PHOTOCATALYST-COATED BODY

RELATED APPLICATION

[0001] This application is based upon and claims the benefit of priority from the prior Japanese Patent Application No. 070197/2010 filed on March 25, 2010 and PCT/JP2010/068790 filed on October 18, 2010, the entire contents of which are incorporated herein by reference.

TECHNICAL FIELD

[0002] The present invention relates to a photocatalyst-coated body and more specifically relates to a photocatalyst-coated body that is excellent in a self-cleaning function developed upon exposure to rain fall, as well as in a harmful gas decomposition function and can exhibit good weatherability over a long period of time.

BACKGROUND ART

[0003] Photocatalysts such as titanium oxide have recently become utilized in many applications such as exterior materials for buildings. Activity of photocatalysts excited by photoenergy can be utilized to decompose various harmful materials or can be utilized to hydrophilize the surface of a base material coated with the photocatalyst and thus to allow contaminants deposited on the surface to be easily washed away with water. The following techniques are known for obtaining photocatalyst-coated bodies coated with such photocatalysts.

[0004] Films as described, for example, in a pamphlet of WO 98/03607 (PTL 1), i.e., films comprising photocatalyst particles formed of a metal oxide, and at least one material selected from the group consisting of fine particles of silica, silicone resin film precursors that can form silicone resin films, and silica film precursors that can form silica films, are known as photocatalyst films that have an excellent photocatalyst-based hydrophilization capability and are provided on composite materials. It is also known that, in the sense that hydrophilicity is developed from an early stage of coating film formation, fine particles of silica, or cured products of silica film precursors that can form silica films are highly suitable as a component of the photocatalyst film.

[0005] When a photocatalytic hydrophilic film is formed on an organic base material, as described in a pamphlet of WO 97/00134 (PTL 2), a technique in which an intermediate layer resistant to corrosion by a

photocatalyst, for example, silicones, is interposed between the base material and the photocatalytic hydrophilic film is used from the viewpoint of solving a problem that the organic material is decomposed or deteriorated by the photocatalytic activity possessed by the photocatalyst.

[0006] A technique that can prevent cracking of a photocatalyst layer while imparting corrosion resistance to a photocatalyst to an intermediate layer between a base material and photocatalyst layer has been proposed. For example, JP 2007-168135 (PTL 3) discloses a composite material formed of a coated body comprising a ceramic base material 1 and an organic coating film 2, an inorganic coating film 3, and a photocatalyst-containing inorganic coating film 4 that have been provided in that order on the ceramic base material 1, the inorganic coating film 3 having an elongation at break of 0.8% to 3.0%. In the photocatalyst-containing inorganic coating film 4, a photocatalyst-containing silicone resin film precursor that can form a silicone resin film , and that is less fragile than the fine particles of silica or the silica film precursor is used as an inorganic coating agent.

[0007] For example, JP H10(1998)-202794 (PTL 4) discloses a technique for immobilizing photocatalyst particles on the surface of an elastic material, i.e. a silicone elastomer coated sheet-like material, the surface layer portion of which(a silicone elastomer coated sheet-like material) a titanium oxide powder having a photocatalytic activity is immobilized on. The silicone elastomer coated sheet-like material is produced by a unique process comprising applying a silicone elastomer composition to a sheet-like material, then supporting a titanium oxide powder having a photocatalytic activity on the surface of the coating, and then curing the silicone elastomer composition.

[Citation List]

[Patent Literature]

[0008] [PTL 1] Pamphlet of WO 98/03607

[PTL 2] Pamphlet of WO 97/00134

[PTL 3] JP 2007-168135

[PTL 4] JP H10(1998)-202794

[PTL 5] JP 2008-272718

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

[0009] The present inventors have now found that a highly elastic photocatalyst-coated body can be realized by providing a layer having specific physical properties so as to come into contact with the underside of a photocatalyst. The present inventors have also found that this photocatalyst-coated body can also meet basic properties required of photocatalyst-coated bodies. The present invention has been made based on such finding.

[0010] Accordingly, an object of the present invention is to provide a photocatalyst-coated body that can meet basic property requirements and has good elasticity while possessing a high level of weatherability.

Means for Solving the Problems

[0011] According to the present invention, there is provided a photocatalyst-coated body comprising a base material, a photocatalyst-containing photocatalyst layer, and an intermediate layer that is interposed between the base material and the photocatalyst layer and is in contact with the underside of the photocatalyst layer, wherein

the intermediate layer contains a resin component containing a silicone component and a flexible non-silicone component and has a loss tangent of 0.2 (exclusive) to 1.5 (exclusive) as measured with a solid-matter viscoelasticity measuring device at 25°C according to JIS (Japanese Industrial Standards) K 7244-4, and the intermediate layer, as measured with a solid-matter viscoelasticity measuring device according to JIS K 7244-4, exhibits spectral peaks in a curve for a change in in a loss elastic modulus as a function of a temperature change, at least one of which appears at a temperature of -80 (exclusive) °C to 30°C.

EFFECT OF THE INVENTION

[0012] The photocatalyst-coated body according to the present invention possesses good elasticity while possessing a high level of weatherability. Specifically, in a photocatalyst-coated body according to the present invention that has been provided outdoors, even when cracking occurs in the photocatalyst layer due to a change in temperature on the surface of the photocatalyst layer, for example, due to a seasonal variation, the propagation/extension of cracking toward the surface, as well as toward the base material can be suppressed while ensuring the adhesion between the base material and the photocatalyst

layer. In a preferred embodiment, advantageously, the photocatalyst-coated body according to the present invention can develop hydrophilicity from an early stage of the coating film formation, thus can exert an excellent self-cleaning function developed upon exposure to rain fall from substantially just after the coating film formation, and can maintain the hydrophilicity over a long period of time.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] [Fig. 1] Fig. 1 is a graph showing a curve for a change in loss elastic modulus of an aqueous urethane polyether resin dispersion used in Example 1 as a function of a temperature change, as measured with a solid-matter viscoelasticity measuring device according to JIS K 7244-4.

[Fig. 2] Fig. 2 is electron photomicrographs 1 to 5 of respective coating films after adhesion evaluation tests for Examples 1 to 3, 7, and 8.

MODE FOR CARRYING OUT THE INVENTION

[0014] Photocatalyst-coated body

The photocatalyst-coated body according to the present invention has a basic structure comprising a base material, a photocatalyst-containing photocatalyst layer, and an intermediate layer that is interposed between the base material and the photocatalyst layer and is in contact with the underside of the photocatalyst layer. The intermediate layer comprises a resin component. The resin component comprises a silicone component and a flexible non-silicone component. The intermediate layer has a loss tangent of 0.2 (exclusive) to 1.5 (exclusive) as measured with a solid-matter viscoelasticity measuring device at 25°C according to JIS K 7244-4. The photocatalyst-coated body according to the present invention possesses a high level of weatherability and, at the same time, possesses good elasticity. Specifically, even when cracking occurs in the photocatalyst layer, the propagation/extension of cracking toward the base material can be significantly suppressed while ensuring the adhesion between the base material and the photocatalyst layer and, at the same time, a high level of photocatalytic function such as a gas decomposition function can be exerted. Accordingly, in the coated body according to the present invention, the following members (1) to (6) can be provided as the base material. However, it should be noted that the base material is not

limited to these members only. Specifically, members include (1) structures such as bridges, to which vibration is applied, (2) members that are porous materials such as unglazed ceramic wares, concretes, cement boards, woods, and stone materials and are exposed to an atmosphere having a temperature of 0°C or below, (3) members that are formed of flexible materials such as metallic materials, rubbers, and flexible film resins and, after the formation of the photocatalyst layer thereon, are bent, (4) members used in places where a one-day temperature change is 20°C or more, (5) members formed of materials having a coefficient of thermal expansion of not less than $10^{-5}K^{-1}$ in terms of a coefficient of linear expansion, for examples, metals, resins, rubbers, silicone sealants, and gaskets, and (6) members used in environments where an annual temperature range is 30°C and more. The surface of these members is irradiated with light that is emitted from a light source and that can photoexcite photocatalysts, for example, sunlight.

[0015] In a preferred embodiment of the present invention, the photocatalyst layer contains photocatalyst particles and inorganic oxide particles as a particulate component, and the content of the particulate component is not less than 70% by mass, preferably not less than 90% by mass, based on the photocatalyst layer. When the photocatalyst layer is constructed as described above, the photocatalyst layer is likely to develop hydrophilicity from an early stage of the coating film formation and can exert an excellent self-cleaning function developed upon exposure to rain fall from substantially just after the coating film formation. Further, in this embodiment, particularly when the photocatalyst layer is fragile, the propagation/extension of cracking can be more significantly suppressed.

[0016] The photocatalyt layer, particularly a photocatalyst layer formed of an inorganic component, is generally fragile and thus sometimes undergoes cracking upon exposure to a temperature change involved in a seasonal variation. In the photocatalyst-coated body according to the present invention, however, it is considered that cracking does not extend toward the surface or the base material due to the following two reasons combined although it should be noted that the following reasons are hypothetical and do not limit the scope of the functions and effects of the present invention. One of the reasons is

that, when the intermediate layer is configured so that the loss tangent at 25°C of the intermediate layer in contact with the underside of the photocatalyst layer is more than 0.2, propagated energy is absorbed by the intermediate layer. Further, when not less than 70% of the photocatalyst layer is accounted for by particulate materials such as photocatalyst particles or inorganic oxide particles as in one embodiment of the present invention, it is considered that interstices are present among the particles in the photocatalyst layer and suppress the extension of cracking. By virtue of these effects, cracks produced in the photocatalyst layer are less likely to be propagated/extended in a surface direction, as well as in a cross-sectional direction, a poor appearance such as opacification involved in cracking does not occur on the surface, and, further, the intermediate layer and the base material are less likely to be broken. Further, when the loss tangent at 25°C of the intermediate layer in contact with the underside of the photocatalyst layer is less than 1.5, the hydrophilicity level on the surface of the photocatalyst layer is maintained at less than 20 degrees for a long period of time. The incorporation of a silicone component as the resin component in the intermediate layer can suppress a deterioration in the base material caused by attack with the photocatalyst.

[0017] Preferably, the surface of the photocatalyst layer in the photocatalyst-coated body according to the present invention exhibits a hydrophilicity level of less than 20 degrees in terms of a contact angle with water in response to photoexcitation by the photocatalyst. This constitution can allow a high self-cleaning function to be developed upon exposure to rain fall.

[0018] The content of the photocatalyst in the photocatalyst layer in the photocatalyst-coated body according to the present invention is preferably 1% by mass to 20 (exclusive) % by mass, more preferably 5% by mass to 15% by mass. In one embodiment of the present invention, it is considered that, when the content of the phocatalyst incorporated in the photocatalyst layer is in the above-defined range which is considerably lower than the content of the inorganic oxide particles, direct contact between the photocatalyst particles and the base material can be minimized and, thus, attack on the base material (particularly organic base material) can be suppressed. At the same time, this

constitution can provide a photocatalyst-coated body having a high level of harmful gas decomposition capability and desired various film properties (for example, transparency and film strength) while preventing attack of the base material (particularly organic base material) by the photocatalyst.

