

MULTILAYER COATING FILM, AND METHOD FOR FORMING MULTILAYER COATING FILM

TECHNICAL FIELD

The present invention relates to a multilayer coating film, and a method for forming a multilayer coating film.

BACKGROUND ART

Heretofore, energy saving has also been required in buildings such as residence, from the viewpoint of a reduction in environmental burden and a reduction in costs.

Therefore, it is believed that, in order to reduce energy to be consumed in buildings such as a residence, an external surface of a roof and an exterior wall of buildings is coated with a coating material having heat insulating properties and heat shielding properties to form a coating film having heat insulating properties and heat shielding properties, thus leading to suppression of a rise in room temperature. There has been known, such a coating film having heat insulating properties and heat shielding properties, a heat shielding insulation laminate (multilayer coating film) comprising of a base material layer (A), a heat insulating under coating layer (B) to be formed of an under coating material including a binder and hollow particles, and a decorative material layer (C) to be formed of a decorative coating material including an organic binder and colored particles, which are sequentially formed on an external surface, the heat shielding insulation

laminate further including, as colored particles, particles in which elementary particles are coated with an infrared-reflecting powder and/or particles made of an assembly of an infrared-reflecting powder (see Patent Document 1).

There has also been known technology in which a building is subjected to single layer coating using a coating material composition having heat shielding properties, comprising a hollow resin prepared by adhering calcium carbonate and talc to a shell, a hollow glass, whitish marble, and a synthetic resin emulsion (see Patent Document 2).

Patent Document 1: Japanese Unexamined Patent Application, Publication No. 2009-90527

Patent Document 2: Japanese Unexamined Patent Application, Publication No. 2011-79999

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

The multilayer coating film of Patent Document 1 has heat insulating properties because it including hollow particles, and also has heat shielding properties because of including the infrared-reflecting powder. However, satisfactory heat insulating properties and heat shielding properties have never been obtained.

In the heat insulating under coating layer (B) of the multilayer coating film of Patent Document 1, the hollow particles and infrared-reflecting powder are individually mixed, so that there is a need to increase the pigment weight

content (PWC) of the coating material so as to improve the heat insulating properties and heat shielding properties of the coating film. However, an increase in PWC of the coating material may impart brittleness to the coating film and also cause deterioration of water-resistant adhesiveness.

Also in the multilayer coating film of Patent Document 1, because of insufficient heat insulating properties and heat shielding properties, steam is likely to be generated from the base material layer (A). Generation of steam from the base material layer (A) leads to accumulation of steam at the interface between the heat insulating under coating layer (B) and the decorative material layer (C), thus resulting in blistering of the decorative material layer (C). Accordingly, the decorative material layer (C) is limited to those having steam transmissivity.

Since the coating film of Patent Document 2 include no infrared-reflecting powder, sufficient heat insulating properties and heat shielding properties have never been obtained.

In the hollow resin in which calcium carbonate and talc are adhered to the shell disclosed in Patent Document 2, calcium carbonate and talc each having large specific gravity are adhered to the shell section so as to solve such a problem that the hollow resin itself has small specific gravity and is likely to scatter during mixing. In Patent Document 2, a shell surface of the hollow resin is not coated for the purpose of improving heat insulating properties and heat shielding

properties of the coating film.

Currently, there has never been obtained a coating film to be formed on an external surface of a building, which has both satisfactory heat insulating properties and heat shielding properties, and also has satisfactory water-resistant adhesiveness.

In light of the above circumstances, the present invention has been made and an object thereof is to provide a multilayer coating film to be formed on an external surface of a building, which has both higher heat insulating properties and heat shielding properties than a conventional one, and also has satisfactory water-resistant adhesiveness; and a method for forming a multilayer coating film.

Means for Solving the Problems

In order to achieve the above object, the present invention provides a multilayer coating film to be formed on an external surface of a building, comprising of a base layer (A), and an upper coating layer (B) to be formed on the base layer (A), wherein the base layer (A) is formed of a base coating material, the base coating material includes particles having hollow sections, and a resin, at least one part of the particles having hollow sections is coated with an infrared-reflecting powder, and the infrared-reflecting powder includes a metal oxide having a refractive index of 1.7 to 3.0.

The content of the particles in the solid component of the base coating material is preferably within a range of 10 to 70% by mass.

It is preferred that the resin included in the base coating material is a synthetic resin emulsion particle, the base coating material further includes a particle crosslinking agent, and the particle crosslinking agent crosslinks the synthetic resin emulsion particles.

It is preferred that the synthetic resin emulsion particles are obtained by polymerizing a monomer mixture including a ketone group- or aldehyde group-containing acrylic monomer, the particle crosslinking agent is a compound having two or more hydrazide groups in a molecule, and the content of the ketone group- or aldehyde group-containing acrylic monomer in the monomer mixture is within a range of 0.1 to 30% by mass.

It is preferred that the synthetic resin emulsion particles are obtained by polymerizing a monomer mixture including a carboxyl group-containing acrylic monomer, the particle crosslinking agent is a compound having two or more carbodiimide groups in a molecule, and the content of the carboxyl group-containing acrylic monomer in the monomer mixture is within a range of 0.1 to 5% by mass.

It is preferred that the upper coating layer (B) is formed of an upper coating material, the upper coating material does not substantially include any black pigment, and the brightness is determined in accordance with JIS K 5675 7.8 c) of the coating film formed of the upper coating material is 50 or less.

It is preferred that the upper coating material includes

a resin and an infrared-reflecting powder, and the content of the infrared-reflecting powder in the upper coating material is 30% by mass or less.

The present invention also provides a method for forming a multilayer coating film in which the multilayer coating film is formed on an external surface of a building, the method comprising the steps of: coating the external surface of the building with a base coating material including particles having hollow sections, and a resin to form a base layer (A), and forming an upper coating layer (B) on the base layer (A), wherein at least one part of a surface of the particles having hollow sections is coated with an infrared-reflecting powder, and the infrared-reflecting powder includes a metal oxide having a refractive index of 1.7 to 3.0.

