

## DESCRIPTION

TITLE OF INVENTION:

FINE PIGMENT PARTICLES

5 TECHNICAL FIELD

The present invention relates to fine pigment particles to be added to or mixed in a coating material, particularly fine pigment particles which impart heat shielding property, abrading endurance, etc. to a coating film to be formed on a surface of an artificial construction.

10

BACKGROUND ART

Artificial structures as typically represented by asphalt pavement bodies are likely to absorb solar radiation energy of sunlight, which causes internal heat storage, and thereby the surface temperature becomes high, and heat island effect results in urban areas. Accordingly, it is desired to take countermeasures to improve urban area-heat environments including overcoming the heat island effect in urban areas. As one of such countermeasures, a means to coat the surface of a pavement body with a coating film having solar heat shielding property, has been studied.

As a conventional technique to form a coating film having solar heat shielding property, a means has been mainly adopted to adjust the solar radiation reflectivity of a surface coating film stipulated in JIS A5759 to wavelengths as broad as possible so as to reflect solar radiation energy in the visible light and infrared light ranges on the coating film surface without absorbing, whereby coating film components can be prevented from energetically excited due to absorption, and the solar radiation energy can be prevented from being converted to heat energy.

Specifically, a heat shielding coating material comprising a pigment which absorbs sunlight in the visible light range and reflects sunlight in the infrared range, a vehicle and as a case requires a white pigment has been proposed, and as the pigment to be used here, a sunlight shielding pigment (excluding the white pigment) having a solar radiation reflectivity of at least 10% and an L\* value of at most 80 in CIE 1976 L\*a\*b\* color space is mentioned as a color pigment (excluding white pigment) which reflects sunlight in the infrared range, and a titanium dioxide pigment is mentioned as the white

pigment (for example, Patent Document 1).

Further, a pavement body having plural coating layers having functions to obtain a solar heat shielding effect has been proposed, and such a pavement body comprises a first coating layer containing a white pigment and a second coating layer containing a pale color pigment, and as the white pigment, a white pigment having a solar radiation reflectivity of at least 15% is mentioned and as the pale color pigment, a pigment having a brightness ( $L^*$  value) of at most 40 is mentioned (for example, Patent Document 2).

## PRIOR ART DOCUMENTS

### 10 PATENT DOCUMENTS

Patent Document 1: JP-A-2004-251108

Patent Document 2: JP-A2005-61042

## DISCLOSURE OF INVENTION

### 15 TECHNICAL PROBLEM

As described above, various pigments have been used in order to shield solar heat, and various combinations have been studied. However, particularly in an application to an asphalt pavement body, there is a problem such that a load is always applied by traffic vehicles such as automobiles and thereby such an asphalt pavement body is abraded, and a part of the coating film is lost without lasting until the time of replacing the asphalt pavement. Therefore, one having an excellent lifespan (durability) of the coating film is preferred. .

However, heretofore, no study has been made from such a viewpoint. It is an object of the present invention to provide fine pigment particles which are white pigments having a heat shielding effect, and by using them, the heat shielding property of a coating film can be improved, while the abrading endurance can be improved, and the lifespan of the coating film can be prolonged.

## SOLUTION TO PROBLEM

30 The present invention has the following constructions.

(1) Fine pigment particles for a coating material, which comprise, as chemical components, from 50 to 95 mass% of  $Al_2O_3$ , from 5 to 40 mass% of  $ZrO_2$  and from 0 to

10 mass% of  $\text{SiO}_2$ , wherein the total amount of  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  is at least 80 mass%, in addition as crystals at least alumina crystal and zirconia crystal are contained, and the particle size  $D_{50}$  is from 0.1 to 80  $\mu\text{m}$ .

(2) The fine pigment particles for a coating material according to the above (1),  
5 wherein the fine pigment particles are used for a heat shield coating material.

(3) The fine pigment particles for a coating material according to the above (1) or (2), wherein the fine pigment particle size  $D_{90}$  is from 0.5 to 200  $\mu\text{m}$ .

(4) The fine pigment particles for a coating material according to any one of the above (1) to (3), wherein the total amount of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  contained in the fine  
10 pigment particles is at most 0.5 mass%.

(5) The fine pigment particles for a coating material according to any one of the above (1) to (4), wherein the solar radiation reflectivity of the fine pigment particles in all wavelength ranges is at least 80%.