[0019] In the present invention, when the photocatalyst is a particulate form, The average particle diameter of the photocatalyst particles in the photocatalyst-coated body is preferably 10 nm to 1000 nm (exclusive), more preferably 10 nm to 100 (exclusive) nm, most preferably 10 nm to 60 nm. The average particle diameter of the photocatalyst particles as used herein is calculated as a number average value as determined by measuring the length of 100 randomly selected particles in a visual field at a magnification of 20,000 times to 200,000 times under a scanning electron microscope. The shape of the particles is most preferably spherical and may also be substantially circular or elliptical. In this case, the length of the particles is approximately calculated as ((major axis + minor axis)/2). An average particle diameter of the photocatalyst particles in the above-defined range is advantageous in that the air flow rate in the photocatalyst and the gas decomposition activity are satisfactorily exerted and a satisfactory decomposition activity of the photocatalyst is exerted and, at the same time, a good balance between various film properties such as weatherability can be provided. Further, when the average particle diameter of the photocatalyst particles is in the above-defined range, the photocatalyst layer has good transparency.

[0020] The average particle diameter of the inorganic oxide particles in the photocatalyst-coated body according to the present invention is preferably 5 nm to 100 (exclusive) nm. More preferably, the lower limit of the average particle diameter of the inorganic oxide particles is 10 nm, and the upper limit of the average particle diameter of the inorganic oxide particles is 40 nm. As with the average particle diameter of the photocatalyst particles, the average particle diameter of the inorganic oxide particles as herein is calculated as a number average value as determined by measuring the length of 100 randomly selected particles in a visual field at a magnification of 200000 times under a scanning electron microscope. An average particle diameter of the

inorganic oxide particles in the above-defined range has advantages in that the air flow rate in the photocatalyst layer is improved, the gas decomposition reactivity is improved, and the abrasion resistance and the cracking resistance can be improved.

[0021] The thickness of the photocatalyst layer in the photocatalyst-coated body according to the present invention is preferably not more than 3 μm. When the thickness of the photocatalyst layer is not more than 3 μm, the transparency and the film strength are excellent and the effect of preventing a poor appearance attained by preventing extension of cracking toward the surface is significant. In a preferred embodiment of the present invention, the thickness of the photocatalyst layer is not less than 0.2 μm, more preferably not less than 0.5 μm. When the thickness of the photocatalyst layer is not less than 0.2 μm, good hydrophilicity can be exerted. Further, since the amount of the ultraviolet light that reaches the interface of the photocatalyst layer and the base material is satisfactorily reduced, the effect of improving the weatherability can also be attained.

[0022] In one embodiment of the present invention, interstices are present among particles in the photocatalyst layer in the photocatalyst-coated body. This constitution can allow the harmful gas decomposition function of the photocatalyst to be improved and, at the same time, can suppress extension of cracking toward the surface and the cross section.

[0023] The interstices among the particles in the photocatalyst-coated body according to the present invention is preferably 20% by volume to 35% by volume in terms of porosity. When the porosity is in the above-defined range, it is considered that the probability of contact between the harmful gas and the photocatalyst particles is high. Consequently, the organic gas decomposition activity is improved. The presence of interstices on this level among the particles can satisfactorily suppress extension of cracking toward the surface and the cross section.

[0024] The porosity as used herein is a value obtained by measuring five points or more per sample, preferably 10 points or more per sample, with a reflection spectral film thickness meter, preferably using FE-3000 manufactured by Otsuka Electronics Co., Ltd. and

averaging the measured values. The procedure of the measurement of the porosity will be described as follows.

[0025] Step 1. Determination of refractive index of glass plate

1-1. The reflectance of the glass plate at a wavelength of 230 nm to 800 nm is measured under the following conditions.

Measuring method: Absolute reflectance

Lens: Refrec. 25X

Reference reflector plate: Al-S-13

Filter: Not used

Slit: 0.2 mm × 2 mm

Sampling time: 1000 msec

Cumulated number: 9

Gain: Normal

[0026] 1-2. The reflectance of the glass plate at a wavelength range of 230 - 800 nm is calculated by n-Cauchy equation and a Fresnel's amplitude reflection coefficient at the interface between air and the glass plate.,where constituent media are air and the glass plate, a light incident angle φ is 0 degree, and the coefficient uses reflected light from the glass plate. In the n-Cauchy dispersion equation, the initial values of constants (C_{m1}, C_{m2}, and C_{m3}) are C_{m1} = 1.5, C_{m2}=0, and C_{m3} = 0, respectively; the refractive index of air is 1; and the extinction coefficient of air is 0 (zero) (Mitsunobu Kobiyama, "Kogaku Haku Maku no Kiso Riron (Basic Theory of Optical Thin Film)," pp. 20-65 (2003, Optronics Co., Ltd.)).

[0027] 1-3. The measured reflectance (1-1) was compared with the calculated reflectance (1-2), and C_{m1}, C_{m2}, and C_{m3} were determined at a minimum sum of square residuals. In this case, the upper limit of the sum of the square residuals is 0.02.

[0028] 1-4. C_{m1}, C_{m2}, and C_{m3} determined in 1-3 are introduced into the n-Cauchy dispersion equation to determine the refractive index nm of the glass substrate.

[0029] Step 2. Determination of porosity of photocatalyst layer

2-1. The reflectance of the photocatalyst layer at a wavelength of 230 nm to 800 nm is measured under the following conditions.

Measuring method: Absolute reflectance

Lens: Refrec. 25X

Reference reflector plate: Al-S-13
Filter: Not used
Slit: 0.2 mm × 2 mm
Sampling time: 1000 msec
Cumulated number: 9
Gain: Normal

[0030] 2-2. The reflectance on the single-layer thin film composed of photocatalyst at a wavelength range of 230 - 800 nm is calculated by Bruggeman equation and a Fresnel's amplitude reflection coefficient at the interface between air and the single-layer thin film, where constituent media are air, a single-layer thin film (the photocatalyst layer), and a glass plate, a light incident angle φ is 0 degree, and the coefficient uses reflected light from the single-layer thin film and transmitted light derived from multipath reflection of light between top and bottom of the single-layer thin film (Mitsunobu Kobiyama, "Kogaku Haku Maku no Kiso Riron (Basic Theory of Optical Thin Film)," pp. 20-65 (2003, Optronics Co., Ltd.), and D.E. Aspnes, Thin Solid Films, 89, 249 (1982)). The initial values of C_1 (volume fraction of SiO_2), C_2 (volume fraction of TiO_2), and C_3 (volume fraction of air) are 0.70, 0.05, and 0.25, respectively. The refractive index of air is 1, and the extinction coefficient of air is 0 (zero). The refractive index (n_1, n_2) and extinction coefficient (k_1, k_2) of SiO_2 and TiO_2 are extracted from E.D. Palik, "Handbook of Optical Constants of Solids," (1998, Academic Press, San Diego).

[0031] 2-3. The film thickness d and the volume fractions, C_1 of SiO_2, C_2 of TiO_2, and C_3 of air are varied, and the measured reflectance (2-1) is compared with the calculated reflectance (2-2), and C_1, C_2, and C_3 are determined at a minimum sum of square residuals. C_3 when the sum of square residuals is less than 0.02 and is minimum is adopted as the porosity. Other conditions are as follows.

Film thickness search method: Optimization method
Search range (wavelength): 400 to 800 nm
Search range (film thickness): 0 to 2000 nm
Film thickness step: 10 nm

The C_3 value determined here is regarded as the porosity (% by volume) of the photocatalyst layer according to the present invention.

[0032] The content of the flexible non-silicone resin in the resin

component in the photocatalyst-coated body according to the present invention is preferably 1 (exclusive) % to 99.5 (exclusive) %, more preferably 10 (exclusive) % to 99.5 (exclusive) %, most preferably 50 (exclusive) % to 99.5 (exclusive) %. When the content of the flexible non-silicone resin is in the above-defined range, the adhesion between the intermediate layer and the photocatalyst layer can be improved while suppressing a deterioration in the intermediate layer caused by attack with the photocatalyst.

[0033] The content of the silicone component in the resin component in the photocatalyst-coated body according to the present invention is preferably 0.5% to 30% in terms of SiO_2. When the content of the silicone component in the resin component is in the above-defined range, a deterioration in the intermediate layer caused by attack with the photocatalyst can be more effectively suppressed.

[0034] Photocatalyst layer

In the present invention, when the photocatalyst is present, preferably in a particulate form, on the surface of the base material, the photocatalyst layer may be completely in a film form, or alternatively may be in a partially film form. Further, the photocatalyst layer may be present in an island-like discrete form on the surface of the base material. In a preferred embodiment of the present invention, the photocatalyst layer is formed by applying a coating liquid.

[0035] In a preferred embodiment of the present invention, the photocatalyst layer in the photocatalyst-coated body contains photocatalyst particles and inorganic oxide particles as the particulate component, and the content of the particulate component in the photocatalyst layer is not less than 70% by mass, preferably not less than 75% by mass, more preferably not less than 80% by mass, still more preferably not less than 90% by mass.

[0036] In the present invention, the particulate component refers to a component having a shape. The particulate component comprises photocatalyst particles and inorganic oxide particles as indispensable components and optional components which will be described later. The shape of the particulate component is not particularly limited, and any of spherical, rod, fibrous, whisker, flat plate, and irregular shapes may be adopted.

[0037] In the present invention, for example, at least one of crystalline titanium oxides such as anatase form of titanium oxide, rutile form of titanium oxide, and brookite form of titanium oxide and metal oxides such as ZnO, SnO_2, $SrTiO_3$, WO_3, Bi_2O_3, and Fe_2O_3 may be used as the photocatalyst. Only one type thereof may be utilized, or alternatively, a combination of a plurality of types thereof may be utilized. For example, a combination of crystalline titanium oxide with SnO_2 and a combination of crystalline titanium oxide with WO_3 are particularly preferred as a suitable combination of a plurality of types. Any of metal oxides exemplified herein is suitable for use in combination with the constitutions described above.

[0038] The photocatalyst particles are preferably crystalline titanium oxide particles. The crystalline titanium oxide has better water resistance than ZnO. Further, as compared with SnO_2, the crystalline titanium oxide more effectively exerts a photocatalytic function such as gas decompositon upon exposure to light with wavelengths of 380 nm to 420 nm contained in a large amount in sunlight. Furthermore, as compared with $SrTiO_3$, fine particles of nano-order size can be more easily obtained, and, thus, fine particles that have a large specific surface area and has a photocatalytic activity high enough to be used in practical use can be more easily obtained. Furthermore, as compared with WO_3, Bi_2O_3, and Fe_2O_3, the crystalline titanium oxide has a larger bandgap and thus has a satisfactory oxidizing power and, at the same time, is less likely to produce a recombination of conduction electrons and holes after photoexcitation and has an activation energy high enough to cause gas decomposition. The crystalline titanium oxide is harmless, chemically stable, and easily available at low cost. Further, the crystalline titanium oxide has a high bandgap energy and thus requires ultraviolet light for photoexcitation and does not absorb visible light in the course of photoexcitation, and, consequently, color development derived from a complementary color component does not occur.

