B-X	Al	0.049	Si	23.5	0.007	148	89	81	1276
B-5	B-Y	Al	0.050	Si	2.5	0.014	75	89	75	950
B-6	B-Z	Al	0.050	Si	2.5	0.536	2	47	23	30
B-7	B- α	—	—	—	—	0.021	50	89	89	22870000

(Analysis method B)

The composition of the ultrafine zinc oxides obtained in Examples B-1 to B-20 and Comparative Examples B-1 to B-7 was analyzed.

5 In 50 ml of pure water, each 0.2 g sample of the ultrafine zinc oxide was added. Then, hydrochloric acid (for analysis use) was further added thereto and mixed the mixture until it became a completely transparent solution. The obtained aqueous solution was transferred to a 100 ml measuring flask,
10 and pure water was added in the flask to adjust the total volume to be 100 ml.

The obtained aqueous solution was analyzed by ICP emission spectrophotometer (SPS 1700 HVR model, Seiko Instruments Inc., Chiba, Japan). Using a previously produced
15 analytical curve, the amount of the element having a valence number of 3 or more and the amount of the metal compound were determined. Then the determined amounts of the element or silica were converted by calculation to the amount relative to the amount of zinc oxide.

20 Table 3 illustrates the amounts of the element having a valence number of 3 or more represented by mol amount per mol of ZnO. The amounts of the metal compound are represented by mass% in the prepared substance.

25 (Evaluation Example B-1) - Evaluation of heat ray shielding ability in the form of thin film

The ultrafine zinc oxides obtained in the above-mentioned Examples B-1 to B-20 and Comparative Examples B-1 to B-7 was tested as follows.

30 Each ultrafine zinc oxide-dispersed coating material was obtained by mixing 2.36 g of each ultrafine zinc oxide, 5.5 g of alkyd resin varnish (Beckosol J-524, Dainippon Ink and Chemicals, Inc., Tokyo, Japan), 2.8 g of melamine resin varnish (Super Beckamine J-820, Dainippon Ink and Chemicals, Inc.), and
35 5.7 g of xylene (Extra pure grade) and dispersing them together

with 55 g of 0.8 mmφ zirconia beads using a paint conditioner over 180 minutes. Then, a small amount of the dispersion coating material was sampled on a glass plate and formed into a film using a No. 12 bar coater and successively baked at 130°C over 30 minutes to give each film for evaluation. The optical transmittance of the film for evaluation was measured by UV-VIS-NIR spectrophotometers (V-570 type spectrophotometer and ILN 471 type integration apparatus manufactured by JASCO Corp., Tokyo, Japan). The transmittance values at 550 nm and 1900 nm are illustrated in Table 3. Further, the optical transmittance spectrum curves of Examples B-4 and B-5 which had significant effect of the present invention and Comparative Examples B-3 and B-7 are illustrated in Fig. 1.

(Evaluation Example B-2) - Evaluation of volume resistivity value

The volume resistivity values of ultrafine zinc oxides obtained in Examples B-1 to B-20 and Comparative Examples B-1 to B-7 were determined by the following method.

A cylinder made of vinyl chloride and having an inner diameter of 20 mmφ was loaded with 0.8 g of each sample and the sample was sandwiched between conductive cores having a function as electrodes in both sides and a load of 200 kgf was added to the sample by hand press. Keeping this state, the resistivity value between both ends of the electrodes was measured by a tester. The volume resistivity value was calculated from the resistivity value according to the following equation:

[Volume resistivity value (Ωcm)]

= [resistivity value (Ω)] × [press surface area (cm²) of sample]/[thickness (cm) at the time of pressing]

(Evaluation Example B-3) - Observation by scanning electron microscope

The ultrafine zinc oxides were observed by a scanning

electronmicroscope (JSM-7000 FTM, JEOL Ltd., Tokyo, Japan). The transmission electron microscopic photographs of Example B-5 and Comparative Example B-3 are illustrated in Fig. 2 and Fig. 3.

(Evaluation Example B-4) - Temperature measurement

Each of the ultrafine zinc oxide-dispersed coating materials obtained in the method of Evaluation Example B-1 was sampled on a glass plate with a size of 10 cm x 12 cm and a thickness of 3 mm and formed into a film on the entire surface of one face using a No. 14 bar coater and baked at 130°C over 30 minutes to give each evaluation film. A 17 x 21 x 12.5 cm (depth x width x height) box, which insulates heat radiation to outside or reception from outside was used for evaluation. The center of the top face of the box was cut off in 9 cm square. The evaluation film was set on the cut off part of the top face of the box and an incandescent lamp was turned on at a distance of 12.5 cm above the evaluation film. The temperature was measured using a thermocouple set at a distance of 12.5 cm under the evaluation film. The schematic drawing of an apparatus is illustrated in Fig. 4. The relation of time from the turning on of the incandescent lamp and the temperature are illustrated in Fig. 5.