(6) The fine pigment particles for a coating material according to any one of the  
15 above (1) to (5), wherein the  $L^*$  value of the fine pigment particles in CIE1976  $L^*a^*b^*$  color space is at least 80.

(7) The fine pigment particles for a coating material according to any one of the above (1) to (6), wherein the specific gravity of the fine pigment particles is from 3.4 to 4.0.

(8) The fine pigment particles for a coating material according to any one of the  
20 above (1) to (7), wherein the solar radiation reflectivity of the fine pigment particles in a near infrared range is at least 80%.

(9) The fine pigment particles for a coating material according to any one of the above (1) to (8), which contain from 3 to 8 mass% of  $\text{SiO}_2$ .

(10) The fine pigment particles for a coating material according to any one of the  
25 above (1) to (8), wherein the mass ratio of  $\text{Al}_2\text{O}_3$  to  $\text{ZrO}_2$  (amount of  $\text{Al}_2\text{O}_3$ /amount of  $\text{ZrO}_2$ ) is at least 2.

(11) A coating composition which comprises the fine pigment particles for a coating material as defined in any one of the above (1) to (10).

(12) A coating film formed from the coating composition as defined in the above  
30 (11).

(13) The coating film according to the above (12), wherein in the abrading

endurance test on a coating material for a traffic sign in accordance with JIS K5665, the mass reduction of the coating film subjected to abrasion for 1000 times rotation under the press load of 250 g is at most 40 g.

## 5 ADVANTAGEOUS EFFECTS OF INVENTION

The fine pigment particles of the present invention are white fine pigment particles having a high solar radiation reflectivity and a high  $L^*$  value in the CIE 1976  $L^*a^*b^*$ , whereby the heat shielding property is excellent, and a coating film in which the fine pigment particles are incorporated is excellent particularly in the heat shielding effect of solar heat. Further, the fine pigment particles of the present invention have a high durability and an effect to improve the abrading endurance of a coating film and are thereby preferably used as a coating film to be formed on a surface of artificial structures required to have a durability, particularly a coating film for asphalt pavements.

## 15 DESCRIPTION OF EMBODIMENTS

The fine pigment particles of the present invention (hereinafter may be referred to also as "the fine pigment particles") comprises from 50 to 95 mass% of  $Al_2O_3$ , from 5 to 40 mass% of  $ZrO_2$  and from 0 to 10 mass% of  $SiO_2$ , wherein the total amount of  $Al_2O_3$  and  $ZrO_2$  is at least 80 mass%, and as crystals, at least alumina crystal and zirconia crystal are contained. The alumina (corundum) crystal and the zirconia (vaterite) crystal are identified by X-ray diffraction. Further, hereinafter, in the specification, "mass%" is represented simply by "%".

In the fine pigment particles,  $Al_2O_3$  and  $ZrO_2$  are main components to form fine pigment particles, and except for a case where they form amorphous with a component such as  $SiO_2$ , they exist in the form of alumina crystal and zirconia crystal respectively. When the alumina crystal and the zirconia crystal exist as an alumina-zirconia eutectic crystal, the strength of the fine pigment particles themselves is improved, such being preferred. Whether the eutectic crystal is formed or not can be identified by structure observation by a scanning electron microscope.

Here, if the content of  $Al_2O_3$  is less than 50% or exceeds 95%, the content of  $ZrO_2$  becomes relatively excessive or too low, and the amount of alumina crystal and zirconia crystal, and a eutectic crystal thereof which constitute structure becomes low, whereby the strength of fine pigment particles may be low, such being not preferred.

Further, if the content of  $\text{ZrO}_2$  exceeds 40%, coloration may result, and cost may be extremely high.

In the fine pigment particles, the content of  $\text{Al}_2\text{O}_3$  is preferably from 50 to 95%, more preferably from 70 to 90%. Further, the content of  $\text{ZrO}_2$  is preferably from 5 to 40%, more preferably from 5 to 25%. Further, the ratio of contents of  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  (amount of  $\text{Al}_2\text{O}_3$ /amount of  $\text{ZrO}_2$ ) is preferably at least 2, more preferably at least 3, particularly preferably at least 5, so that a eutectic crystal could be sufficiently formed. Further, the amount of  $\text{Al}_2\text{O}_3$ /amount of  $\text{ZrO}_2$  is preferably at most 19.