[0039] Among the crystalline titanium oxide particles, anatase form of titanium oxide is preferred as the photocatalyst particles. The anatase form of titanium oxide has a higher oxidizing power than rutile form of titanium oxide and exerts a higher photocatalytic function such as

a gas decomposition activity. Further, the anatase form of titanium oxide particles as the photocatalyst particles are suitable for combination with the above constitutions and can exert the above function and effect without sacrificing the effect.

[0040] Suitable inorganic oxide particles include silica particles, alumina particles, zirconia particles, and ceria particles. Preferred are silica particles. In addition to photocatalyst particles and inorganic oxide particles (silica particles), in the photocatalyst layer inorganic binders, metals or metal compounds, and surfactants may be added in such an amount that is preferably not more than 30% by mass, more preferably not more than 10% by mass, up to the amount that does not harm the photocatalytic hydrophilization function.

[0041] Other particles that may be contained as optional components in the photocatalyst layer include resin particles such as fluoro resin particles, latex, and acrylic beads, colored pigment particles, extender pigment particles such as colored pigment particles, whiskers, fibers, and fillers, and design material particles such as mica, talc, and glass beads.

[0042] In a preferred embodiment of the present invention, the photocatalyst layer may contain an inorganic binder. Examples thereof include amorphous titanium oxide, amorphous silica; cured products of precursors that can form silica films, (the precursors such as alkali silicates, alkyl silicates), amorphous zirconia, and cured products of precursors that can form zirconia films, (the precursors such as, zirconium ammonium carbonate, zirconium acetate, and zirconium formate).

[0043] In a preferred embodiment of the present invention, the photocatalyst layer may contain metals or metal compounds. Examples thereof include Cu (copper) or Cu compounds such as Cu_2O and CuO; Ag (silver) or Ag compounds such as Ag_2O; Pt (platinum) or Pt compounds; Fe (iron) or Fe compounds; and Pd (palladium) or Pd compounds.

[0044] The photocatalyst layer in the photocatalyst-coated body according to the present invention may be formed by applying a coating liquid comprising the above components dispersed in a solvent and drying or baking the coating. In a preferred embodiment of the present

invention, in the formation of the photocatalyst layer, the coating liquid may contain a surfactant from the viewpoints of dispersion stability of the photocatalyst and the inorganic oxide particles and a capability of wetting the intermediate layer when the coating liquid is applied on the intermediate layer. The surfactant may be properly selected from nonionic surfactants, anionic surfactants, cationic surfactants, and amphoteric surfactants. Among them, nonionic surfactants are particularly preferred. More preferred are ether-type nonionic surfactants, ester-type nonionic surfactants, polyalkylene glycol nonionic surfactants, fluoro nonionic surfactants, and silicone nonionic surfactants.

[0045] The level of hydrophilization in response to photoexcitation of the photocatalyst used in the present invention is such that the contact angle with water varied to a hydrophobic nature caused by placing the photoctalyst overnight in such a state that the photocatalyst remains unexposed to light can be restored after a 24-hr sunshine carbon arc lamp-type weatherability test. A tester manufactured by Suga Test Instruments Co., Ltd. (conditions: light irradiation 30 W/m^2, atmosphere temperature 60°C, spraying of water for 18 min during 120-min light irradiation, water temperature 16 ± 5°C) is used in the sunshine carbon arc lamp-type weatherability test. The contact angle with water is measured by a method specified in JIS R 1703-1.

[0046] Intermediate layer

The intermediate layer in the photocatalyst-coated body according to the present invention is provided so as to be interposed between the base material and the photocatalyst layer and to be in contact with the underside of the photocatalyst layer. The intermediate layer comprises a resin component. The resin component contains a silicone component and a flexible non-silicone resin and has a loss tangent at 25°C of 0.2 (exclusive) to 1.5 (exclusive), more preferably 0.2 (exclusive) to 1.0 (exclusive).

[0047] What is required for the state "provided so as to be interposed between the base material and the photocatalyst layer and to be in contact with the underside of the photocatalyst layer" is only that the underside of the photocatalyst layer is in contact with the upper side of the intermediate layer, and the interface of the photocatalyst layer and the intermediate layer may be substantially linear or may be partially

entangled.

[0048] The loss tangent of the intermediate layer in the photocatalyst-coated body as used herein is a value obtained by installing the intermediate layer in a solid-matter viscoelasticity measuring device according to JIS K 7244-4 (Plastics - Determination of dynamicmechanical properties - Part 4: Tensile vibration - Non-resonance method) and performing measurement in a tensile mode at a frequency of 1 Hz.

[0049] In the present invention, the intermediate layer comprises a resin component. The resin component contains a silicone component and a flexible non-silicone component. Silicone resins or silicone segments are suitable for use as the silicone component, and flexible non-silicone resins or flexible non-silicone segments are suitable for as the flexible non-silicone component. The resin component may consist of the two components only or alternatively may contain other resins or segments in addition to the two components. The resin component is obtained by polymerizing, mixing, or crosslinking either the two components or the two components in combination with other resins or segments.

[0050] In the present invention, the content of the resin component in the intermediate layer is preferably 10% by mass to 100% by mass, more preferably 50% by mass to 100% by mass, still more preferably 55% by mass to 100% by mass, most preferably 60% by mass to 100% by mass.

[0051] In the present invention, the flexible non-silicone component is a flexible non-silicone resin or a flexible non-silicone segment, preferably a component that exhibits a spectral peak which appears at -80 (exclusive) °C to 30°C in a curve for a change in loss elastic modulus as a function of a temperature change, as measured with a solid-matter viscoelasticity measuring device according to JIS K 7244-4. When the flexible non-silicone component contained in the intermediate layer has the above properties, at least one of spectral peaks in a curve for a change in loss elastic modus of the intermediate layer as a function of temperature change, as measured with a solid-matter viscoelasticity measuring device according to JIS K 7244-4, appears at a temperature of -80 (exclusive) °C to 30°C.

[0052] The content of the flexible non-silicone component is preferably 20% by mass to 100000% by mass, more preferably 100% by mass to 20000% by mass, still more preferably 200% by mass to 16000% by mass, based on the amount of Si (silicon) in the silicone component.

[0053] Examples of flexible non-silicone resins usable herein include urethane polyethers, urethane polyesters, urethane polycarbonates, polyethers, polyesters, polyacrylates, polymethacrylates, polyacrylic acids, polymethacrylic acids, polyvinyl resins, their composites, and silicone-modified or halogen-modified products thereof.

[0054] Examples of flexible non-silicone segments usable herein include urethane polyether segments, urethane polyester segments, urethane polycarbonate segments, polyether segments, polyester segments, polyacrylate segments, polymethacrylate segments, polyacrylic acid segments, polymethacrylic acid segments, polyvinyl segments, and silicone-modified or halogen-modified segments thereof.

[0055] Preferred silicone resins are silicones represented by average composition formula (1):

$$R^1{}_pSi(OR^2)_qO_{(4-p-q)/2} \cdots (1)$$

wherein R^1 represents an unsubstituted or substituted monovalent hydrocarbon group; R^2 represents at least one of a hydrogen atom, unsubstituted monovalent hydrocarbon groups having 1 to 6 carbon atoms, and alkoxy-substituted monovalent hydrocarbon groups having 1 to 6 carbon atoms; and p and q are each a number that meets a requirement of $0 < p < 4$, $0 < q < 4$, and $0 < (p + q) < 4$.

[0056] In the formula, preferably, the unsubstituted or substituted monovalent hydrocarbon group indicated by R^1 has 1 to 18 carbon atoms. Specific examples of unsubstituted monovalent hydrocarbon groups include alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, t-butyl, hexyl, cyclohexyl, octyl, and decyl groups; alkenyl groups such as vinyl, allyl, 5-hexenyl, and 9-decenyl groups; aryl groups such as a phenyl group; and aralkyl groups such as benzyl and phenyl ethyl groups. The substituted monovalent hydrocarbon group is one obtained by substiting a part or all of hydrogen atoms in the unsubstituted monovalent hydrocarbon group by a substituent, and examples of substituents include 1) halogen atoms such as fluorine and chlorine, 2) epoxy

functional groups such as glycidyloxy and epoxycyclohexyl groups, 3) (meth)acryl functional groups such as methacryl and acryl groups, 4) amino functional groups such as amino, aminoethylamino, phenylamino, and dibutylamino groups, 5) sulfur-containing functional groups such as mercapto and tetrasulfide groups, 6) alkyl ether groups such as (polyoxyalkylene) alkyl ether groups, 7) anionic groups such as carboxyl and sulfonyl groups, and 8) groups containing quaternary ammonium salt structures. Preferred reactive groups are groups 2) and 3), and groups containing epoxy functional groups are particularly preferred. Specific examples of substituted monovalent hydrocarbon groups include trifluoropropyl, perfluorobutylethyl, perfluorooctylethyl, 3-chloropropyl, 2-(chloromethylphenyl)ethyl, 3-glycidoxypropyl, 2-(3,4-epoxycyclohexyl)ethyl, 3-(meth)acryloxypropyl, (meth)acryloxymethyl, 3-aminopropyl, N-(2-aminoethyl)aminopropyl, 3-(N-phenylamino)propyl, 3-dibutylaminopropyl, 3-mercaptopropyl, polyoxyethyleneoxypropyl, 3-hydroxycarbonylpropyl, and 3-tributylammoniumpropyl groups. Among them, methyl, propyl, hexyl, and phenyl groups are preferred.

[0057] Examples of unsubstituted or substituted monovalent hydrocarbon groups having 1 to 6 carbon atoms indicated by R^2 include unsubstituted monovalent hydrocarbon groups including alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, and t-butyl groups, alkenyl groups such as an isopropenyl group or aryl groups such as a phenyl group and alkoxy-substituted monovalent hydrocarbon groups, for example, alkoxyalkyl groups such as methoxymethyl, ethoxyethyl, ethoxymethyl, and methoxyethyl groups.

[0058] In one embodiment of the present invention, difunctional silane derivative monomers (monomers that contain two hydrolyzable groups X per molecule and form a difunctional siloxane bond comprising two oxygen atoms bonded to each silicon atoms) may be contained in the silicone resin from the viewpoint of imparting flexibility. Examples of suitable hydrolyzable difunctional silane derivative monomers include diphenyldichlorosilane, diphenyldibromosilane, diphenyldimethoxysilane, diphenyldiethoxysilane, phenylmethyldichlorosilane, phenylmethyldibromosilane, phenylmethyldimethoxysilane, phenylmethyldiethoxysilane, γ-glycidoxypropylmethyldimethoxysilane, γ-glycidoxypropylmethyldiethoxysilane, γ-

(meth)acryloxypropylmethyldimethoxysilane, γ-(meth)acryloxypropylmethyldiethoxysilane, γ-aminopropylmethyldimethoxysilane, γ-aminopropylmethyldiethoxysilane, heptadecafluorooctylmethyldimethoxysilane, and heptadecafluorooctylmethyldiethoxysilane.