Effects of the Invention

According to the present invention, it is possible to provide a multilayer coating film to be formed on an external surface of a building, which has both higher heat insulating properties and heat shielding properties than a conventional one, and also has satisfactory water-resistant adhesiveness; and a method for forming a multilayer coating film. In the present invention, it is believed that mixing a base layer of the multilayer coating film with particles having hollow sections, at least part of a surface of the particles being coated with an infrared-reflecting powder, enables a decrease in a pigment weight content (PWC) of a coating material as compared with the case of individually mixing conventional

particles with an infrared-reflecting powder, thus leading to an improvement in brittleness of the coating film, so that water-resistant adhesiveness of the coating film is improved. In the present invention, it is believed that coating of at least one part of particles having hollow sections with an infrared-reflecting powders enables enhancement in surface reflectance, thus leading to an improvement in heat shielding properties of the coating film as compared with the case of mixing with the infrared-reflecting powder alone.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

Embodiments of the present invention will be described in detail below.

Multilayer Coating Film

The multilayer coating film according to the embodiment of the present invention is a multilayer coating film to be formed on an external surface of a building, comprising of a base layer (A), and an upper coating layer (B) to be formed on the base layer (A), wherein the base layer (A) is formed of a base coating material, the base coating material includes particles having hollow sections, at least one part of a surface of the particles being coated with an infrared-reflecting powder, and a resin, and the infrared-reflecting powder includes a metal oxide having a refractive index of 1.7 to 3.0. The multilayer coating film according to the present embodiment is formed on an external surface of a building, and has both high heat insulating properties and heat shielding

properties.

There is no particular limitation on an external surface (base material) of a building on which the multilayer coating film according to the present embodiment is formed. Examples of the base material on which the multilayer coating film of the present embodiment is formed include a metal base material, a plastic base material, an inorganic material base material, and the like. Examples of the metal base material include an aluminum sheet, an iron sheet, a galvanized steel sheet, an aluminum-zinc plate steel sheet, a stainless steel sheet, a tin sheet, and the like. Examples of the plastic base material include an acrylic sheet, a polyvinyl chloride sheet, a polycarbonate sheet, an ABS sheet, a polyethylene terephthalate sheet, a polyolefin sheet, and the like. Examples of the inorganic material base material include concrete, mortar, a cement board, an extruded sheet, a slate sheet, a PC sheet, an ALC sheet, ceramic building materials mentioned in JIS A 5422, JIS A 5430, etc., such as a ceramic siding material and a fiber-reinforced cement sheet, a glass base material, and the like. A so-called coated old coating film may also exist on the external surface. The multilayer coating film according to the present embodiment is preferably formed on a surface of inorganic material base materials which are used for an external surface of an exterior wall and a roof of a residence or a building, and more preferably used on a surface of inorganic building materials such as a ceramic building material, concrete, mortar, ALC, and others.

[Base Layer (A)]

The base layer (A) is formed on an external surface of a building. The base layer (A) is formed from a base coating material, and the base coating material includes particles having hollow sections, at least one part of a surface of the particles being coated with an infrared-reflecting powder, and a resin.

Particles having hollow sections, at least one part of a surface of the particles being coated with an infrared-reflecting powder (hereinafter sometimes referred to as "infrared-reflecting particles") included in the base coating material are particles having one or more hollow sections in particles. The infrared-reflecting powder include a metal oxide having a refractive index of 1.7 to 3.0. Examples of the metal oxide having a refractive index of 1.7 to 3.0 include titanium dioxide (having a refractive index of 2.76), zinc oxide (having a refractive index of 1.95), magnesium oxide (having a refractive index of 1.72), zirconium oxide (having a refractive index of 2.76), yttrium oxide (having a refractive index of 1.82), alumina (having a refractive index of 1.76), and the like. If the refractive index of the metal oxide included in the infrared-reflecting powder is less than 1.7, infrared rays may not satisfactorily diffuse and reflect in the base layer (A), thus failing to obtain the objective heating shielding function. Whereas, if the refractive index is more than 3.0, non-white metal oxide such as Bengal red or vermilion is included, so that see through may cause

deterioration of design properties in the case of coating with a white upper coating material. The metal oxide included in the infrared-reflecting powder is preferably a titanium dioxide. When the infrared-reflecting powder includes the titanium dioxide, the multilayer coating film exhibits high heat shielding performance. Calcium carbonate has a refractive index of 1.57 and talc has a refractive index of 1.59.

Infrared-reflecting particles may be either particles in which at least one part of a surface of particles made of an organic or inorganic substance is coated with an infrared-reflecting powder, or particles having hollow sections formed by an infrared-reflecting powder having hollow sections.

Infrared-reflecting particles made of an organic substance are produced, for example, in the following manner. First, a liquid, which is converted into a gas at a softening temperature or lower of a shell, is included in a shell made of a vinyl chloride resin, a vinyl alcohol resin, an acrylic resin, or the like. Next, titanium dioxide exemplified as one of infrared-reflecting powders is adhered to a surface of the shell in a state where the shell is thermally softened to a hollow resin in which the shell is thermally expanded by heating to a softening temperature or higher or the shell to obtain infrared-reflecting particles made of an organic substance (see, for example, JP 1993-285376 A). Infrared-reflecting particles made of an inorganic substance are produced, for example, in the following manner. First, an inorganic micro hollow body made of a vitreous raw material is

softened by heating. Next, titanium dioxide as one of infrared-reflecting powders is adhered to a surface in a state where the inorganic micro hollow body is softened to obtain infrared-reflecting particles made of an inorganic substance (see, for example, JP 1998-25139 A).

The base layer (A) exhibits both high heat insulating properties and heat shielding properties by including the above-mentioned particles having hollow sections, at least one part of a surface of the particle being coated with an infrared-reflecting powder. In more detail, air in a hollow space of particles imparts heat insulating properties to the base layer (A), and the infrared-reflecting powder (metal oxide) of a particle surface imparts heat shielding properties of the base layer (A) by diffuse reflection of infrared rays. Here, the base layer (A) including hollow particles in which a metal oxide having a refractive index of 1.7 to 3.0 exists on a surface in the present embodiment enables infrared rays to diffuse and reflect more strongly than the case where the metal oxide and hollow particle separately exist in the coating film. The reason is not necessarily clear, but it is assumed that an air layers and a resin layer, each having a different refractive index, are adjacent to each other via a metal oxide having a refractive index of 1.7 to 3.0, thus leading to amplification of diffuse reflection of infrared rays.