When the total amount of components of such  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  is at least 80%, the solar radiation reflectivity and the  $L^*$  value will be good. Further, in the case of the above total amount, the strength of fine pigment particles to be obtained is improved, and the abrading endurance of a coating film to be formed is improved.

Further, in the present specification,  $\text{ZrO}_2$  means the total content of  $\text{ZrO}_2$  and  $\text{HfO}_2$ , because particularly in a case where  $\text{ZrO}_2$  is obtained by melting, it is difficult to chemically separate  $\text{HfO}_2$  from  $\text{ZrO}_2$ . However,  $\text{HfO}_2$  is not intentionally added as a starting material and always exists naturally in a  $\text{ZrO}_2$  source. Thus, without distinguishing the trace amount of  $\text{HfO}_2$ ,  $\text{HfO}_2$  is considered to be included in the content of  $\text{ZrO}_2$ .

Further, the fine pigment particles may contain  $\text{SiO}_2$ .  $\text{SiO}_2$  is a component of an amorphous structure with which alumina crystal and zirconia crystal are filled, and when  $\text{SiO}_2$  is contained, irregular breakage at a step of pulverization decreases, such being preferred. The content of  $\text{SiO}_2$  in the fine pigment particles is from 0 to 10%, more preferably from 3 to 8%.

Further, fine pigment particles to be obtained by the above composition has a high solar radiation reflectivity and a high  $L^*$  value, whereby such fine pigment particles are preferred as white fine pigment particles for shielding heat. Further, in order to improve the above properties, the above total amount is preferably at least 95%, more preferably at least 98%.

The solar radiation reflectivity of the fine pigment particles of the present invention is preferably at least 80%, more preferably from 90 to 99%. Here, so long as not particularly restricted, the solar radiation reflectivity in the present specification is a solar radiation reflectivity in the range of all wavelengths measured and calculated by the

calculation method in accordance with JIS K5602. The range of all wavelengths mentioned here is a range of a wavelength of from 300 to 2,500 nm including a near ultraviolet and visible light range (300 to 780 nm) and a near infrared range (780 to 2,500 nm). However, as samples for measuring a solar radiation reflectivity in the present specification, being different from a coating film defined in JIS, plate samples formed by dry pressing fine pigment particles are used.

Further, sunlight has energy in an infrared range in addition to the visible light range, and therefore, considering the solar radiation reflectivity in the near infrared range is effective to evaluate the heat shielding property (influence on heat storage).

Here, the solar radiation reflectivity in the near infrared range is preferably at least 80%, more preferably from 90 to 99%. The solar radiation reflectivity in the near infrared range is calculated by the same method under the same condition as mentioned above, except that the wavelength range to be measured is from 780 to 2,500 nm.

The  $L^*$  value of the fine pigment particles of the present invention is preferably at least 80, more preferably from 90 to 98. Here, the  $L^*$  value in the present specification is a brightness index defined by the CIE 1976  $L^*a^*b^*$  color space. The CIE 1976  $L^*a^*b^*$  color space is color space recommended by CIE (commission international de l'Eclairage) in 1976,  $L^*$  represents brightness, and  $a^*$  and  $b^*$  represent hue and chroma which are chromaticity. At present, the  $L^*$  value is widely used in various fields.

In the fine pigment particles,  $TiO_2$  and  $Fe_2O_3$  components are components which cause coloration, whereby the  $L^*$  value tends to be low. Thus, it is preferred that such components are not contained in the fine pigment particles as far as possible, and the total of the respective amounts of  $TiO_2$  component and  $Fe_2O_3$  component ( $TiO_2 + Fe_2O_3$ ) is preferably at most 0.5%, more preferably at most 0.3%, further preferably at most 0.1%.

In the fine pigment particles, oxides of transition metal elements are components which cause coloration. The total amount of contents of all oxides of these transition metal elements (including  $TiO_2$  component and  $Fe_2O_3$  component) is further preferably at most 1.0%, and the total amount of contents of all transition metal element oxides (including  $TiO_2$  component and  $Fe_2O_3$  component) is particularly preferably at most 0.5%. As oxides of transition metal elements other than  $TiO_2$  and  $Fe_2O_3$ ,  $MnO$ ,  $Co_2O_3$ ,  $NiO$ ,  $CuO$  and  $ZnO$  are mentioned as specific examples.