[0059] Preferred silicone segments are silicones as described above and represented by average composition formula (1):

$$R^1{}_pSi(OR^2)_qO_{(4-p-q)/2} \ldots (1)$$

wherein R^1 represents an unsubstituted or substituted monovalent hydrocarbon group; R^2 represents a group selected from a hydrogen atom, unsubstituted monovalent hydrocarbon groups having 1 to 6 carbon atoms, or alkoxy-substituted monovalent hydrocarbon groups having 1 to 6 carbon atoms; and p and q are each a number that meets a requirement of $0 < p < 4$, $0 < q < 4$, and $0 < (p + q) < 4$.

[0060] In the formula, preferably, the unsubstituted or substituted monovalent hydrocarbon group indicated by R^1 has 1 to 18 carbon atoms. Specific examples of unsubstituted monovalent hydrocarbon groups include alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, t-butyl, hexyl, cyclohexyl, octyl, and decyl groups; alkenyl groups such as vinyl, allyl, 5-hexenyl, and 9-decenyl groups; aryl groups such as a phenyl group; and aralkyl groups such as benzyl and phenylethyl groups. The substituted monovalent hydrocarbon group is one obtained by substiting a part or all of hydrogen atoms in the unsubstituted monovalent hydrocarbon group by a substituent, and examples of substituents include 1) halogen atoms such as fluorine and chlorine, 2) epoxy functional groups such as glycidyloxy and epoxycyclohexyl groups, 3) (meth)acryl functional groups such as methacryl and acryl groups, 4) amino functional groups such as amino, aminoethylamino, phenylamino, and dibutylamino groups, 5) sulfur-containing functional groups such as mercapto and tetrasulfide groups, 6) alkyl ether groups such as (polyoxyalkylene) alkyl ether groups, 7) anionic groups such as carboxyl and sulfonyl groups, and 8) groups containing quaternary ammonium salt structures. Preferred reactive groups are groups 2) and 3), and groups containing epoxy functional groups are particularly preferred. Specific examples of substituted monovalent hydrocarbon groups include trifluoropropyl, perfluorobutylethyl, perfluorooctylethyl, 3-chloropropyl, 2-

(chloromethylphenyl)ethyl, 3-glycidoxypropyl, 2-(3,4-epoxycyclohexyl)ethyl, 3-(meth)acryloxypropyl, (meth)acryloxymethyl, 3-aminopropyl, N-(2-aminoethyl)aminopropyl, 3-(N-phenylamino)propyl, 3-dibutylaminopropyl, 3-mercaptopropyl, polyoxyethyleneoxypropyl, 3-hydroxycarbonylpropyl, and 3-tributylammoniumpropyl groups. Among them, methyl, propyl, hexyl, and phenyl groups are preferred.

[0061] Examples of unsubstituted or substituted monovalent hydrocarbon groups having 1 to 6 carbon atoms indicated by R^2 include unsubstituted monovalent hydrocarbon groups including alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, and t-butyl groups, alkenyl groups such as an isopropenyl group or aryl groups such as a phenyl group and alkoxy-substituted monovalent hydrocarbon groups, for example, alkoxyalkyl groups such as methoxymethyl, ethoxyethyl, ethoxymethyl, and methoxyethyl groups.

[0062] In one embodiment of the present invention, difunctional silane derivative monomers (monomers that contain two hydrolyzable groups X per molecule and form a difunctional siloxane bond comprising two oxygen atoms bonded to each silicon atoms) may be contained in the silicon segment from the viewpoint of imparting flexibility. Examples of suitable hydrolyzable difunctional silane derivative monomers include diphenyldichlorosilane, diphenyldibromosilane, diphenyldimethoxysilane, diphenyldiethoxysilane, phenylmethyldichlorosilane, phenylmethyldibromosilane, phenylmethyldimethoxysilane, phenylmethyldiethoxysilane, γ-glycidoxypropylmethyldimethoxysilane, γ-glycidoxypropylmethyldiethoxysilane, γ-(meth)acryloxypropylmethyldimethoxysilane, γ-(meth)acryloxypropylmethyldiethoxysilane, γ-aminopropylmethyldimethoxysilane, γ-aminopropylmethyldiethoxysilane, heptadecafluorooctylmethyldimethoxysilane, and heptadecafluorooctylmethyldiethoxysilane.

[0063] Resins other than the above two types of resin that may be contained in the intermediate layer according to the present invention include, for example, polyesters, polyacrylates, polymethacrylates, polyacrylic acids, polymethacrylic acids, polystyrene, polyvinyl, epoxy resins, polycarbonates, polyacrylamides, polyamides, polyamines, polyols, polyurethanes, polyethers, polysulfides, polyphenols,

composites thereof, and silicone-modified or halogen-modified products thereof.

[0064] Segments other than the two segments that may be contained in the intermediate layer according to the present invention include, for example, polyester segments, polyacrylate segments, polymethacrylate segments, polyacrylic acid segments, polymethacrylic acid segments, polystyrene segments, polyvinyl segments, polycarbonate segments, polyacrylamide segments, polyamide segments, polyamine segments, polyol segments, polyurethane segments, polyethers segments, polysulfide segments, polyphenol segments, and silicone-modified or halogen-modified of these segments.

[0065] In the present invention, the intermediate layer may contain, in addition to the resin component, colorants, extender pigments, matting agents, ultraviolet absorbers, photostabilizers, film forming assistants, curing agents, surfactants, viscosity modifiers, antifoaming agents, pH adjustors and the like.

[0066] Inorganic pigments, organic pigments, dyes and the like are suitable for use as the colorant.

[0067] Suitable inorganic pigments usable herein include metal oxide pigments such as titanium oxide, zinc flower, iron oxide red, chrome oxide, cobalt blue, and iron black; metal hydroxide pigments such as alumina white and yellow iron oxide; ferrocyanic compounds such as iron blue; lead chromate poigments such as chrome yellow, zinchromate, and molybdenum red; sulfide pigments such as zinc sulfide, vermillion, cadmium yellow, and cadmium red; sulfate pigments such as selenium compounds, barite, and precipitated barium sulfate; carbonate pigments such as heavy calcium carbonate, and precipitated calcium carbonate; silicate pigments such as hydrous silicates, clay, and ultramarine blue; carbon pigments such as carbon black; metal powder pigments such as aluminum powder, bronze powder, and zinc powder; and pearl pigments such as mica and titanium oxide pigments.

[0068] Suitable organic pigments usable herein include nitroso pigments such as naphthol green B; nitro pigments such as naphthol S; azo pigments such as lithol red, lake red C, fast yellow, and naphthol red; and condensed polycyclic pigments such as alkali blue red, rhodamine chelate, quinacridone red, dioxazine violet, and isoindolinone

yellow.

[0069] Suitable dyes usable herein include disperse dyes, basic dyes, direct dyes, and acid dyes.

[0070] Examples of suitable extender pigments usable herein include titanium oxide whisker, calcium carbonate whisker, potassium titanate whisker, aluminum borate whisker, mica, talc, barium sulfate, potassium carbonate, quartz sand, diatomaceous earth, kaolin, clay, porcelain clay, and barium carbonate.

[0071] Examples of suitable matting agents usable herein include inorganic matting agents and organic matting agents. Inorganic matting agents include, for example, dry-type silica, wet-type silica, calcium carbonate, mica, boron nitride, and titanium oxide. Examples of organic matting agents include resin beads such as acrylic resin beads, urethane resin beads, silicone resin powders, and fluoro resin powders.

[0072] Suitable ultraviolet absorbers usable herein include benzophenone, benzotriazole, and triazine ultraviolet absorbers.

[0073] Specific examples of suitable benzophenone ultraviolet absorbers include polymerizable benzophenone ultraviolet absorbers such as 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid, 2-hydroxy-4-n-octoxybenzophenone, 2-hydroxy-4-n-dodecyloxybenzophenone, 2-hydroxy-4-benzyloxybenzophenone, bis(5-benzoyl-4-hydroxy-2-methoxyphenyl)methane, 2,2'-dihydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, 2,2',4,4'-tetrahydroxybenzophenone, 4-dodecyloxy-2-hydroxybenzophenone, 2-hydroxy-4-methoxy-2'-carboxybenzophenone, 2-hydroxy-4-stearyloxybenzophenone, octabenzone, 2-hydroxy-4-acryloxybenzophenone, 2-hydroxy-4-methacryloxybenzophenone, 2-hydroxy-5-acryloxybenzophenone, 2-hydroxy-5-methacryloxybenzophenone, 2-hydroxy-4-(acryloxy-ethoxy)benzophenone, 2-hydroxy-4-(methacryloxyethoxy)benzophenone, 2-hydroxy-4-(methacryloxydi-ethoxy)benzophenone, 2-hydroxy-4-(acryloxy-triethoxy)benzophenone, and (co)polymers thereof.

[0074] Specific examples of suitable benzotriazole ultraviolet absorbers usable herein include polymerizable benzotriazole ultraviolet

absorbers such as 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-5'-tert-butylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)benzotriazole, 2-(2-hydroxy-5-tert-octylphenyl)benzotriazole, 2-(2-hydroxy-3,5-di-tert-octylphenyl)benzotriazole, 2-[2'-hydroxy-3',5'-bis(α,α'-dimethylbenzyl)phenyl]benzotriazole), a condensate of methyl-3[3-tert-butyl-5-(2H-benzotriazol-2-yl)-4-hydroxyphenyl]propionate with polyethylene glycol (molecular weight 300), isooctyl-3-[3-(2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyphenyl]propionate, 2-(3-dodecyl-5-methyl-2-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-di-tert-amylphenyl)benzotriazole, 2-(2'-hydroxy-4'-octoxyphenyl)benzotriazole, 2-[2'-hydroxy-3'-(3",4",5",6"-tetrahydrophthalimidomethyl)-5'-methylphenyl]benzotriazole, 2,2-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-(2H-benzotriazol-2-yl)phenol], 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol, 2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole, 2-(2'-hydroxy-5'-methacryloxyethyl-3-tert-butylphenyl)-2H-benzotriazole, 2-(2'-hydroxy-5'-methacryloxypropyl-3-tert-butylphenyl)-5-chloro-2H-benzotriazole, and 3-methacryloyl-2-hydroxypropyl-3-[3'-(2"-benzotriazolyl)-4-hydroxy-5-tert-butyl]phenyl propionate, and (co)polymers thereof.