Infrared-reflecting particles preferably have an average particle diameter of 0.1 to 300 μm . If the average particle

diameter of infrared-reflecting particles is less than 0.1 μm , heat shielding properties of the multilayer coating film may deteriorate. Whereas, if the average particle diameter of infrared-reflecting particles is more than 300 μm , hollow sections may burst during preparation of the base coating material, thus failing to exhibit heat insulating properties. Therefore, infrared-reflecting particles are not sufficiently coated with the resin, thus leading to a decrease in strength of the coating film. The average particle diameter of infrared-reflecting particles is a volume average particle diameter measured by Laser Diffraction Particle Size Analyzer (e.g., LA-920 manufactured by HORIBA, Ltd., Model SALD-1100 manufactured by Shimadzu Corporation, etc.) having measurement principle [light scattering method (25°C)] mentioned in JIS Z 8825-1:2001.

The content of infrared-reflecting particles in the solid component of the base coating material is preferably 10 to 70% by mass. If the content of the above particles in the solid component of the base coating material is less than 10% by mass, heat insulating properties and heat shielding properties of the coating film may deteriorate. Whereas, if the content of the above particles is more than 70% by mass, hollow sections in the base layer (A) may increase, thus causing a decrease in strength of the coating film. The content of the above particles is more preferably 20 to 50% by mass.

There is no particular limitation on the resin included in the base coating material. The resin included in the base

coating material is a synthetic resin emulsion particle, and it is preferred that the base coating material further include a particle crosslinking agent capable of crosslinking synthetic resin emulsion particles. When the base coating material includes synthetic resin emulsion particles and a particle crosslinking agent, whereby, these components undergoes crosslinking at normal temperature so that a strong coating film can be formed in the case of forming the base layer (A).

Synthetic resin emulsion particles can be obtained by polymerizing a monomer mixture including a ketone group- or aldehyde group-containing acrylic monomer, and the particle crosslinking agent preferably includes a compound having two or more hydrazide groups in a molecule. When employing a combination of the synthetic resin emulsion particles and particle crosslinking agent, a ketone group and an aldehyde group react with a hydrazide group at normal temperature to form a crosslinked structure between synthetic resin emulsion particles, so that a strong coating film can be formed.

Specific examples of the ketone group or aldehyde group-containing acrylic monomer include acrolein, diacetone (meth)acrylamide, formyl styrol, vinyl alkyl ketone having 4-7 carbon atoms (e.g., vinyl methyl ketone, vinyl ethyl ketone, vinyl butyl ketone, etc.), acetoacetoxyethyl methacrylate, and the like. Among these monomers, diacetone (meth)acrylamide is preferably used since the thus obtained synthetic resin emulsion particles have high reactivity with the particle

crosslinking agent.

As mentioned above, when the base coating material includes synthetic resin emulsion particles obtained by polymerizing a monomer mixture including a ketone group- or aldehyde group-containing acrylic monomer, the content of the ketone group or aldehyde group-containing acrylic monomer in the monomer mixture is preferably 0.1 to 30% by mass, more preferably 0.5 to 10% by mass, and still more preferably 1 to 10% by mass. If the content of the ketone group or aldehyde group-containing acrylic monomer in the monomer mixture is less than 0.1% by mass, the strength of the coating film may decrease since crosslinkability becomes insufficient. Whereas, if the content of the ketone group or aldehyde group-containing acrylic monomer is more than 30% by mass, an adverse influence may be exerted on physical properties of the coating film.

It is also preferred that the base coating material include synthetic resin emulsion particles obtained by polymerization of a monomer mixture including a carboxyl group-containing acrylic monomer, and a particle crosslinking agent including a compound having two or more carbodiimide groups in a molecule. When employing a combination of the synthetic resin emulsion particles and particle crosslinking agent, a carboxyl group reacts with a carbodiimide group at normal temperature to form a crosslinked structure between synthetic resin emulsion particles, so that a strong coating film can be formed.

Specific examples of the carboxyl group-containing acrylic monomer include (meth)acrylic acid, maleic acid, maleic anhydride, itaconic acid, itaconic anhydride, crotonic acid, and the like. Among these monomers, (meth)acrylic acid is preferably used since the thus obtained synthetic resin emulsion particles have high reactivity with the particle crosslinking agent.

As mentioned above, when the base coating material includes synthetic resin emulsion particles obtained by polymerizing a monomer mixture including a carboxyl group-containing acrylic monomer, the content of the carboxyl group-containing acrylic monomer in the monomer mixture is preferably 0.1 to 5% by mass, and more preferably 0.1 to 3% by mass. If the content of the ketone group or aldehyde group-containing acrylic monomer in the monomer mixture is less than 0.1% by mass, stability of emulsion particles may deteriorate. Whereas, if the content of the ketone group or aldehyde group-containing acrylic monomer is more than 5% by mass, water resistance of the thus formed coating film may deteriorate.

In addition to the above ketone group or aldehyde group-containing acrylic monomer and carboxyl group-containing acrylic monomer, an optional monomer component may be included in the monomer mixture serving as raw materials of synthetic resin emulsion particles. Examples of the optional monomer component include methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, t-butyl (meth)acrylate, isobutyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl

(meth)acrylate, 2-ethylhexyl (meth)acrylate, cyclohexyl (meth)acrylate, styrene, glycidyl (meth)acrylate, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, each having a hydroxyl group, (meth)acrylamide having an amide group, M90G, M230G (both of which are manufactured by Shin-Nakamura Chemical Co., Ltd.), BLEMME AE-350, BLEMME PE-90, BLEMME PE-200, BLEMME PE-350 (all of which are manufactured by NOF CORPORATION), each including a polyalkylene oxide unit, and the like. Two or more monomers may be used in combination as these monomer components.