The particle size  $D_{50}$  of the fine pigment particles is from 0.1 to 80  $\mu\text{m}$ , whereby the dispersibility in a coating material is excellent, and the heat shielding effect of a coating film is made to be uniform. Further, from the viewpoint of handling efficiency and low cost, the particle size  $D_{50}$  is preferably at least 1  $\mu\text{m}$ , more preferably at least 5  $\mu\text{m}$ , particularly preferably at least 10  $\mu\text{m}$ . Further, the particle size is preferably at most 50  $\mu\text{m}$ , more preferably at most 40  $\mu\text{m}$ , particularly preferably at most 30  $\mu\text{m}$ . However, depending on film thickness to be applied, the particle size to be used is selected, and for example, in a case where a thin coating film at a level of a film thickness of 25  $\mu\text{m}$  is formed, the particle size  $D_{50}$  is preferably at most 10  $\mu\text{m}$ .

Further, the particle size  $D_{90}$  is preferably from 0.5 to 200  $\mu\text{m}$ , and in the case of such a particle size distribution, the dispersion in a coating material is excellent, such being preferred. The particle size  $D_{90}$  is preferably at most 100  $\mu\text{m}$ , more preferably at most 80  $\mu\text{m}$ , particularly preferably at most 70  $\mu\text{m}$ , whereby the agglomeration of a coating film, chunk of a coating film and clogging of a device for blowing to form a coating film can be prevented.

Further, the particle sizes  $D_{50}$  and  $D_{90}$  mentioned in the present specification are particle sizes having integrated amount of 50% and 90% by volume standard in a cumulative particle size curve of a particle size-distribution measured by a laser diffraction/scattering type particle size distribution measuring apparatus.

The specific gravity of the fine pigment particles is preferably from 3.4 to 4.0, whereby the dispersibility at a time of blending the fine pigment particles in a base resin to prepare a coating material is good. The specific gravity is more preferably from 3.8 to 4.0. If the specific gravity is less than 3.4, the fine pigment particles tend to easily separate from other components in a coating material, and if the specific gravity exceeds 4.0, the fine pigment particles tend to easily precipitate, and the dispersibility tends to deteriorate. The specific gravity is a value calculated from the ratio of the composition of respective components.

Next, the process for producing the fine pigment particles of the present invention (hereinafter referred to as also "the production process") will be described. The production process may, for example, be a process wherein an alumina material, a zirconia material and other essential materials are mixed to prepare a mixed material of which chemical components are adjusted to be the above mentioned contents, the

mixed material is melted by an arc electric furnace or the like, and a high temperature melt is discharged from the furnace and grain refining to prepare ceramic particles (hereinafter referred to simply as "melting method") or a method of sintering a prepared material to prepare ceramic particles (hereinafter referred to simply as "sintering method"), and the obtained ceramic particles are further subjected to grain refining by a pulverization means.

In a case where the melting method is employed as the production process, the type of the melting furnace for melting prepared materials is not particularly restricted, however, a heating type such as a burner, an electric resistance, arc or cokes may be mentioned. Particularly, the arc type is preferred, whereby a high temperature can be relatively easily obtained, the uniformity of a melt is high, the facility of the furnace is simple, and the handling efficiency is excellent.

In a case where the melting process is employed as the production process, as the operating conditions for melting materials in a melting furnace, when the materials are melted by using a trans of 500 kVA to 5,000 kVA as a power source, it is usually preferred that the voltage at a time of arc is from 80 to 300 (V), and the electric current is from 500 to 12,000 (A), whereby the distance between electrodes and a melt can be appropriately kept, a product in the electric furnace can be appropriately maintained, and the stable melting can be realized. The final melting temperature is preferably from 1,950 to 2,100 (°C).

In a case where the melting process is employed as the production process, after melting the prepared materials, the melt is discharged to outer atmosphere from an outlet installed on an outer wall of the melting furnace. For the discharge, it is preferred to tilt the melting furnace, whereby the discharging can be easily carried out. The melt is flown out from the outlet cooled and solidified to be a ceramic ingot by outer atmosphere.

As a case requires, the discharged and formed ceramic particles are roughly pulverized by a crusher or the like to the desired particle size (for example, particle size at a level of 0.5 to 5 mm larger than the fine pigment particles).