[0075] Suitable triazine ultraviolet absorbers usable herein include hydroxyphenyltriazine compounds.

[0076] The additional incorporation of photostabilizers such as hindered amines and/or hindered phenols is advantageous in that the weatherability is further improved by a synergistic effect of the ultraviolet absorbers and the photostabilizers.

[0077] Specific examples of suitable hindered amine photostabilizers usable herein include polymerizable hindered amine ultraviolet absorbers such as bis(2,2,6,6-tetramethyl-4-piperidyl) succinate, bis(2,2,6,6-tetramethylpiperidyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)2-(3,5-di-tert-butyl-4-hydroxybenzyl)-2-butyl malonate, 1-[2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]ethyl]-4-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propinyloxy]-2,2,6,6-tetramethylpiperidine, a mixture of bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate with methyl-1,2,2,6,6-pentamethyl-4-piperidyl sebacate, bis(1-octoxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate, 1,2,2,6,6-pentamethyl-

4-piperidyl methacrylate, 1,2,2,6,6-pentamethyl-4-piperidyl acrylate, 2,2,6,6-tetramethyl-4-piperidyl methacrylate, 2,2,6,6-tetramethyl-4-piperidylacrylate, 1,2,2,6,6-pentamethyl-4-iminopiperidyl methacrylate, 2,2,6,6,-tetramethyl-4-iminopiperidyl methacrylate, 4-cyano-2,2,6,6-tetramethyl-4-piperidyl methacrylate, and 4-cyano-1,2,2,6,6-pentamethyl-4-piperidylmethacrylate, and (co)polymers thereof.

[0078] Specific examples of suitable hindered phenol photostabiizers usable herein include bis(3,5-tert-butyl)-4-hydroxytoluene.

[0079] In a preferred embodiment of the present invention, the liquid for the intermediate layer formation may contain a film forming assistant for intermediate layer formation improvement purposes. Film forming assistants include ester organic solvents such as isoamyl acetate, oxohexyl acetate, methylmethoxybutyl acetate, ethylethoxy propionate, ethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, 2,2,4-trimethyl-1,3-pentanediol monoisobutylate, 2,2,4-trimethyl-1,3-pentanediol diisobutylate, 2,2,4-trimethyl-1,3-pentanediol mono-2-ethylhexanoate, and 2,2,4-trimethyl-1,3-pentanediol di-2-ethylhexanoate; alcoholic organic solvents such as benzyl alcohol, texanol, diethylene glycol, isotridecanol, 1,3-octylene glycol, and glycerin; and etheric organic solvents such as ethylene glycol monohexyl ether, ethylene glycol mono-2-ethylhexyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol monobutyl ether, diethylene glycol dibutyl ether, diethylene glycol mono-2-ethylhexyl ether, propylene glycol monophenyl ether, and tripropylene glycol methyl ether. One of or a combination of these film forming assistants may be used.

[0080] In a preferred embodiment of the present invention, if necessary, the intermediate layer may additionally contain a curing agent reactive with a functional group contained in the silicone component and the non-silicone component.

[0081] Specific examples of such curing agents include compounds containing a silanol group and/or a hydrolyzable silyl group, polyepoxy compounds, polyoxazoline compounds, and polyisocyanates. In particular, when compounds containing a carboxyl or carboxylate group as the functional group contained in the silicone component and the non-silicone component are used, a combination of compounds

containing an epoxy group and a silanol group and/or a hydrolyzable silyl group, polyepoxy compounds, and polyoxazoline compounds is preferred.

[0082] Compounds containing a silanol group and/or a hydrolyzable silyl group include, for example, organotrialkoxysilanes such as methyltrimethoxysilane, methyltriethoxysilane, methyltri-n-butoxysilane, ethyltrimethoxysilane, n-propyltrimethoxysilane, iso-butyltrimethoxysilane, cyclohexyltrimethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, vinyltrimethoxysilane, or 3-(meth)acryloyloxypropyltrimethoxysilane; diorganodialkoxysilanes such as dimethyldimethoxysilane, dimethyldiethoxysilane, dimethyldi-n-butoxysilane, diethyldimethoxysilane, diphenyldimethoxysilane, methylcyclohexyldimethoxysilane, or methylphenyldimethoxysilane; various chlorosilanes such as methyltrichlorosilane, ethyltrichlorosilane, phenyltrichlorosilane, vinyltrichlorosilane, 3-(meth)acryloyloxypropyltrichlorosilane, dimethyldichlorosilane, diethyldichlorosilane, or diphenyldichlorosilane; and partially hydrolyzed condensates thereof. Among them, organotrialkoxysilanes and diorganodialkoxysilanes are preferred. One of or a combination of these silane compounds may be used. Other examples thereof include 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 3-glycidoxypropyltriethoxysilane, 3-glycidoxypropylmethyldiethoxysilane, β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, and hydrolyzed condensates thereof.

[0083] Examples of such polyepoxy compounds usable herein include polyglycidyl ethers having aliphatic or alicyclic polyol-derived structures such as ethylene glycol, hexanediol, neopentyl glycol, trimethylolpropane, pentaerythritol, sorbitol, and hydrogenated bisphenol A; polyglycidyl ethers of aromatic diols such as bisphenol A, bisphenol S, and bisphenol F; polyglycidyl ethers of polyether polyols such as polyethylene glycol, polypropylene glycol, and polytetramethylene glycol; polyglycidyl ethers of tris(2-hydroxyethyl) isocyanurate; polyglycidyl esters of aliphatic or aromatic polycarboxylic acids such as adipic acid, butanetetracarboxylic acid, phthalic acid, and terephthalic acid; bisepoxides of hydrocarbon dienes such as cyclooctadine and vinylcyclohexene; and alicyclic polyepoxy compounds such as bis(3,4-

epoxycyclohexylmethyl) adipate and 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexyl carboxylate.

[0084] Examples of polyoxazoline compounds usable herein include 2,2'-p-phenylene-bis(1,3-oxazoline), 2,2'-tetramethylene-bis(1,3-oxazoline), 2,2'-octamethylene-bis(2-oxazoline), 2-isopropenyl-1,3-oxazoline, or polymers thereof.

[0085] Examples of polyisocyanates usable herein include aromatic diisocyanates such as tolylenediisocyanate and diphenylmethane-4,4'-diisocyanate; aralkyldiisocyanates such as m-xylenediisocyanate, and $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-m-xylylenediisocyanate; hexamethylenediisocyanate, lysinediisocyanate, 1,3-bisisocyanatemethylcyclohexane, 2-methyl-1,3-diisocyanatecyclohexane, 2-methyl-1,5-diisocyanatecyclohexane, and isophoronediisocyanate.

[0086] Isocyanate group-containing various prepolymers, isocyanurate ring-containing prepolymers, biuret structure-containing polyisocyanates, and isocyanate group-containing vinyl monomers may also be used as the polyisocyanate.

[0087] The isocyanate group in the polyisocyanate as the curing agent may if necessary have been blocked with publicly known blocking agents such as methanol.

[0088] The intermediate layer in the photocatalyst-coated body according to the present invention may be formed by applying a coating liquid comprising the above components dispersed in a solvent and drying or baking the coating.

[0089] The coating liquid may contain a surfactant for coatability improvement purposes. Examples of suitable surfactants usable herein include anionic surfactants such as ammonium salt of polyoxyethylene alkyl phenyl ether sulfonic acid, sodium salt of polyoxyethylene alkyl phenyl ether sulfonic acid, fatty acid sodium soap, fatty acid potassium soap, sodium dioctylsulfosuccinate, alkyl sulfates, alkyl ether sulfates, soda salt of alkyl sulfates, soda salt of alkyl ether sulfates, polyoxyethylene alkyl ether sulfates, soda salt of polyoxyethylene alkyl ether sulfates, TEA salt of alkyl sulfates, TEA salt of polyoxyethylene alkyl ether sulfates, sodium salt of 2-ethylhexyl alkyl sulfate esters, sodium acylmethyltaurate, sodium lauroylmethyltaurate, sodium dodecylbenzenesulfonate, disodium sulfosuccinate lauryl, disodium

polyoxyethylenesulfosuccinate lauryl, polycarboxylic acid, oleoylsarcosin, amide ether sulfate, lauroyl sarcosinate, and sodium salt of sulfo-FA ester; nonionic surfactants such as polyoxyethylene lauryl ether, polyoxyethylene tridecyl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene alkyl ether, polyoxyethylene alkyl ester, polyoxyethylene alkyl phenol ether, polyoxyethylene nonylphenyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene laurate, polyoxyethylene stearate, polyoxyethylene alkyl phenyl ether, polyoxyethylene oleate, sorbitan alkyl ester, polyoxyethylene sorbitan alkyl ester, polyether-modified silicone, polyester-modified silicone, sorbitan laurate, sorbitan stearate, sorbitan palmitate, sorbitan oleate, sorbitan sesquioleate, polyoxyethylene sorbitan laurate, polyoxyethylene sorbitan stearate, polyoxyethylene sorbitan palmitate, polyoxyethylene sorbitan oleate, glycerol stearate, polyglycerin fatty acid ester, alkyl alkylolamide, lauric acid diethanol amide, oleic acid diethanol amide, oxyethylene dodecylamine, polyoxyethylene dodecyl amine, polyoxyethylene alkyl amine, polyoxyethylene octadecyl amine, polyoxyethylene alkyl propylene diamine, polyoxyethylene oxypropylene block polymer, and polyoxyethylene stearate; amphoteric surfactants such as dimethyl alkyl betaine, alkyl glycine, amide betaine, and imidazoline; and cationic surfactants such as octadecyl dimethylbenzylammonium chloride, alkyl dimethylbenzylammonium chloride, tetradecyl methylbenzylammonium chloride, dioleyl dimethylammonium chloride, 1-hydroxyethyl-2-alkylimidazoline quaternary salt, alkylisoquinolinium bromide, polymeric amine, octadecyl trimethylammonium chloride, alkyl trimethylammonium chloride, dodecyl trimethylammonium chloride, hexadecyl trimethylammonium chloride, behenyl trimethylammonium chloride, alkylimidazoline quaternary salt, dialkyl dimethylammonium chloride, octadecylamine acetate salt, tetradecyl amine acetate salt, alkyl propylene diamine acetate salt, and didecyl dimethylammonium chloride.

[0090] The coating liquid forming the intermediate layer according to the present invention may properly contain viscosity modifiers, antifoaming agents, pH adjustors and the like.

[0091] Base material

The base material used in the present invention may be various materials regardless of whether the materials are inorganic materials or organic materials as long as the photocatalyst layer can be formed thereon. The shape of the base material is not also limited. Examples of preferred base materials from the viewpoint of material include metals, ceramics, glasses, plastics, rubbers, stones, cement, concretes, fibers, fabrics, woods, papers, combinations thereof, laminates thereof, and these materials with at least one layer formed on a surface thereof. Cements and concretes are more preferred from the viewpoint of allowance of expansion deformation caused by water absorption, and metals and resins are more preferred from the viewpoint of expansion deformation caused by heat.