Synthetic resin emulsion particles in the present embodiment can be obtained by emulsion polymerization of a ketone group or aldehyde group-containing acrylic monomer, a carboxyl group-containing acrylic monomer, and other monomer components. There is no particular limitation of the method of emulsion polymerization for obtaining a synthetic resin emulsion, and it is possible to use a method which is generally known to a person with an ordinary skill in the art.

The resin of synthetic resin emulsion particles in the present embodiment preferably has a glass transition temperature (T_g) of -20°C to 50°C . If the glass transition temperature (T_g) of synthetic resin emulsion particles is lower than -20°C , the coating film may be softened by heat generated due to sunlight in the case of coating an external surface of a building, so that blister and peeling of the coating film are likely to occur. Whereas, if the glass transition temperature is higher than 50°C , flexibility of the

coating film may become insufficient, so that cracks of the coating film are likely to occur. T_g of the polymer made of n kinds of monomers can be determined by the FOX equation (equation (1) mentioned below). In the following equation (1), T_{gi} ($^{\circ}\text{C}$) denotes a glass transition temperature of each monomer constituting a polymer made of n kinds of monomers, and W_i denotes a mass fraction of each monomer of a homopolymer. Namely, a relationship $W_1 + W_2 + \dots + W_i + \dots + W_n = 1$ is established.

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} + \dots + W_i/T_{gi} + \dots + W_n/T_{gn} \quad (1)$$

Examples of the compound having two or more hydrazide groups in a molecule (particle crosslinking agent), which is used together with synthetic resin emulsion particles obtained by polymerizing a monomer mixture including a ketone group- or aldehyde group-containing acrylic monomer, include oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide, sebacic acid dihydrazide, dodecanoic acid dihydrazide, carbonic acid dihydrazide, phthalic acid dihydrazide, terephthalic acid dihydrazide, isophthalic acid dihydrazide, pyromellitic acid dihydrazide, polyhydrazide of polyacrylic acid having 20-100 hydrazide groups, nitrilotriacetic acid trihydrazide, ethylenediaminetetraacetic acid tetrahydrazide, ditrihydrazine-triazine, trihydrazine-triazine, thiocarbohydrazide, N,N' -diaminoguanidine, 2-hydrazinopyridine-5-carboxylic acid hydrazide, 3-chloro-2-hydrazinopyridine-5-carboxylic acid hydrazide, 6-chloro-2-

hydrazinopyridine-4-carboxylic acid hydrazide, 2,5-dihydrazinopyridine-4-carboxylic acid, 1,4-dihydrazinobenzole, 1,3-dihydrazinobenzole, 2,3-dihydrazine naphthalene, maleic acid dihydrazide, fumaric acid dihydrazide, itaconic acid dihydrazide, 1,3-bis(hydrazinocarboethyl)-5-isopropyl hidantoin, and the like. Among these compounds, adipic acid dihydrazide is preferably used in view of availability and 1,3-bis(hydrazinocarboethyl)-5-isopropyl hidantoin is preferably used in view of high water solubility.

Examples of the compound having two or more carbodiimide groups in a molecule (particle crosslinking agent), which is used together with synthetic resin emulsion particles obtained by polymerizing a monomer mixture including a carboxyl group-containing acrylic monomer, include a modified polycarbodiimide compound which will be described below. The modified polycarbodiimide compound has at least two carbodiimide groups in a molecule, and includes a polyalkylene oxide unit blocked with a monoalkoxy group having 4 or more carbon atoms at one end. The number of the carbodiimide groups included in a molecule of the modified polycarbodiimide compound is at least two, and is preferably twenty or less taking account of reaction efficiency. Specific examples of the compound having two or more carbodiimide groups in a molecule include CARBODILITE V-02-L2 (polyvalent carbodiimide, manufactured by Nisshinbo Chemical Inc.), CARBODILITE E-01 (polyvalent carbodiimide, manufactured by Nisshinbo Chemical Inc.), and the like.

Examples of the combination of a crosslinkable reactive group of the synthetic resin emulsion particles and particle crosslinking agent which is used in the case of forming the base layer (A) include, in addition to the above combination of a ketone group or an aldehyde group and a hydrazide group and the above combination of a carboxyl group and a carbodiimide group, a combination of an epoxy group and an amino group, a combination of an epoxy group and a carboxyl group, a combination of a carboxyl group and an aziridine group, a combination of a carboxyl group and an oxazoline group, a combination of alkoxyl groups, and the like. It is possible to use, as the particle crosslinking agent to be used for synthetic resin emulsion particles having a carboxyl group, a substance capable of forming metal ions. In this case, a crosslinked structure is formed by coordination of a carboxyl group of synthetic resin emulsion particles to metal ions.

[Upper Coating Layer (B)]

An upper coating layer (B) is formed on a base layer (A). It is preferred that the upper coating layer (B) does not absorb infrared rays as much as possible, and reflects or transmits infrared rays. If the upper coating layer (B) reflects a large amount of infrared rays, the entire multilayer coating film exhibits high heat shielding properties. Even if the upper coating layer (B) does not reflect infrared rays so much, when the upper coating layer transmits infrared rays, the base layer (A) including the

above-mentioned infrared-reflecting particles reflects a large amount of infrared rays, and also it is possible to decrease heat storage due to absorption of infrared rays of the upper coating layer (B). Even in this case, the entire multilayer coating film can exhibit high heat shielding properties.

The upper coating layer (B) is formed of an upper coating material. There is no particular limitation on the upper coating material. Although the upper coating material can include carbon black as a black pigment, and examples of a method of toning optional hue without including carbon black in the upper coating material include a method of toning using heat shielding black pigment in place of carbon black. Examples of the heat shielding black pigment include composite metal oxides such as iron chromium and bismuth manganese; and organic black pigments such as a perylene-based black pigment and an azomethineazo-based pigment. All of these pigments scarcely reflect in a visible wavelength region within a range of 350 nm to less than 780 nm and are almost black, namely, brightness determined in accordance with JIS K 5675 7.8 c) is less than 30. Meanwhile, infrared rays are reflected or transmitted in a near infrared wavelength region within a range of 780 nm to 2,500 nm, the amount of infrared rays to be absorbed decreases as compared with carbon black.