In a case where the melting process is employed as the production process, it is preferred that smaller particles are formed at a time of discharging, whereby a subsequent fine pulverization can be easily carried out. For example, as one means,

particles are dropped from at a level of 100 mm, and compressed air is blown from behind, whereby the ceramic ingot can be formed into small particles.

The ceramic particles thus obtained are further formed into smaller particles so as to have a particle size  $D_{50}$  of from 0.1 to 80  $\mu\text{m}$  by a pulverization means such as a vibration mill, a ball mill, an air type jet mill or the like, whereby the fine pigment particles of the present invention are obtained.

Further, the fine pigment particles thus obtained can be used also as a coating material to be used in a field of coating materials or may be mixed with another pigment to prepare a coating material for shielding heat. Usually, color pigments mentioned below may be incorporated in the fine pigment particles to control color tone for use.

The pigment is not restricted, so long as it is commonly used for a coating material. At least one selected from the group consisting of a color pigment such as titanium dioxide, phthalocyanine blue, phthalocyanine green, quinacridone, indanthrone, isoindolinone, perylene, anthrapyrimidine, benzimidazolone, yellow iron oxide or red iron oxide, and as a case requires an extender pigment such as barium sulfate or aluminum silicate may be used. Further, as a glitter, a mica pigment, an aluminum foil, a bronze foil, a tin foil, a silver foil, a titanium metal foil, a stainless steel foil, an alloy foil such as nickel-copper, a foil covered with a plastic or a metal foil pigment such as a foil form phthalocyanine blue, may be used. As the extender pigment, calcium carbonate, gypsum, clay, talc or the like may also be used.

The type and the form of the coating material is not particularly restricted, for example, a heat curing coating material, a thermoplastic coating material, a normal temperature drying coating material, a normal temperature curing coating material or an activation energy radiation curing coating material may be used. Further, as the form of the coating material, the coating material may be used in any form of a solvent coating material, an aqueous coating material, a non-hydro emulsion coating material, a solvent-free coating material, a powdery coating material, etc.

Here, a resin for a coating material which is a base is not particularly restricted, so long as it is commonly used for a coating material. For example, an acrylic resin, a methyl methacrylate (MMA) resin, an alkyd resin, a polyester resin, a silicone modified polyester resin, a silicone modified acrylic resin, an epoxy resin, a polycarbonate resin, a silicate resin, an urea resin, an urethane resin, a chlorine type resin or a fluorine type

resin may be mentioned. As a case requires, as a curing agent, an amino resin such as a melamine resin or a crosslinkable resin such as isocyanate or block isocyanate may be contained.

The coating composition of the present invention comprises the fine pigment particles of the present invention and a resin for a coating material. The mass ratio of the fine pigment particles to the resin for a coating material in the coating composition, namely the fine pigment particles : the resin for a coating material, is preferably 5 to 150:100, more preferably 20 to 50:100. The coating composition of the present invention preferably further contains a solvent such as an organic solvent or water.

As a case requires, a fine particle state filler, an additive, a solvent or the like may be added to the coating composition of the present invention. The fine particle state filler is not particularly restricted, so long as it is one commonly used for a coating material, and for example, fine particles made of  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , zirconium silicate or the like may be mentioned.

Further, as another additive, a conventionally used additive such as a delustering agent such as silica or alumina; an anti-foaming agent; a leveling agent; an anti-sagging agent; a surface adjustor; a viscosity adjustor; a dispersant; an ultraviolet absorber or a wax may, for example, be mentioned.

Further, the solvent is not particularly restricted, so long as it is ordinarily used for a coating material. For example, an aromatic hydrocarbon such as toluene, xylene, Solvesso 100 or Solvesso 150; an ester such as ethyl acetate or butyl acetate; a ketone such as methyl ethyl ketone, methyl isobutyl ketone, cyclohexane or isophorone; or water may be mentioned. The solvent is optionally selected depending on the solubility, the rate of evaporation, the safety, etc. Such a solvent may be used alone, or two or more solvents may be used in combination.

A coating composition may, for example, be prepared by using them as described below. First, a dispersion paste containing a resin and a pigment is prepared by using a device commonly used for preparing a pigment dispersion such as a roller mill, a paint shaker, a pot mill, a disperser or a sand grind mill, and a resin, each additive, an organic solvent, a curing agent, a catalyst, etc. are added thereto and uniformized to prepare a coating composition.