[0092] Examples of preferred base materials from the viewpoint of applications include external walls, roofs, soundproof walls, guardrails, and bridges. Building materials include external walls and roofs. The shape of the base material is not particularly limited and may be in a flat plate form or a curved form. Any of these base materials is suitable for use in a combination with each of the constructions.

[0093] the present invention is particularly suitable for application to base materials, the surface of which is formed of an organic material. Any of a base material, the whole of which is formed of an organic material, and a base material formed of an inorganic material having a surface covered with an organic material (for example, decorative plate) is embraced in the base material having a surface formed of an organic material.

[0094] Use of coated-body

In the photocatalyst-coated body according to the present invention, even when cracking occurs in the photocatalyst layer, the propagation/extension of the cracking toward the surface as well as toward the base material can be significantly suppressed while ensuring the adhesion between the base material and the photocatalyst layer and, at the same time, a high level of photocatalytic function such as a gas decomposition function can be exerted. Accordingly, the coated body according to the present invention is particularly suitable for use, for example, under the following conditions. (1) vibration is applied to the base material such as bridge, (2) the base material is porous materials

such as unglazed ceramic wares, concretes, cement boards, woods, and stone materials, and the photocatalyst-coated body is exposed to an atmosphere having a temperature of 0°C or below, (3) the base material is formed of flexible materials such as metallic materials, rubbers, and flexible film resins and, after the formation of the photocatalyst layer thereon, the photocatalyst-coated body is bent, (4) the photocatalyst-coated body is placed under the environment where a one-day temperature change is 20°C or above, (5) base materials have a coefficient of thermal expansion of not less than $10^{-5}K^{-1}$ in terms of a coefficient of linear expansion, for examples, metals, resins, rubbers, silicone sealants, and gaskets, and (6) the photocatalyst-coated body is used under the environment where an annual temperature range is not less than 30°C. Furthermore, the surface of the photocatalyst layer is exposed to light that is emitted from a light source and can photoexcite the photocatalyst, for example, sunlight.

[0095] Further, the coated body, when placed in an environment where the surface of the photocatalyst layer can be sometimes exposed to rain, can develop a self-cleaning function upon exposure to rain fall. Furthermore, when the coated body is configured so that a hydrophilicity is less than 20 degrees, more preferably less than 10 degrees, still more preferably less than 5 degrees in terms of a contact angle with water, from an early stage of the coating film formation, an excellent self-cleaning function can be exerted upon exposure to rain fall from substantially just after the coating film formation and, at the same time, the hydrophilicity can be maintained for a long period of time.

EXAMPLES

[0096] Preparation of photocatalyst coating liquids

Photocatalyst coating liquid 1

An aqueous titania dispersion (or a titania water dispersion) (average particle diameter: 30 nm to 60 nm) as a photocatalyst, a water dispersed colloidal silica (average particle diameter: 20 nm to 30 nm) as an inorganic oxide, and water were mixed together to obtain a composition (photocatalyst coating agent) having a solid content of 5.5% by mass, a colloidal silica content (on a solid basis) of 90% by mass, and a photocatalyst content (on a solid basis) of 10% by mass. In order that the photocatalyst coating liquid, when coated on

a base material, has a wetting capability high enough to wet the base material, 0.3 part by mass of a nonionic surfactant was mixed into 100 parts by mass of the photocatalyst coating agent to obtain a photocatalyst coating liquid.

[0097] Photocatalyst coating liquid 2

An aqueous titania dispersion (average particle diameter: 30 nm to 60 nm) as a photocatalyst, a water dispersed colloidal silica (average particle diameter: 20 to 30 nm) and tetraethoxysilane as inorganic oxides, and water were mixed together to obtain a composition (photocatalyst coating agent) having a solid content of 5.5% by mass, a colloidal silica content (on a solid basis) of 66.2% by mass, a tetraethoxysilane content (on a solid basis) of 26.5% by mass, and a photocatalyst content (on a solid basis) of 7.4% by mass. In order that the photocatalyst coating liquid, when coated on a base material, has a wetting capability high enough to wet the base material, 0.3 part by mass of a nonionic surfactant was mixed into 100 parts by mass of the photocatalyst coating agent to obtain a photocatalyst coating liquid.

[0098] Photocatalyst coating liquid 3

An aqueous titania dispersion (average particle diameter: 30 nm to 60 nm) as a photocatalyst, a water dispersed colloidal silica (average particle diameter: 20 nm to 30 nm) and tetraethoxysilane as inorganic oxides, and water were mixed together to obtain a composition (photocatalyst coating agent) having a solid content of 5.5% by mass, a colloidal silica content (on a solid basis) of 31% by mass, a tetraethoxysilane content (on a solid basis) of 62.1% by mass, and a photocatalyst content (on a solid basis) of 6.9% by mass. In order that the photocatalyst coating liquid, when coated on a base material, has a wetting capability high enough to wet the base material, 0.3 part by mass of a nonionic surfactant was mixed into 100 parts by mass of the photocatalyst coating agent to obtain a photocatalyst coating liquid.

[0099] Photocatalyst coating liquid 4

An aqueous titania dispersion (average particle diameter: 30 nm to 60 nm) as a photocatalyst, a water dispersed colloidal silica (average particle diameter: 20 nm to 30 nm) and an alkoxy oligomer as inorganic oxides , and water were mixed together to obtain a composition having a solid content of 5.5% by mass, a colloidal silica content (on a

solid basis) of 86.9% by mass, an alkoxy oligomer content (on a solid basis) of 3.5% by mass, and a photocatalyst content (on a solid basis) of 9.7% by mass. In order that the photocatalyst coating liquid, when coated on a base material, has a wetting capability high enough to wet the base material, 0.3 part by mass of a nonionic surfactant was mixed into 100 parts by mass of the photocatalyst coating agent to obtain a photocatalyst coating liquid.

[0100] Photocatalyst coating liquid 5

An aqueous titania dispersion (average particle diameter: 30 nm to 60 nm) as a photocatalyst, tetraethoxysilane as an inorganic oxide, and water were mixed together to obtain a composition (photocatalyst coating agent) having a solid content of 5.5% by mass, a tetraethoxysilane content (on a solid basis) of 78.3% by mass, and a photocatalyst content (on a solid basis) of 21.7% by mass. In order that the photocatalyst coating liquid, when coated on a base material, has a wetting capability high enough to wet the base material, 0.3 part by mass of a nonionic surfactant was mixed into 100 parts by mass of the photocatalyst coating agent to obtain a photocatalyst coating liquid.

[0101] Photocatalyst coating liquid 6

An aqueous titania dispersion (average particle diameter: 30 nm to 60 nm) as a photocatalyst, an alkoxy oligomer as an inorganic oxide, and water were mixed together to obtain a composition (photocatalyst coating agent) having a solid content of 5.5% by mass, an alkoxy oligomer content (on a solid basis) of 26.5% by mass, and a photocatalyst content (on a solid basis) of 73.5% by mass. In order that the photocatalyst coating liquid, when coated on a base material, has a wetting capability high enough to wet the base material, 0.3 part by mass of a nonionic surfactant was mixed into 100 parts by mass of the photocatalyst coating agent to obtain a photocatalyst coating liquid.

[0102] Preparation of intermediate layer coating liquids

An aqueous acrylic silicone resin dispersion and an aqueous urethane polyether resin dispersion used in the following Examples have a solid content of 35% and a solid content of 30%, respectively.

[0103] In the following Examples, the loss tangent at 25°C of the film coated with intermediate layer coating liquids was measured as

follows. Specifically, the intermediate layer coating liquid was applied to a Teflon (registered trademark) sheet with a bar coater #20, and the intermediate layer coating liquid was dried. Further, the intermediate coating liquid was overcoated on the coating film with a bar coater #20, and the coating was dried. This procedure was repeated until the dried film thickness reached about 20 μm. The coating film thus formed was cut into a strip having a size of 5 mm × 50 mm. The strip was then separated from the Teflon (registered trademark) sheet and was mounted on a solid-matter viscoelasticity measuring device, and the loss tangent was measured in a tensile mode at a frequency of 1 Hz.

[0104] Intermediate layer coating liquid 1

An aqueous urethane polyether resin dispersion (202 parts by mass), 14 parts by mass of a film forming assistant, 5.4 parts by mass of a curing agent, and 82 parts by mass of water were successively added to 100 parts by mass of an aqueous acrylic silicone resin dispersion having a silicone content of 75% by mass in terms of SiO_2. The mixture thus obtained was stirred with a stirrer for 30 min to obtain an intermediate layer coating liquid 1 having a solid content of 25% by mass. The proportion of polysiloxane in the intermediate layer coating liquid 1 was 30% by mass.

[0105] A curve for a change in a loss elastic modulus of the aqueous urethane polyether resin dispersion as a function of a temperature change as measured with a solid-matter viscoelasticity measuring device according to JIS K 7244-4 was as shown in Fig. 1. As shown in the drawing, a spectral peak appeared at -30°C. The loss tangent at 25°C of the coating film was 0.28.

[0106] Intermediate layer coating liquid 2

An aqueous urethane polyether resin dispersion (875 parts by mass), 45 parts by mass of a film forming assistant, 5.4 parts by mass of a curing agent, and 187 parts by mass of water were successively added to 100 parts by mass of an aqueous acrylic silicone resin dispersion having a silicone content of 75% by mass. The mixture thus obtained was stirred with a stirrer for 30 min to obtain an intermediate layer coating liquid 2 having a solid content of 25% by mass. The proportion of polysiloxane in the intermediate layer coating liquid 2 was 10% by mass. A spectral peak in a curve for a change in a loss

elastic modulus of the aqueous urethane polyether resin dispersion as a function of a temperature change as measured with a solid-matter viscoelasticity measuring device according to JIS K 7244-4 appeared at -30°C. The loss tangent at 25°C of a coating film obtained from the intermediate layer coating liquid 2 was 0.48.

[0107] Intermediate layer coating liquid 3

An aqueous urethane polyether resin dispersion (1885 parts by mass), 90 parts by mass of a film forming assistant, 5.4 parts by mass of a curing agent, and 343 parts by mass of water were successively added to 100 parts by mass of an aqueous acrylic silicone resin dispersion having a silicone content of 75% by mass. The mixture thus obtained was stirred with a stirrer for 30 min to obtain an intermediate layer coating liquid 3 having a solid content of 25% by mass. The proportion of polysiloxane in the intermediate layer coating liquid 3 was 5% by mass. One of spectral peaks in a curve for a change in a loss elastic modulus of the aqueous urethane polyether resin dispersion as a function of a temperature change as measured with a solid-matter viscoelasticity measuring device according to JIS K 7244-4 appeared at -30°C. The loss tangent at 25°C of a coating film obtained from the intermediate layer coating liquid 3 was 0.52.