The method of toning optional hue also includes a method of toning by performing subtractive color mixing using a plurality of colored pigments.

Examples of performing subtractive color mixing using a

plurality of colored pigments include a method of toning using one, or two or more pigments selected from the group of colored pigments consisting of a red-colored pigment, a yellow-colored pigment, an orange-colored pigment, a blue-colored pigment, a green-colored pigment, and a violet-colored pigment; and titanium dioxide which is an infrared-reflecting powder.

In this way, various pigments can be included in the upper coating material in the present embodiment, and it is preferred that the upper coating material substantially include no black pigment. Examples of the black pigment include carbon black, and the above-mentioned heat shielding black pigment. It is possible to suppress infrared rays from being absorbed in to the coating film (upper coating layer (B)) without using the black pigment as the pigment to be mixed in the upper coating material. By suppressing infrared rays from being absorbed in to the upper coating layer (B), most of the infrared rays irradiation on the upper coating layer (B) are reflected on a surface of the upper coating layer (B) surface, or transmitted through the upper coating layer (B) and then reflected on the base layer (A), so that heat storage due to absorption of infrared rays of the upper coating layer (B) decreases, thus leading to satisfactory heat shielding properties of the entire multilayer coating film.

The phrase "substantially including no black pigment" is not intended to exclude a slight amount of the black pigment. Specifically, the content of the black pigment in the solid

component of the upper coating material is preferably less than 3.0% by mass.

Here, in comparison with an organic colored pigment, an inorganic colored pigment generally exhibits high reflectance in a near infrared wavelength region within a range of 780 nm to 2,500 nm, and also exhibits absorption of infrared rays to some extent. Whereas, the organic colored pigment exhibits small reflectance of infrared rays, and also may exhibit smaller absorption of infrared rays and large transmissivity of infrared rays. Accordingly, in the case of toning the upper coating layer by subtractive color mixing of selectively using the organic pigment as the colored pigment (hereinafter referred to as "organic subtractive color mixing"), larger amount of infrared rays transmitted through the upper coating layer are reflected on the under coating layer, thus enabling an increase in solar reflectance of the multilayer coating film.

As mentioned above, since there is no particular limitation on the upper coating material, brightness of the coating film formed of the upper coating material is not also particularly limited. Therefore, brightness of the coating film formed of the upper coating layer (B) is preferably 50 or less. Here, "brightness" is determined in accordance with JIS K 5675 7.8 c). If brightness of the upper coating layer (B) becomes dark, for example, 50 or less, the amount of titanium dioxide as the infrared-reflecting powder to be mixed in the upper coating layer (B) decreases. In this case, reflection

performance of the base layer (A) is effectively exhibited by performing organic subtractive color mixing without using a black pigment, and it is possible to increase solar reflectance of the multilayer coating film when compared with toning using an inorganic colored pigment or toning using a substitute black pigment.

Examples of the red-colored pigment to be used in the upper coating material in the present embodiment include Pigment Red (hereinafter referred to as "PR") 3, PR5, PR48, PR58, PR63, PR88, PR112, PR122, PR123, PR144, PR146, PR149, PR168, PR170, PR171, PR175, PR177, PR179, PR189, PR190, PR194, PR202, PR207, PR209, PR214, PR216, PR224, PR255, PR242, PR254, PR260, PR264, and the like, which are classified by Colour Index Pigment Number (hereinafter referred to as "C.I. No.") of The Society of Dyer and Colourists in Great Britain.

Examples of the orange-colored pigment to be used in the upper coating material in the present embodiment include Pigment Orange (hereinafter referred to as "PO") 5, PO13, PO16, PO34, PO36, PO38, PO43, PO60, PO62, PO64, PO65, PO69, PO73, and the like, which are classified by C.I. No.

Examples of the yellow-colored pigment to be used in the upper coating material in the present embodiment include Pigment Yellow (hereinafter referred to as "PY") 1, PY3, PY12, PY13, PY14, PY16, PY17, PY55, PY73, PY74, PY81, PY83, PY93, PY95, PY97, PY98, PY108, PY109, PY110, PY116, PY117, PY120, PY127, PY128, PY129, PY130, PY137, PY138, PY139, PY147, PY150, PY151, PY153, PY154, PY155, PY165, PY168, PY173, PY174, PY175,

PY176, PY180, PY183, PY184, and the like, which are classified by C.I. No.

Examples of the green-colored pigment to be used in the upper coating material in the present embodiment include Pigment Green (hereinafter referred to as "PG") 7, PG8, PG10, PG36, and the like, which are classified by C.I. No.

Examples of the blue-colored pigment to be used in the upper coating material in the present embodiment include Pigment Blue (hereinafter referred to as PB) 15:1, PB15:2, PB15:3, PB15:4, PB15:6, PB60, PB75, PB76, PB80, and the like, which are classified by C.I. No.

Examples of the violet-colored pigment to be used in the upper coating material in the present embodiment include Pigment Violet (hereinafter referred to as PV) 19, PV23, PV27, PV29, and the like, which are classified by C.I. No.

The total amount of the pigment to be used in the upper coating material in the present embodiment is preferably within a range of 2 to 70% by mass in the solid component of the upper coating material. If the total amount of the pigment to be used in the upper coating material is less than 2% by mass in the solid component of the upper coating material, pigmenting power decreases, so that the film thickness required to obtain the objective color increases. Whereas, if the total amount of the pigment to be used in the upper coating material is more than 70% by mass in the solid component of the upper coating material, weatherability may deteriorate.

In the upper coating material, solid components such as a resin component in a vehicle and optionally added other additives are included, in addition to the pigment in the present embodiment.

The upper coating material preferably includes a resin and an infrared-reflecting powder. When the upper coating material include the infrared-reflecting powder together with the resin, the upper coating layer (B) has heat shielding properties, in addition to the base layer (A), so that shielding properties of the entire multilayer coating film are also improved. The infrared-reflecting powder includes a metal oxide included in the upper coating material. The metal oxide included in the infrared-reflecting powder of the upper coating material is the same as that included in the infrared-reflecting powder in the base coating material.