As described above, a coating film formed from the coating composition of the

present invention has excellent heat shielding property and practically useful abrading endurance. The abrading endurance of the coating film of the present invention can be tested in accordance with the abrading endurance test for a coating material for a traffic sign limited in JIS K5665. In the abrading endurance test, the mass reduction of the coating material subjected to abrasion for 1,000 times rotation under the press load of 250 g is preferably at most 40 g, preferably from 10 to 30 g.

## EXAMPLES

Now, the present invention will be described with reference to Examples, but it should be understood that the present invention is by no means limited to these Examples. Ex. 1, 2 and 3 are Working Examples, and Ex. 4 and 5 are Comparative Examples.

The measuring methods in Examples will be described.

[Solar radiation reflectivity]

The obtained fine pigment particles were subjected to dry press molding by applying a pressing load of 30 t so as to be a disk shape molded product having a diameter 40 mm and thickness 4 mm, the spectral reflectance between 300 nm to 2,500 nm was measured by a spectrophotometer (tradename: U-4100, manufactured by Hitachi High-Technologies Corporation) in accordance with JIS K5602, and the solar radiation reflectivity was calculated based on the weight coefficient of the standard solar light.

[L\* value in CIE 1976 L\*a\*b\* color space]

The obtained fine pigment particles were subjected to dry press molding by applying a pressing load of 30 t so as to be a disk shape molded product having a diameter 40 mm and thickness 4 mm, the spectral reflectivity in a visible light range was measured by a spectrophotometer (tradename: U-4100, manufactured by Hitachi High-Technologies Corporation) in accordance with JIS K5602, and an L\* was calculated.

[Abrading endurance]

A test sample coating film was prepared by spray coating/drying on a steel plate of 10 cm<sup>2</sup>. In accordance with the abrading endurance test of a coating material for a traffic sign limited in JIS K5665, the abrading endurance of the test sample coating film was tested. Here, as the Taber abrading test condition, an abrading wheel was CS-17

(manufactured by TABER INDUSTRIES), the mass reduction of the coating film subjected to abrasion for 1,000 times rotation under each press load of 250 g was measured.

(Ex. 1)

5        A Bayer alumina having a purity of at least 99.3% was used as an  $\text{Al}_2\text{O}_3$  material, an electromelting zirconia material having a purity of at least 99% was used as a  $\text{ZrO}_2$  material, and a silica sand having a purity of at least 99% was used as an  $\text{SiO}_2$  material. These materials were mixed so as to be the predetermined proportion and melted in a melting furnace.

10        An arc type melting furnace having a core diameter of 1.5 m, a height of 1.5 m and a core volume of  $2.5 \text{ m}^3$  was used as the melting furnace, and a 1,100 kVA trans was prepared as a power source. Further, as a lining refractory material in the melting furnace, an electrocast refractory having an alumina content of 95% was used. As electrodes, three electrodes having a diameter of 15 cm were used.

15        Under the melting condition of a voltage of from 100 V to 250 V and an electric power of 800 kW to 1,000 kW, 600 kg of one time amount to be added was divided to three times and added in the furnace separately at an interval of 10 minutes to 15 minutes. The total time for adding materials was from 30 minutes to 45 minutes, and the melting time was from 80 minutes 100 minutes.

20        Then, water was added at a rate of 2 L/min to compressed air compressed at a pressure of 4 MPa, followed by spraying from a nozzle. An exhausted melt was dropped from a height of 100 mm, and compressed air was blown to the melt from the bottom at a high speed to form particles. The particles were collected in a collection container made of a metal and protected with a refractory material, whereby ceramic  
25        particles having a diameter of 0.1 to 5.0 mm were formed.

      The obtained ceramic particles were adjusted to ceramic particles having a mill volume ratio of 50% by a ball mill having a diameter of 1.5 m and a volume amount of 2,000 L, filled and pulverized for 6 hours so as to be small particles, and thereby fine  
30        pigment particles having the particle size  $D_{50}$  of 13  $\mu\text{m}$  and  $D_{90}$  of 40  $\mu\text{m}$  were obtained. Further, the obtained pigment particles were analyzed by X-ray diffraction (RINT2000 powder X-ray diffraction apparatus, manufactured by Rigaku Corporation), and peaks of alumina crystal and zirconia crystal were observed. Further, by the

structure observation by a scanning electron microscope (TM3000 Miniscope, manufactured by Hitachi High-Technologies Corporation), it was observed that the alumina crystal and the zirconia crystal were eutectic structure (alumina-zirconia eutectic crystal).