[0108] Intermediate layer coating liquid 4

An aqueous acrylic resin emulsion (10300 parts by mass), 779 parts by mass of a film forming assistant, 5.4 parts by mass of a curing agent, and 9578 parts by mass of water were successively added to 100 parts by mass of an aqueous acrylic silicone resin dispersion having a silicone content of 75% by mass. The mixture thus obtained was stirred with a stirrer for 30 min to obtain an intermediate layer coating liquid 4 having a solid content of 25% by mass. The proportion of polysiloxane in the intermediate layer coating liquid 4 was 0.5% by mass. One of spectral peaks in a curve for a change in a loss elastic modulus of the aqueous acrylic resin emulsion as a function of a temperature change as measured with a solid-matter viscoelasticity measuring device according to JIS K 7244-4 appeared at 2°C. The loss tangent at 25°C of a coating film obtained from the intermediate layer coating liquid 4 was 0.60.

[0109] Intermediate layer coating liquid 5

An aqueous acrylic resin emulsion (11444 parts by mass), 779 parts by mass of a film forming assistant, 5.4 parts by mass of a curing agent, and 8433 parts by mass of water were successively added to 100 parts by mass of an aqueous acrylic silicone resin dispersion (solid content: 35% by mass) having a silicone content of 75% by mass. The mixture thus obtained was stirred with a stirrer for 30 min to obtain an intermediate layer coating liquid 5 having a solid content of 25% by mass. The proportion of polysiloxane in the intermediate layer coating liquid 5 was 0.5% by mass. One of spectral peaks in a curve for a change in a loss elastic modulus of the aqueous acrylic resin emulsion as a function of a temperature change as measured with a solid-matter viscoelasticity measuring device according to JIS K 7244-4 appeared at -35°C. The loss tangent at 25°C of a coating film obtained from the intermediate layer coating liquid 5 was 0.48.

[0110] Intermediate layer coating liquid 6

An aqueous acrylic resin emulsion (10300 parts by mass), 779 parts by mass of a film forming assistant, 5.4 parts by mass of a curing agent, and 9578 parts by mass of water were successively added to 100 parts by mass of an aqueous acrylic silicone resin dispersion having a silicone content of 75% by mass. The mixture thus obtained was stirred with a stirrer for 30 min to obtain an intermediate layer coating liquid 6 having a solid content of 25% by mass. The proportion of polysiloxane in the intermediate layer coating liquid 6 was 0.5% by mass. One of spectral peaks in a curve for a change in a loss elastic modulus of the aqueous acrylic resin emulsion as a function of a temperature change as measured with a solid-matter viscoelasticity measuring device according to JIS K 7244-4 appeared at 24°C. The loss tangent at 25°C of a coating film obtained from the intermediate layer coating liquid 6 was 1.00.

[0111] Intermediate layer coating liquid 7

An aqueous acrylic resin emulsion (9346 parts by mass), 776 parts by mass of a film forming assistant, 5.4 parts by mass of a curing agent, and 10495 parts by mass of water were successively added to 100 parts by mass of an aqueous acrylic silicone resin dispersion having a silicone content of 75% by mass. The mixture thus obtained was stirred with a stirrer for 30 min to obtain an intermediate

layer coating liquid 7 having a solid content of 25% by mass. The proportion of polysiloxane in the intermediate layer coating liquid 7 was 0.6% by mass. One of spectral peaks in a curve for a change in a loss elastic modulus of the aqueous acrylic resin emulsion as a function of a temperature change as measured with a solid-matter viscoelasticity measuring device according to JIS K 7244-4 appeared at 24°C. The loss tangent at 25°C of a coating film obtained from the intermediate layer coating liquid 7 was 0.49.

[0112] Intermediate layer coating liquid 8

An aqueous urethane polyether resin dispersion (159 parts), 14 parts of a film forming assistant, 7.7 parts of a curing agent, and 100 parts of water were successively added to 100 parts of an aqueous acrylic silicone resin dispersion having a silicone content of 30% by mass. The mixture thus obtained was stirred with a stirrer for 30 min to obtain an intermediate layer coating liquid 8 having a solid content of 25% by mass. The proportion of polysiloxane in the intermediate layer coating liquid 8 was 15% by mass. One of spectral peaks in a curve for a change in a loss elastic modulus of the aqueous urethane polyether resin dispersion as a function of a temperature change as measured with a solid-matter viscoelasticity measuring device according to JIS K 7244-4 appeared at -30°C. The loss tangent at 25°C of a coating film obtained from the intermediate layer coating liquid 8 was 0.48.

[0113] Intermediate layer coating liquid 9 (comparative example)

An aqueous urethane polyether resin dispersion (67 parts), 8.3 parts of a film forming assistant, 5.4 parts of a curing agent, and 61 parts of water were successively added to 100 parts of an aqueous acrylic silicone resin dispersion having a silicone content of 75% by mass. The mixture thus obtained was stirred with a stirrer for 30 min to obtain an intermediate layer coating liquid 9 having a solid content of 25% by mass. The proportion of polysiloxane in the intermediate layer coating liquid 9 was 50% by mass. One of spectral peaks in a curve for a change in a loss elastic modulus of the aqueous urethane polyether resin dispersion as a function of a temperature change as measured with a solid-matter viscoelasticity measuring device according to JIS K 7244-4 appeared at -30°C. The loss tangent at 25°C

of a coating film obtained from the intermediate layer coating liquid 4 was 0.13.

[0114] Intermediate layer coating liquid 10 (comparative example)

An aqueous urethane polyether resin dispersion (34 parts), 6.8 parts of a film forming assistant, 5.4 parts of a curing agent, and 56 parts of water were successively added to 100 parts of an aqueous acrylic silicone resin dispersion having a silicone content of 75% by mass. The mixture thus obtained was stirred with a stirrer for 30 min to obtain an intermediate layer coating liquid 10 having a solid content of 25% by mass. The proportion of polysiloxane in the intermediate layer coating liquid 10 was 60% by mass. The loss tangent at 25°C of a coating film obtained from the intermediate layer coating liquid 5 was 0.09.

[0115] Intermediate layer coating liquid 11 (comparative example)

A film forming assistant (7.2 parts), 7.9 parts of a curing agent, and 76.5 parts of water were successively added to 100 parts of an aqueous acrylic silicone resin dispersion having a silicone content of 30% by mass. The mixture thus obtained was stirred with a stirrer for 30 min to obtain an intermediate layer coating liquid 11 having a solid content of 25% by mass. The proportion of polysiloxane in the intermediate layer coating liquid 11 was 30% by mass. One of spectral peaks in a curve for a change in a loss elastic modulus of the aqueous urethane polyether resin dispersion as a function of a temperature change as measured with a solid-matter viscoelasticity measuring device according to JIS K 7244-4 appeared at 60°C. The loss tangent at 25°C of a coating film obtained from the intermediate layer coating liquid 11 was 0.10.

[0116] Production and evaluation of photocatalyst-coated bodies

The aqueous acrylic resin coating material was sprayed on a flexible board to a thickness on a dry basis of about 20 μm, and the coated board was dried at 80°C for 30 min. Subsequently, the aqueous acrylic urethane resin coating material was spray-coated thereon to a thickness on a dry basis of about 200 μm, and the coated board was then dried at 80°C for 30 min to obtain an undercoated base material for an adhesion test.

[0117] Each of the intermediate layer coating liquids 1 to 11 was

sprayed on an undercoated base material prepared above and preheated to 50°C so that the coated base material can have a intermediate layer thickness of 10 μm after dried at 90°C for 2 min. Subsequently, each of the photocatalyst liquid coating liquids 1 to 6 was spray-coated thereon to a thickness on a dry basis of 0.3 to 0.7 μm to obtain a photocatalyst-coated body. The combination of the intermediate layer coating liquid and the photocatalyst coating liquid was as specified in tables below.

[0118] Evaluation of adhesion

For the photocatalyst-coated bodies thus obtained, the adhesion was evaluated as follows. At the outset, the photocatalyst-coated body (specimen) was introduced into a sunshine weather-o-meter (S-300C, manufactured by Suga Test Instruments Co., Ltd.) specified in JIS B 7753 and, 100 hr after the introduction, was taken out of the sunshine weather-o-meter. The specimen was immersed in water of 60°C for 10 hr, was then dried at 100°C for one hr, and was then placed under and exposed to light (wavelength 254 nm) from a sterilization lamp (manufactured by TOSHIBA LIGHTING & TECHNOLOGY CORPORATION) adjusted so that the illuminance on the surface of the specimen was 10 W/m^2, for 12 hr. This procedure was repeated 8 times in total (total testing time 184 hr). The contact angle of the coated bodies with water was measured with a contact angle goniometer (model CA-X150, manufactured by Kyowa Interface Science Co., Ltd.). Further, the surface of the coated bodies was observed under a scanning electron microscope (S800, manufactured by Hitachi, Ltd.) at a magnification of 100 times to visually evaluate an approximate retention ratio of the photocatalyst layer.

[0119] Thermal shock test

A thermal shock test was carried out as follows. At the outset, the photocatalyst-coated body (specimen) was introduced into a sunshine weather-o-meter (S-300C, manufactured by Suga Test Instruments Co., Ltd.) specified in JIS B 7753 and, 100 hr after the introduction, was taken out of the sunshine weather-o-meter. The specimen was heated at 100°C for one hr and was then cooled at -20°C for one hr. This procedure was repeated 10 times in total (total testing time 20 hr). Further, the coated body was again introduced into a sunshine weather-o-meter (S-300C, manufactured by Suga Test

Instruments Co., Ltd.) specified in JIS B 7753 and, 100 hr after the introduction, was taken out of the sunshine weather-o-meter. The contact angle of the coated body with water was measured with a contact angle goniometer (model CA-X150, manufactured by Kyowa Interface Science Co., Ltd.).

[0120] Flex resistance test

A flex resistance test was carried out as follows. At the outset, the photocatalyst-coated body (specimen) was introduced into a sunshine weather-o-meter (S-300C, manufactured by Suga Test Instruments Co., Ltd.) specified in JIS B 7753 and, 100 hr after the introduction, was taken out of the sunshine weather-o-meter. The coated body was flexed under conditions of 10φ and 180 degrees and was then visually evaluated for cracks in the flexed portion. Further, the contact angle of the flexed portion with water was measured with a contact angle goniometer (model CA-X150, manufactured by Kyowa Interface Science Co., Ltd.).

[0121] Vibration resistance test

A vibration resistance test was carried out as follows. At the outset, the photocatalyst-coated body (specimen) was introduced into a sunshine weather-o-meter (S-300C, manufactured by Suga Test Instruments Co., Ltd.) specified in JIS B 7753 and, 100 hr after the introduction, was taken out of the sunshine weather-o-meter. The coated body was fixed to a vibration tester, and vibration was applied to the coated body under conditions of a vibration frequency of 5 Hz and a vibration acceleration of 1 G for 10 min. The contact angle of the coated body with water after the application of the vibration was measured with a contact angle goniometer (model CA-X150, manufactured by Kyowa Interface Science Co., Ltd.).