Even if the upper coating material includes the infrared-reflecting powder, together with the resin, the content of the infrared-reflecting powder in the solid component of the upper coating material is preferably 30% by mass or less, and more preferably 20% by mass or less. If the content of the infrared-reflecting powder in the solid component of the upper coating material is more than 30% by mass, weatherability may deteriorate.

Method for Forming Multilayer Coating Film

The method for forming a multilayer coating film according to the present embodiment is a method of forming a multilayer coating film according to the above embodiment. In

other words, the method for forming a multilayer coating film according to the present embodiment includes the steps of: coating an external surface of a building with a base coating material including particles having hollow sections, at least one part of a surface of the particles being coated with an infrared-reflecting powder, and a resin to form a base layer (A), and forming an upper coating layer (B) on the base layer (A), wherein the infrared-reflecting powder includes a metal oxide having a refractive index of 1.7 to 3.0.

Examples of the method of forming the base layer (A) and the upper coating layer (B) of the multilayer coating film according to the present embodiment (method of coating with a base coating material and an upper coating material) include, but are not limited to, generally used coating methods using immersion, brush, roller, roll coater, air spray, airless spray, curtain flow coater, roller curtain coater, die coater, and the like. These coating methods can be appropriately selected according to the object to be coated and applications.

The present invention is not limited to the above-mentioned embodiments, and includes modifications and improvements as long as the object of the present invention can be achieved.

For example, an intermediate coating layer may be formed between the base layer (A) and the upper coating layer (B) in the above-mentioned embodiment. After forming the base layer (A), it is possible to form between the intermediate coating

layer and the upper coating layer (B), each having different hue and to form a tile-like coating film in which hue of joints is different from that of upper coating. It is also possible to form a clear coating layer on the upper coating layer (B).

EXAMPLES

The present invention will be described in detail by way of Examples, but the present invention is not limited thereto. Unless otherwise specified, "parts" and "percentages" are by mass.

[Preparation of Synthetic Resin Emulsions 1 to 3]

Preparation Example 1

In a beaker, 45 parts by mass of deionized water, 2 parts by mass of AQUALON HS-10 (reactive emulsifier, manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.), 30 parts by mass of styrene, 25 parts by mass of methyl methacrylate, parts by mass of n-butyl acrylate, 20 parts by mass of 2-ethylhexyl acrylate, 3 parts by mass of diacetone acrylamide, and 2 parts by mass of acrylic acid were charged, followed by stirring to obtain an emulsified material. Separately, in a reaction vessel equipped with a stirrer, a condenser tube, a dropping funnel, and a thermometer, 60 parts by mass of deionized water and 0.4 part by mass of AQUALON HS-10 were charged. After raising the temperature to 80°C, the above-mentioned emulsified material was added dropwise over 3 hours and, at the same time, 20 parts by mass of an aqueous 10% ammonium

persulfate solution was added dropwise. After completion of the dropwise addition and keeping at 80°C for 2 hours, the reaction solution was cooled to room temperature and then the pH was adjusted to 8 by adding 10% ammonia water. Then, the solution was filtered through a 200 mesh woven metal wire to prepare a synthetic resin emulsion 1. The solid component NV in the synthetic resin emulsion 1 was 45%.

Preparation Example 2

In the same manner as in the above-mentioned Preparation Example 1, except that each monomer mixing amount of the above-mentioned emulsified material as shown in Table 1, a synthetic resin emulsion 2 was prepared. The solid component NV in the synthetic resin emulsion 2 was 45%.

Preparation Example 3

In a reaction vessel, 50 parts by mass of deionized water and 0.5 part by mass of AQUALON HS-10 (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) as a reactive emulsifier and the temperature of contents was set at 85°C. In the reaction vessel, a pre-emulsified solution including 20 parts by mass of styrene, 45 parts by mass of n-butyl acrylate, 5 parts by mass of glycidyl methacrylate, 40 parts by mass of deionized water, and 1 part by mass of AQUALON HS-10 (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) and an aqueous polymerization initiator solution including 0.1 part by mass of ammonium persulfate as a water-soluble polymerization initiator and 10 parts by mass of deionized water were added dropwise over 2 hours to prepare a core section. During

emulsion polymerization, the pH of the polymerization reaction solution was kept at 3.0. Thereafter, a pre-emulsified solution including 10 parts by mass of styrene, 17 parts by mass of n-butyl acrylate, 3 parts by mass of methacrylic acid, 20 parts by mass of deionized water, and 0.3 part by mass of AQUALON HS-10 (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) and an aqueous polymerization initiator solution including 0.2 part by mass of ammonium persulfate and 10 parts by mass of deionized water were added dropwise over 2 hours, followed by continuous stirring for 3 hours to prepare a shell section. Subsequently, the reaction solution was cooled to 30°C and the pH was adjusted to 8 by adding 10% ammonia water. Then, the solution was filtered through a 200 mesh woven metal wire to prepare a synthetic resin emulsion 3. The synthetic resin emulsion 3 had a solid component NV of 44%.

[Table 1]

		Homo polymer Tg (°C)	Preparation Example 1 (single)	Preparation Example 2 (single)	Preparation Example 3		
					Total of core and shell sections	Core section	Shell section
Mixing amount of monomer (Parts by mass)	ST	100	30	30	30.0	20.0	10.0
	MMA	105	25	25	0.0	0.0	0.0
	BA	-54	20	22	62.0	45.0	17.0
	2EHA	-70	20	20	0.0	0.0	0.0
	DAAM	77	3	1	0.0	0.0	0.0
	GMA	41	0	0	5.0	5.0	0.0
	MAA	187	0	0	3.0	0.0	3.0
	AA	87	2	2	0.0	0.0	0.0
Total			100	100	100	70.0	30.0
Tg of synthetic resin emulsion particles(°C)			12.3	9.5	-14.0	-10.5	-2.5
Solid component of synthetic resin emulsion (NV%)			45	45	44	-	-

ST:styrene

MMA:methyl methacrylate

BA:n-butyl acrylate

2EHA:2-ethylhexyl acrylate

DAAM:diacetone acrylamide

MAA:methacrylic acid

AA:acrylic acid

"Tg in synthetic resin emulsion" in Table 1 is a theoretical glass transition temperature determined by the above-mentioned FOX equation from a glass transition temperature of a homopolymer of each monomer constituting emulsion particles and a mixing amount of each monomer.
[Preparation of Base Coating Materials 1 to 8 and Intermediate Coating Material 1]

The synthetic resin emulsion particles obtained by the above-mentioned Preparation Example were mixed with infrared-reflecting particles, hollow particles, titanium dioxide as an infrared-reflecting powder, and a particle crosslinking agent

in each mixing amount (unit: " parts by mass") shown in Table 2, followed by uniform stirring to prepare base coating materials 1 to 8 and an intermediate coating material 1.