Table 3 shows the ultrafine zinc oxides of B-A to B-J obtained in Examples B-1 to B-10 within the scope of the present invention have excellent properties, such as an average primary particle diameter of 0.1 μm or smaller, high visible light transmittance at 550 nm, and significantly low near infrared ray transmittance at 1900 nm, since they contained the elements having a valence number of 3 or more.

Table 3 further shows that all of the ultrafine zinc oxides of B-A to B-J have a volume resistivity value of 1000 Ωcm or lower and accordingly the ultrafine zinc oxides of the present invention also have good conductivity.

Table 1 shows that the ultrafine zinc oxides of B-K and

B-L obtained in Examples B-11 and B-12, were, ultrafine zinc oxides having both of good near infrared ray shielding ability and conductivity as the same as the above case, even in the case of altering the content of Al, an element having a valence number of 3 or more. Table 1 also shows that the ultrafine zinc oxides of B-M to B-P obtained in Examples B-13 to B-16 were ultrafine zinc oxides having both of good near infrared ray shielding property and conductivity, as the same as the above case, even in the case of using various kinds of sintering-preventing components according to the present invention.

Table 1 further shows that the ultrafine zinc oxides of B-Q and B-R obtained in Examples B-17 and B-18 were ultrafine zinc oxides having both of good near infrared ray shielding property and conductivity, although the amounts of Si, a sintering-preventing component were altered. It was also true for the case of the ultrafine zinc oxides of B-S and B-T obtained in Examples B-19 and B-20, although the reducing firing temperatures were changed.

On the contrary, the ultrafine zinc oxide B-U obtained in Comparative Example B-1 was inferior in infrared ray shielding ability and a high volume resistivity value, although B-U contained Al as an element having a valence number of 3 or more. This is because the amount of Al was insufficient.

The ultrafine zinc oxide B-V obtained in Comparative Example B-2 showed decreased optical transmittance at 550 nm and high optical transmittance at 1900 nm. The reason why the properties were insufficient was assumed that the amount of Al as an element having a valence number of 3 or more was so high that excess Al was deposited in the grain boundaries and visible light was scattered. This resulted in inferior transparency and a low infrared ray shielding property.

The ultrafine zinc oxide B-W obtained in Comparative Example B-3 showed decreased of transmittance at 550 nm. The reason why the properties were insufficient was assumed that amount of Si as a sintering-preventing component is

significantly low, and the particles were sintered to each other at the firing temperature applied in the present invention, and thus the particles were coarsened.

5 The ultrafine zinc oxide B-X obtained in Comparative Example B-4 showed insufficient infrared ray shielding ability, since the amount of Si, as a sintering-preventing component, was large and therefore, the proportion of zinc oxide containing an element having a valence number of 3 or more was lowered. The B-4 showed a high volume resistivity value, since surplus
10 sintering preventing component Si insulated particles each other.

The ultrafine zinc oxide B-Y obtained in Comparative Example B-5 showed a low infrared ray shielding ability since the reducing firing temperature was low, and thus the element
15 having a valence number of 3 or more were not sufficiently diffused in the zinc oxide crystal.

The ultrafine zinc oxide B-Z obtained in Comparative Example B-6 showed a large average primary particle diameter and a significantly low visible light transparency, since the
20 reducing firing temperature was high. Therefore, even if the sintering-preventing agent was added, particles were sintered to each other and coarsened.

The ultrafine zinc oxide B- α of Comparative Example B-7 showed a high volume resistivity value, since it is pure zinc
25 oxide and containing no element having a valence number of 3 or more. Thus, B- α has substantially no infrared ray shielding ability.

Further, Fig. 5 shows the results of temperature measurement with the lapse of time obtained by Evaluation
30 Example B-4. In the case of a binder only and the evaluation film of Comparative Example B-7, the temperature was considerably increased since it has substantially no infrared ray shielding ability. On the contrary, in the case of Examples B-4 and B-5, it is apparent that the infrared ray shielding
35 ability of the evaluation films, which were placed between the

incandescent lamp as a heat source and the thermocouple, contributed to suppress the temperature increase.

INDUSTRIAL APPLICABILITY

5

An ultrafine zinc oxide obtained by a method of producing the ultrafine zinc oxide of the present invention can be used for coating compositions, thermoplastic resin compositions, ink compositions and the like. A coating composition,

10 thermoplastic resin composition, and ink composition provided by the present invention can be applied as an infrared ray shielding material and a conductive material to a substrate of glass or the like.