5        The obtained fine pigment particles had a chemical composition of  $\text{Al}_2\text{O}_3$  of 80%,  $\text{ZrO}_2$  of 10% and  $\text{SiO}_2$  of 9%. Further,  $\text{Fe}_2\text{O}_3$  which lowers a solar radiation reflectivity and brightness was 0.10%, and  $\text{TiO}_2$  was 0.10%.

      Respective properties of the fine pigment particles were measured. As a result, the solar radiation reflectivity was 90%, the solar radiation reflectivity in a near infrared  
10    range was 89%, the  $L^*$  value was 96, and the specific gravity was 3.9.  
(Ex. 2)

      1 part by mass of the fine pigment particles obtained in Ex. 1 was dissolved in 2 parts by mass of a commercially available transparent acrylic lacquer (acrylic lacquer Eight A8-300, manufactured by Natoco Co., Ltd.) and sufficiently stirred to prepare a  
15    properly dispersed coating composition, followed by spray coating a steel plate of 10  $\text{cm}^2$  with the coating composition and drying it to prepare a test sample coating film. The coating composition was sprayed so that the dried film thickness of the coating film would be 240  $\mu\text{m}$  in thickness. The abrading endurance of the test sample coating film was measured in accordance with the abrading endurance test of a coating material for  
20    a traffic sign stipulated in JIS K5665. Here, as the taber abrading test condition, an abrading wheel was CS-17 (manufactured by TABER INDUSTRIES), each press load was 250 g, and the mass reduction of the coating film subjected to 1,000 times rotation was measured as the abraded mass. The test was repeated 6 times, the average abraded mass was 18.3 g, and the standard deviation was 1.7 g.

25    (Ex. 3)

      31 Parts by mass of the fine pigment particles obtained in Ex. 1 was dissolved in 69 parts by mass of A liquid of a commercially available two liquid mixing type methyl methacrylate (MMA) resin (Acrysirup XD-1009, manufactured by RYOKO Co., Ltd.), and  
30    31 parts of the fine pigment particles obtained in Ex. 1 was dissolved in 69 parts by mass of B liquid, followed by mixing and sufficiently stirring so as to be sufficiently dispersed to prepare a coating composition. Then, a 10  $\text{cm}^2$  straight plate was spray coated with the coating composition and dried to prepare a test sample coating film.

The spray coating was carried out so that the dried film thickness of the coating film would be 200  $\mu\text{m}$  in thickness. The abrading endurance of the test sample coating film was measured in accordance with the abrading endurance test of a coating material for a traffic sign stipulated in JIS K5665. Here, as the taber abrading test condition, an  
5 abrading wheel was CS-17 (manufactured by TABER INDUSTRIES), and the mass reduction of the coating film subjected to abrasion for 1,000 times rotation each press load of 250 g was measured as the abraded mass. The test was repeated 3 times, the average abraded mass was 29.6 g, and the standard deviation was 1.4 g.

(Ex. 4)

10 The abrading endurance test was carried out under the same condition, except that instead of the fine pigment particles obtained in Ex. 1, a coating film formed by using conventionally used another type pigments and the same acrylic lacquer by the same method as in Ex.2. Here, as the conventionally used pigments, titanium oxide (CR-EL, manufactured by Ishihara Sangyo Kaisha, Ltd.), zinc oxide (JIS2,  
15 manufactured by Mitsui Mining & Smelting Co., Ltd.) and calcinated kaolin (Snow White 90, manufactured by China Mineral Processing, Ltd.) were respectively used. As the mass reduction in the abrading test under the same condition, in the case of titanium oxide, the average was 69.8 g, and the standard deviation was 5.6 g; in the case of zinc oxide, the average was 54.6 g, and the standard deviation was 8.0 g; and in the case of  
20 calcinated kaolin, and the average was 47.0 g, and the standard deviation was 5.4 g.