[Table 2]

		Base 1	Base 2	Base 3	Base 4	Base 5	Base 6	Base 7	Base 8	Interme diate coating 1
Synthetic resin emulsion	Preparation Example	1	1	1	2	2	3	1	1	1
	Mixing amount	100	100	100	100	100	100	100	100	100
Infrared-reflecting particles 1		12	20	0	0	20	0	250	5	0
Infrared-reflecting particles 2		0	20	100	25	20	0	0	0	0
Hollow particles		0	0	0	0	0	3	0	0	0
Infrared-reflecting powder (titanium dioxide)		0	0	0	5	0	20	0	5	20
Particle crosslinking agent 1		2	2	1	0	0	0	2	2	2
Particle crosslinking agent 2		0	1	2	2	0	0	0	0	0

The following hollow particles and particle crosslinking agent were used as hollow particle and particle crosslinking agents 1 and 2 shown in Table 2.

Hollow particle: closed cell type hollow resin particles (acrylic-acrylonitrile copolymer resin, average particle diameter of 45 μm , density of 0.025 g/cm^3)

Particle crosslinking agent 1: adipic dihydrazide

Particle crosslinking agent 2: CARBODILITE V-02-L2 (polyvalent carbodiimide, manufactured by Nisshinbo Chemical Inc.)

The infrared-reflecting particles shown in Table 2 were prepared as follows.

Infrared-Reflecting Particles 1

After uniformly mixing 340 parts by mass of deionized water, 10 parts by mass of an aqueous 10% adipic acid-diethanolamine condensate solution, and 110 parts by mass of sodium chloride, a solution including 5.0 millimolar parts (0.7 part by mass) of glycidyl methacrylate (GMA), 1,526 millimolar parts (80.9 parts by mass) of acrylonitrile, 5.0 millimolar parts (0.7 part by mass) of hydroxyethyl methacrylate, 2.0 millimolar parts (0.4 part by mass) of ethylene glycol dimethacrylate, 200 millimolar parts (20 parts by mass) of methyl methacrylate, 20 parts by mass of n-pentane and 0.5 part by mass of azobisisobutyronitrile was added for 1 minute using a homomixer (manufactured by Tokushu Kikai Kogyo Co., Ltd., ROBOMICS, 4,000 rpm) to obtain a suspension. This suspension was transferred to a pressure-resistant reaction vessel and polymerized under a gauge pressure of 0.3 MPa at 60°C for 20 hours polymerization to obtain a polymerization solution of resin particles including a volatile expanding agent (n-pentane) which is converted into a gas at a softening temperature (160°C) or lower of the copolymerized resin. This polymerization solution was filtered and then dried at 30°C for 3 hours to obtain thermally expansible resin particles (microcapsules). The shell was thermally expanded by thermally heating expansible resin particles (microcapsules) at 160°C for 3 minutes using a fair wind dryer to form hollow particles (closed cell type hollow resin particles: acrylic-acrylonitrile copolymer resin). Subsequently, titanium dioxide

(having a refractive index of 2.76) was adhered to a surface of a hollow resin in a state where the thermally expanded hollow particle are softened to obtain infrared-reflecting particles 1. Infrared-reflecting particles 1 have an average particle diameter of 51.1 μm .

Infrared-Radiation-Reflecting Particles 2

In a state where an inorganic micro hollow body made of a vitreous raw material (Shirasu balloon) is softened by heating to 1,000°C, titanium dioxide (having a refractive index of 2.76) was adhered to a surface to obtain infrared-reflecting particles 2. The infrared-reflecting particles 2 have an average particle diameter of 42 μm .

Each average particle diameter of hollow particle and infrared-reflecting particles 1 and 2 mentioned in Table 2 is a volume average particle diameter measured by Model SALD-1100 manufactured by Shimadzu Corporation.

[Upper Coating Material]

The following upper coating materials were used as the upper coating material. The value of brightness of each coating film was measured in accordance with JIS K 5675 7.8 c).

Upper coating material 1: THERMOEYE 4F COOL BLACK

(manufactured by Nippon Paint Co., Ltd., brightness: 10, the content of infrared-reflecting powder in coating material solid component: 0% by mass, substantially including no black pigment)

Upper coating material 2: THERMO EYE 4F NEO SAPPHIRE BLUE

(manufactured by Nippon Paint Co., Ltd., brightness: 42, the content of infrared-reflecting powder in coating material solid component: 30% by mass, substantially including no black pigment)

Upper coating material 3: FINE 4F BEST BLACK (manufactured by Nippon Paint Co., Ltd., brightness: 9, the content of infrared-reflecting powder in coating material solid component: 0% by mass, including black pigment)

Example 1

A slate sheet was uniformly coated with a base coating material 1 so as to obtain a dry film thickness of 500 μm , dried in an atmosphere at 23°C and relative humidity of 50% RH for 24 hours, coated with an upper coating material 1 so as to obtain a dry film thickness of 50 μm , and then aged in an atmosphere at 23°C and relative humidity of 50% RH for 10 days to obtain a test sheet.

Examples 2 to 8 and Comparative Example 1 to 2

In the same manner as in Example 1, except that the base coating material and the upper coating material were changed to those mentioned in Table 3, test sheets were obtained.