[0122] The results were as shown in tables below.

[Table 1]

Example	Photocatalyst coating liquid	Intermediate layer coating liquid	Evaluation of adhesion		Thermal shock resistance	Flex resistance		Vibration resistance
			Contact angle after test	Retention of coating film	Contact angle after test	Cracks in flexed portion	Contact angle in flexed portion	Contact angle after test
1	1	1	<20°	75%	<20°	Absent	<20°	<20°
2	1	2	<20°	100%	<20°	Absent	<20°	<20°
3	1	3	<20°	100%	<20°	Absent	<20°	<20°
4	1	4	<20°	100%	<20°	Absent	<20°	<20°
5	1	5	<20°	100%	<20°	Absent	<20°	<20°
6	1	6	<20°	100%	<20°	Absent	<20°	<20°
7	1	7	<20°	100%	<20°	Absent	<20°	<20°
8	1	8	<20°	100%	<20°	Absent	<20°	<20°
11	2	1	<20°	100%	<20°	Absent	<20°	<20°
12	2	2	<20°	100%	<20°	Absent	<20°	<20°
13	2	3	<20°	100%	<20°	Absent	<20°	<20°
14	2	4	<20°	100%	<20°	Absent	<20°	<20°
15	2	5	<20°	100%	<20°	Absent	<20°	<20°
16	2	6	<20°	100%	<20°	Absent	<20°	<20°
17	2	7	<20°	100%	<20°	Absent	<20°	<20°
18	2	8	<20°	100%	<20°	Absent	<20°	<20°
21	3	1	<20°	100%	<20°	Absent	<20°	<20°
22	3	2	<20°	100%	<20°	Absent	<20°	<20°
23	3	3	<20°	100%	<20°	Absent	<20°	<20°
24	3	4	<20°	100%	<20°	Absent	<20°	<20°
25	3	5	<20°	100%	<20°	Absent	<20°	<20°
26	3	6	<20°	100%	<20°	Absent	<20°	<20°
27	3	7	<20°	100%	<20°	Absent	<20°	<20°
28	3	8	<20°	100%	<20°	Absent	<20°	<20°

[0123]

[Table 2]

Example	Photocatalyst coating liquid	Intermediate layer coating liquid	Evaluation of adhesion		Thermal shock resistance	Flex resistance		Vibration resistance
			Contact angle after test	Retention of coating film	Contact angle after test	Cracks in flexed portion	Contact angle in flexed portion	Contact angle after test
31	4	1	<20°	100%	<20°	Absent	<20°	<20°
32	4	2	<20°	100%	<20°	Absent	<20°	<20°
33	4	3	<20°	100%	<20°	Absent	<20°	<20°
34	4	4	<20°	100%	<20°	Absent	<20°	<20°
35	4	5	<20°	100%	<20°	Absent	<20°	<20°
36	4	6	<20°	100%	<20°	Absent	<20°	<20°
37	4	7	<20°	100%	<20°	Absent	<20°	<20°
38	4	8	<20°	100%	<20°	Absent	<20°	<20°
41	5	1	<20°	100%	<20°	Absent	<20°	<20°
42	5	2	<20°	100%	<20°	Absent	<20°	<20°
43	5	3	<20°	100%	<20°	Absent	<20°	<20°
44	5	4	<20°	100%	<20°	Absent	<20°	<20°
45	5	5	<20°	100%	<20°	Absent	<20°	<20°
46	5	6	<20°	100%	<20°	Absent	<20°	<20°
47	5	7	<20°	100%	<20°	Absent	<20°	<20°
48	5	8	<20°	100%	<20°	Absent	<20°	<20°
51	6	1	<20°	100%	<20°	Absent	<20°	<20°
52	6	2	<20°	100%	<20°	Absent	<20°	<20°
53	6	3	<20°	100%	<20°	Absent	<20°	<20°
54	6	4	<20°	100%	<20°	Absent	<20°	<20°
55	6	5	<20°	100%	<20°	Absent	<20°	<20°
56	6	6	<20°	100%	<20°	Absent	<20°	<20°
57	6	7	<20°	100%	<20°	Absent	<20°	<20°
58	6	8	<20°	100%	<20°	Absent	<20°	<20°
Comp.Ex. 1	1	9	60°	<10%	<20°	Present	<20°	<20°
Comp.Ex. 2	1	10	80°	<10%	<20°	Present	<20°	<20°
Comp.Ex. 3	1	11	80°	<10%	<20°	Present	<20°	<20°

[0124] Electron photomicrographs of the coating films after the adhesion evaluation test were as shown in Fig. 2. In Fig. 2, photographs 1 to 5 are electron photomicrographs of the coating films of Examples 1 to 3 and Comparative Examples 1 and 2.

[CLAIMS]

Claim 1. A photocatalyst-coated body comprising a base material, a photocatalyst layer containing a photocatalyst, and an intermediate layer which is between the base material and the photocatalyst layer and is in contact with the underside of the photocatalyst layer, wherein

the intermediate layer comprises a resin component containing a silicone component and a flexible non-silicone component and has a loss tangent of more than 0.2 to less than 1.5 as measured with a solid-matter viscoelasticity measuring device at 25°C according to JIS K 7244-4, and

the intermediate layer, as measured with a solid-matter viscoelasticity measuring device according to JIS K 7244-4, exhibits spectral peaks in a curve for a change in a loss elastic modulus as a function of a temperature change, at least one of which appears at a temperature of more than -80°C to 30°C.

Claim 2. The photocatalyst-coated body according to claim 1, wherein the loss tangent is more than 0.2 to less than 1.0.

Claim 3. The photocatalyst-coated body according to claim 1, wherein the flexible non-silicone component is a flexible non-silicone resin or a flexible non-silicone segment.

Claim 4. The photocatalyst-coated body according to any one of claims 1 to 3, wherein the spectral peak in a curve for a change in a loss elastic modulus as a function of a temperature change as measured with the solid-matter viscoelasticity measuring device according to JIS K 7244-4 appears at a temperature of -40°C to 30°C.

Claim 5. The photocatalyst-coated body according to any one of claims 1 to 4, wherein the photocatalyst layer contains photocatalyst particles and inorganic oxide particles as particulate components and the content of the particulate components in the photocatalyst layer is not less than 70% by mass.

Claim 6. The photocatalyst-coated body according to any one of claims 1 to 5, wherein the surface of the photocatalyst layer becomes hydrophilic upon photoexcitation of the photocatalyst.

Claim 7. The photocatalyst-coated body according to claim 6, wherein

the surface of the photocatalyst layer becomes hydrophilic on a level of less than 20 degrees in terms of contact angle with water upon photoexcitation of the photocatalyst.

Claim 8. The photocatalyst-coated body according to any one of claims 1 to 7, wherein the content of the photocatalyst in the photocatalyst layer is not less than 1% and less than 20% by mass.

Claim 9. The photocatalyst-coated body according to any one of claims 2 to 8, wherein the photocatalyst particles have an average particle diameter of 10 to less than 1000 nm.

Claim 10. The photocatalyst-coated body according to any one of claims 2 to 9, wherein the photocatalyst particles have an average particle diameter of 10 nm to less than 100 nm.

Claim 11. The photocatalyst-coated body according to any one of claims 1 to 10, wherein the photocatalyst is formed of crystalline titanium oxide.

Claim 12. The photoctalyst-coated body according to any one of claims 2 to 11, wherein the inorganic oxide particles have an average particle diameter of 5 nm to less than 100 nm.

Claim 13. The photocatalyst-coated body according to any one of claims 2 to 12, wherein the inorganic oxide particles are silica particles.

Claim 14. The photocatalyst-coated body according to any one of claims 1 to 12, wherein the photocatalyst layer has a thickness of not more than 3 μm.

Claim 15. The photocatalyst-coated body according to any one of claims 2 to 14, wherein interstices are present among the particles in the photocatalyst layers and 20 to 35% by volume of the photocatalyst layer is occupied by the interstices.

Claim 16. The photocatalyst-coated body according to any one of claims 1 to 15, wherein the content of the silicone component in the resin component is 0.5 to 30% by mass in terms of SiO_2.

Claim 17. The photocatalyst-coated body according to any one of claims 1 to 16, wherein the content of the flexible non-silicone component is 20 % by mass to 100000% by mass based on the amount of Si in the silicone component.

Claim 18. The photocatalyst-coated body according to any one of claims 1 to 17, wherein the flexible non-silicone component is at least

one component selected from the group consisting of urethane polyethers, urethane polyesters, urethane polycarbonates, polyethers, polyesters, polyacrylates, polymethacrylates, polyacrylic acids, polymethacrylic acids, and polyvinyls.

Claim 19. The photocatalyst-coated body according to any one of claims 1 to 18, wherein the flexible non-silicone component is at least one component selected from the group consisting of urethane polyether, urethane polyesters, polyethers, and polyacrylates.

Claim 20. Use of a photocatalyst-coated body according to any one of claims 1 to 19 in an environment where the coated body is vibrated and the surface of the photocatalyst layer is exposed to sunlight.

Claim 21. Use of a photocatalyst-coated body according to any one of claims 1 to 19 in which the base material is porous and the photocatalyst-coated body is provided in an atmosphere in which the temperature reaches 0°C or below, and the surface of the photocatalyst layer is exposed to sunlight.

Claim 22. Use of a photocatalyst-coated body according to any one of claims 1 to 19 in which the base material is flexible and the photocatalyst-coated body is subjected to bending after the formation of the photocatalyst layer and is placed in an environment where the surface of the photocatalyst layer is exposed to sunlight.

Claim 23. Use of a photocatalyst-coated body according to any one of claims 1 to 19 in which the photocatalyst-coated body is provided in a place where a daily temperature change is 20°C or above, and is placed in an atmosphere where the surface of the photocatalyst layer is exposed to sunlight.

Claim 24. Use of a photocatalyst-coated body according to any one of claims 1 to 19 in which the base material has a coefficient of linear expansion of not less than $10^{-5}K^{-1}$ and the photocatalyst-coated body is placed in an environment where the surface of the photocatalyst layer is exposed to sunlight.

Claim 25. Use of a photocatalyst-coated body according to any one of claims 1 to 19 in which the photocatalyst-coated body is provided in a place where an annual range of temperature is 30°C or more, and is placed in an atmosphere where the surface of the photocatalyst layer is exposed to sunlight.

Claim 26. Use of a photocatalyst-coated body according to claim 20, wherein the base material is a bridge.

Claim 27. The use of a photocatalyst-coated body according to claim 21, wherein the base material is an unglazed ceramic ware, concrete, cement board, wood, or stone material.

Claim 28. Use of a photocatalyst-coated body according to claim 22, wherein the base material is at least one of metallic materials, rubbers, and flexible film resins.

Claim 29. Use of a photocatalyst-coated body according to claim 23, wherein the base material is at least one of metals, resins, rubbers, silicone sealants, and gaskets.