(Ex. 5)

The abrading endurance test was carried out under the same condition, except that instead of the fine pigment particles obtained in Ex. 1, a coating film formed by using conventionally used another type pigments and the same methyl methacrylate by  
25 the same method as in Ex.3. Here, as the conventionally used pigments, titanium oxide (CR-EL, manufactured by Ishihara Sangyo Kaisha, Ltd.), zinc oxide (JIS2, manufactured by Mitsui Mining & Smelting Co., Ltd.) and calcium carbonate (SL-700, manufactured by Takehara Kagaku Kogyo Co., Ltd.) were respectively used. As the mass reduction in the abrading test under the same condition, in the case of titanium  
30 oxide, the average was 52.3 g, the standard deviation was 0.6; in the case of zinc oxide, the average was 51.9 g, the standard deviation was 0.9 g; and in the case of calcium carbonate, the average was 44.9 g, and the standard deviation was 1.6 g.

It is evident from these results that when the product of the present invention was used as pigments for a coating film, as compared with the conventionally used pigments, the abraded amount of the coating film remarkably decreased, and such a coating film had a practically excellent abrading endurance.

5 As described above, the fine pigment particles of the present invention have a high solar radiation reflectivity and thereby are preferably used as fine pigment particles for shielding heat. Further, the fine pigment particles of the present invention have excellent abrading endurance, whereby they are preferably used in applications in which the durability is required, particularly an asphalt pavement which continuously  
10 receives load from traffic vehicles.

#### INDUSTRIAL APPLICABILITY

According to the present invention, it is possible to provide fine pigment particles which are excellent in solar radiation reflectivity and preferably used as a heat shielding  
15 coating material for forming a coating film on a surface of asphalt pavements, buildings, etc. Further, in addition to the applications for heat shielding, these fine pigment particles have a high brightness and a high whiteness, whereby they can be used as fine pigment particles blended in conventional coating materials.

20 The entire disclosure of Japanese Patent Application No. 2012-252235 filed on November 16, 2012 including specification, claims, drawings and summary is incorporated herein by reference in its entirety.

## CLAIMS

1. Fine pigment particles for a coating material, which comprise, as chemical components, from 50 to 95 mass% of  $\text{Al}_2\text{O}_3$ , from 5 to 40 mass% of  $\text{ZrO}_2$  and from 0 to 10 mass% of  $\text{SiO}_2$ , wherein the total amount of  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  is at least 80 mass%, in  
5 addition as crystals at least alumina crystal and zirconia crystal are contained, and the particle size  $D_{50}$  is from 0.1 to 80  $\mu\text{m}$ .
2. The fine pigment particles for a coating material according to Claim 1, wherein the fine pigment particles are used for a heat shield coating material.
3. The fine pigment particles for a coating material according to Claim 1 or 2,  
10 wherein the fine pigment particle size  $D_{90}$  is from 0.5 to 200  $\mu\text{m}$ .
4. The fine pigment particles for a coating material according to any one of Claims 1 to 3, wherein the total amount of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  contained in the fine pigment particles is at most 0.5 mass%.
5. The fine pigment particles for a coating material according to any one of Claims 1  
15 to 4, wherein the solar radiation reflectivity of the fine pigment particles in all wavelength ranges is at least 80%.
6. The fine pigment particles for a coating material according to any one of Claims 1 to 5, wherein the  $L^*$  value of the fine pigment particles in CIE1976  $L^*a^*b^*$  color space is at least 80.
- 20 7. The fine pigment particles for a coating material according to any one of Claims 1 to 6, wherein the specific gravity of the fine pigment particles is from 3.4 to 4.0
8. The fine pigment particles for a coating material according to any one of Claims 1 to 7, wherein the solar radiation reflectivity of the fine pigment particles in a near infrared range is at least 80%.
- 25 9. The fine pigment particles for a coating material according to any one of Claims 1 to 8, which contain from 3 to 8 mass% of  $\text{SiO}_2$ .
10. The fine pigment particles for a coating material according to any one of Claims 1 to 8, wherein the mass ratio of  $\text{Al}_2\text{O}_3$  to  $\text{ZrO}_2$  (amount of  $\text{Al}_2\text{O}_3$ /amount of  $\text{ZrO}_2$ ) is at least 2.
- 30 11. A coating composition which comprises the fine pigment particles for a coating material as defined in any one of Claims 1 to 10.
12. A coating film formed from the coating composition as defined in Claim 11.

13. The coating film according to Claim 12, wherein in the abrading endurance test on a coating material for a traffic sign in accordance with JIS K 5665, the mass reduction of the coating film subjected to abrasion for 1,000 times rotation under the press load of 250 g is at most 40 g.