Example 9

In the same manner as in Example 1, except for coating with the base coating material, drying, coating with the intermediate coating material 1 so as to obtain a dry film thickness of 50 μm , drying in an atmosphere at 23°C and relative humidity of 50% RH for 24 hours, and coating with an upper coating material, a test sheet was obtained.

Measurement of Near-Infrared Solar Reflectance of Multilayer Coating Film

An evaluation sheet was obtained by performing a coating step which is the same as in case of test sheets of Examples and Comparative Examples on a monochrome hiding chart in place of the slate sheet. Each evaluation sheet obtained in the coating step, which is the same as in case of test sheets obtained in Examples 1 to 9 and Comparative Example 1 to 2, was used as evaluation sheets of Examples 1 to 9 and Comparative Example 1 to 2. With respect to the evaluation sheets of Examples 1 to 9 and Comparative Example 1 to 2, near-infrared solar reflectance was measured in accordance with JIS K 5675 (high solar reflectance coating material for roof). The results are shown in Table 3. The results of Table 3 are evaluated by the following criteria.

- A: Reflectance of 50% or more
- B: Reflectance of 40% or more and less than 50%
- C: Reflectance of 20% or more and less than 40%
- D: Reflectance of less than 20%

Evaluation of Water-Resistant Adhesiveness

Each test sheet obtained in Examples and Comparative Examples was cut into pieces measuring 70 mm x 150 mm, immersed in water left to stand for twenty-four hours or more and then left to stand in a laboratory in an atmosphere at 23°C and relative humidity of 50% RH for a week. After water was wiped off, the test sheet was cut to form 25 square pieces of 4 mm squares, and then adhesiveness was evaluated by

applying a transparent pressure-sensitive adhesive tape to the test sheet mentioned in JIS K 5600-5,-6 and peeling the transparent pressure-sensitive adhesive tape. The number of square pieces remained without being peeled off by the transparent pressure-sensitive adhesive tape among 25 square pieces of the test sheet was evaluated by the following criteria. The results are shown in Table 3.

A: 25 square pieces

B: 22 to 24 square pieces

C: 20 to 21 square pieces

D: less than 20 square pieces

[Table 3]

		Example									Comparative Example	
		1	2	3	4	5	6	7	8	9	1	2
Number of coating material used	Base coating material	1	2	3	4	1	5	7	8	1	6	1
	Intermediate coating material	-	-	-	-	-	-	-	-	1	-	-
	Upper coating material	1	1	1	1	2	1	1	1	1	1	3
Near-infrared solar reflectance of multilayer coating film		A	A	A	A	A	A	A	C	B	B	C
Water-resistant adhesiveness		A	A	A	A	A	C	D	A	C	D	A

As is apparent from Table 3, a multilayer coating film including a base layer (A) and an upper coating layer (B) to be formed on the base layer (A), the base layer being formed of a base coating material including particles having hollow sections, at least one part of a surface of the particles

being coated with an infrared-reflecting powder (titanium dioxide having a refractive index of 2.76), and a resin, the upper coating layer being formed thereon, exhibits high near-infrared solar reflectance and also exhibits satisfactory water-resistant adhesiveness. In comparison with the multilayer coating film of Comparative Example 2, the multilayer coating film of Example 1 exhibits higher near-infrared solar reflectance. These results revealed that, when the upper coating material containing substantially no black pigment, the base layer formed of a base coating material including infrared-reflecting particles exerts stronger effect of reflecting infrared rays.

CLAIMS

1. A multilayer coating film to be formed on an external surface of a building,
comprising a base layer (A), and an upper coating layer (B) to be formed on the base layer (A), wherein
the base layer (A) is formed of a base coating material,
the base coating material includes particles having hollow sections, and a resin,
at least one part of a surface of the particles having hollow sections is coated with an infrared-reflecting powder,
the infrared-reflecting powder includes a metal oxide having a refractive index of 1.7 to 3.0, and wherein the upper coating layer (B) is formed of an upper coating material,
the upper coating material substantially includes no black pigment, and
brightness determined in accordance with JIS K 5675 7.8 c) of the coating film formed of the upper coating material is 50 or less.
2. The multilayer coating film according to claim 1, wherein the content of the particles in the solid component of the base coating material is within a range of 10 to 70% by mass.
3. The multilayer coating film according to claim 1 or 2, wherein the resin included in the base coating material is a synthetic resin emulsion particle,
the base coating material further includes a particle crosslinking agent, and
the particle crosslinking agent crosslinks the synthetic resin emulsion particles.

4. The multilayer coating film according to claim 3, wherein the synthetic resin emulsion particles are obtained by polymerizing a monomer mixture including a ketone group- or aldehyde group-containing acrylic monomer,

the particle crosslinking agent is a compound having two or more hydrazide groups in a molecule, and

the content of the ketone group- or aldehyde group-containing acrylic monomer in the monomer mixture is within a range of 0.1 to 30% by mass.

5. The multilayer coating film according to claim 3, wherein the synthetic resin emulsion particles are obtained by polymerizing a monomer mixture including a carboxyl group-containing acrylic monomer,

the particle crosslinking agent is a compound having two or more carbodiimide groups in a molecule, and

the content of the carboxyl group-containing acrylic monomer in the monomer mixture is within a range of 0.1 to 5% by mass.

6. The multilayer coating film according to claim 5, wherein the upper coating material includes a resin and an infrared-reflecting powder, and

the content of the infrared-reflecting powder in the upper coating material is 30% by mass or less.

7. A method for forming a multilayer coating film in which the multilayer coating film is formed on an external surface of a building, the method comprising the steps of:

coating the external surface of the building with a base coating material including particles having hollow sections, and a resin to form a base layer (A), and

forming an upper coating layer (B) on the base layer (A), wherein

at least one part of a surface of the particles having hollow sections is coated with an infrared-reflecting powder, and

the infrared-reflecting powder includes a metal oxide having a refractive index of 1.7 to 3.0, and wherein the upper coating layer (B) is formed of an upper coating material,

the upper coating material substantially includes no black pigment, and

brightness determined in accordance with JIS K 5675 7.8 c) of the coating film formed of the upper coating material is 50 or less.