15

We Claim:

1. An ultrafine zinc oxide, comprising
an element having a valence number of 3 or more,
the zinc oxide bearing a Si compound on the surface
thereof, and having an average primary particle diameter of
0.1 μm or smaller,
wherein the element having a valence number of 3 or more
is Ga,
wherein the amount of Ga is within the range of 0.001 to
0.2 mol per mol of zinc oxide, and the amount of the Si
compound is within the range of 0.5 to 20 mass% of surface-
treated zinc oxide to zinc oxide subjected to coating
treatment.
2. A method for producing the ultrafine zinc oxide
according to claim 1 comprising:
 - coating the surface of zinc oxide containing Ga or a
zinc oxide precursor compound containing Ga by firing with
silica and
 - firing the zinc oxide or the precursor compound at 600
to 850°C,wherein the amount of Ga is within the range of 0.001
to 0.2 mol per mol of zinc oxide and the amount of silica is
within the range of 0.5 to 20 mass% as the mass proportion
of SiO_2 in the surface-treated zinc oxide.
3. A coating composition, comprising
the ultrafine zinc oxide according to claim 1.
4. A thermoplastic resin composition, comprising
the ultrafine zinc oxide according to claim 1.

5. An ink composition, comprising
the ultrafine zinc oxide according to claim 1.

6. A laminated article, comprising:

- a glass substrate layer, and
- an infrared ray shielding layer,

wherein the infrared ray shielding layer comprises the
ultrafine zinc oxide according to claim 1 and a binder resin.

Application number/numéro de demande: SP2007/068678

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DRAWINGS

Fig.1

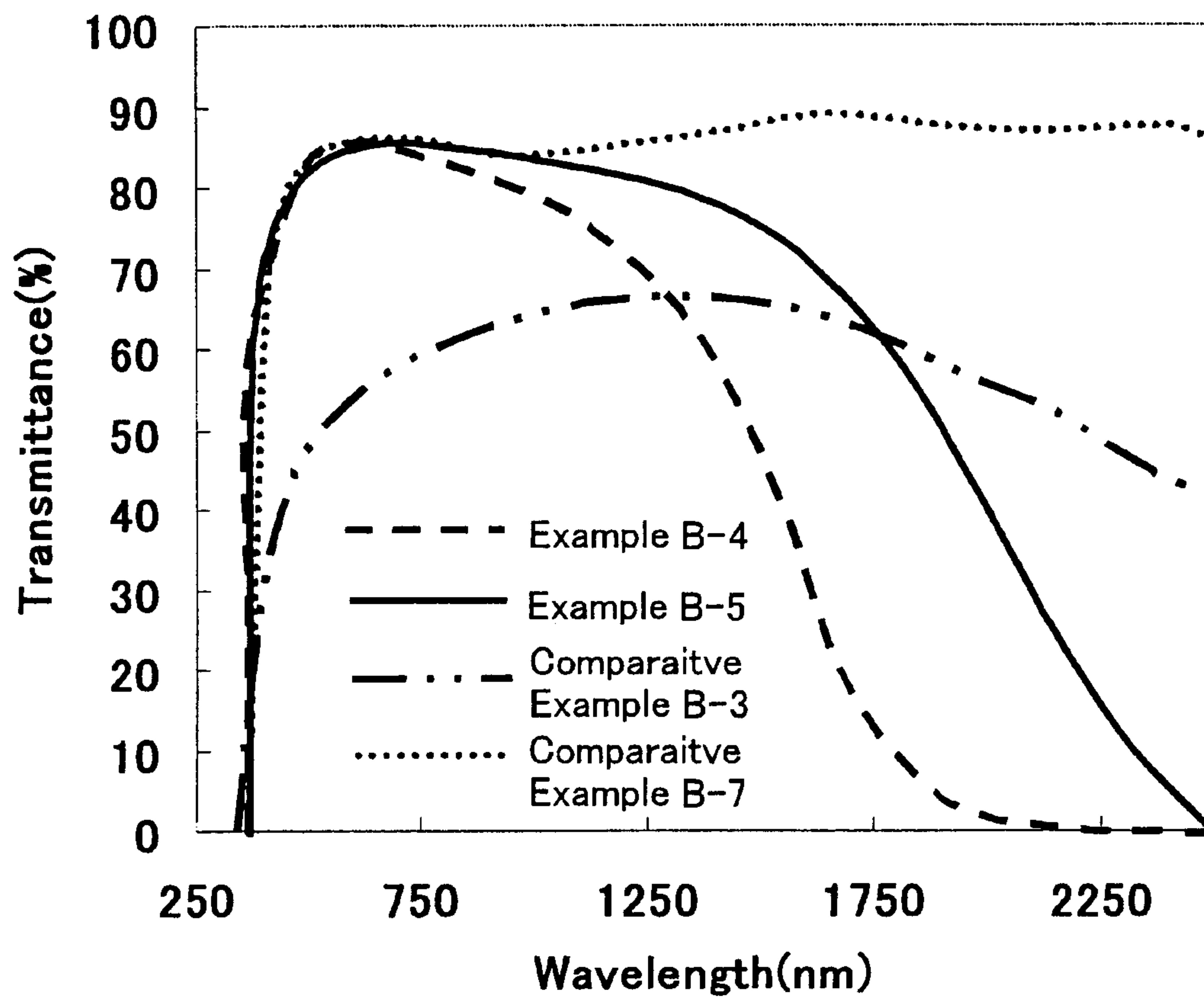


Fig.4

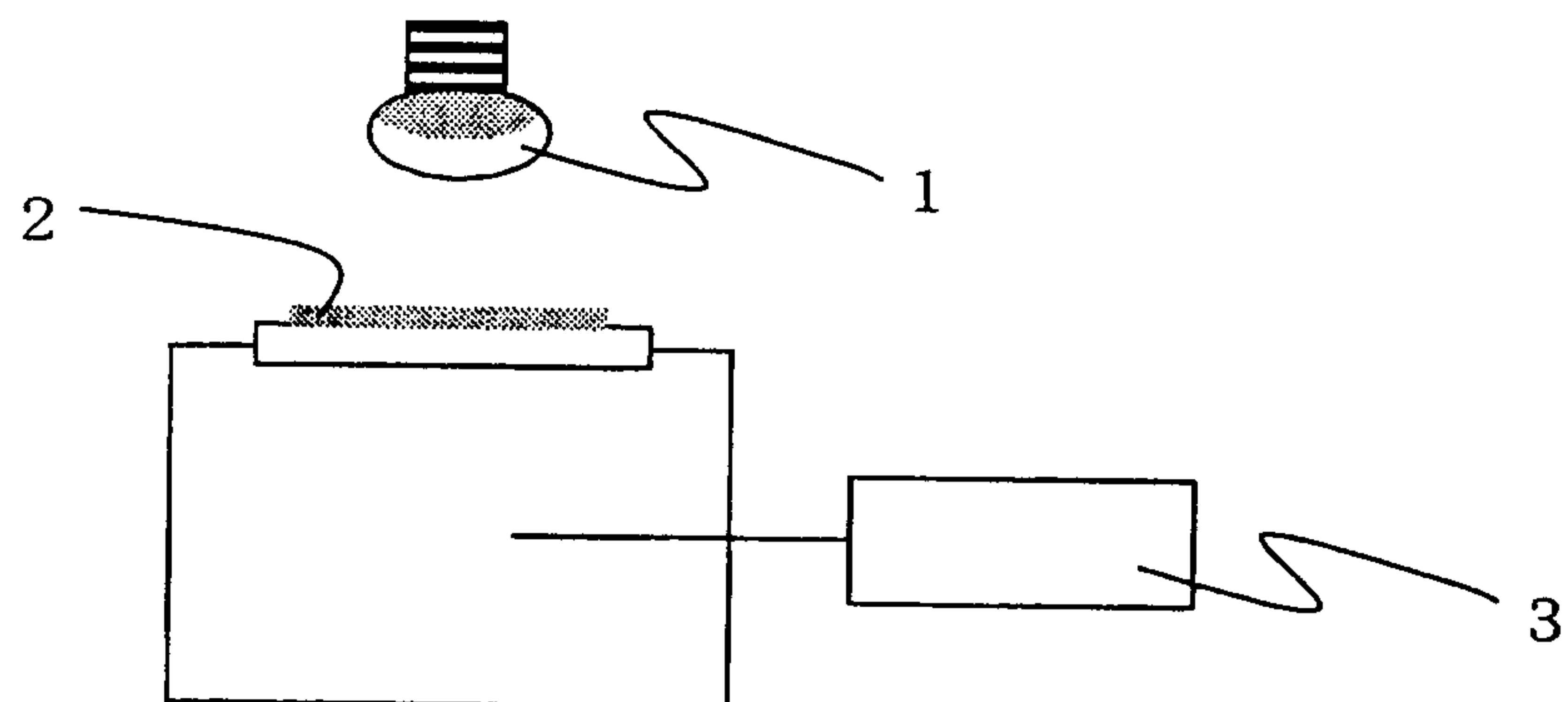


Fig.5

