

DESCRIPTION

Title of Invention PRECOATED STEEL SHEET AND PROCESS FOR
PRODUCING THE SAME

Technical Field

[0001]

The present invention relates to precoated steel sheets for use as, for example, exterior materials of electrical equipment, building interior and exterior materials and roadway members. In particular, the invention relates to precoated steel sheets that are excellent in processability, weather resistance, aesthetic durability and environmental cleanness properties, and to processes for producing the precoated steel sheets.

Background Art

[0002]

Precoated steel sheets, which do not require painting after being shaped or processed, enable one to omit processing steps and improve the working environment. Because of these benefits, precoated steel sheets are used in a wide range of fields as, for example, members in electrical equipment, building exterior materials such as roofs and walls, and building interior materials such as partition members.

[0003]

Prior to use, precoated steel sheets are usually

subjected to various processing operations such as pressing, rolling and embossing which involves 90° bending or 180° bending. Thus, excellent processability and coating layer durability are required. For example, coating resins used in precoated steel sheets are thermosetting polyester resins that can form cured coating layers by being baked at 200°C or above, or fluororesins that are excellent in weather resistance.

[0004]

Recently, there have been increasing demands for improvements in the performance and functions of precoated steel sheets. In particular, the need for aesthetic durability is high. That is, countermeasures should be taken to prevent precoated steel sheets from aesthetic damage caused by bacteria, algae and fungi becoming attached thereto, or caused by airborne combustion products such as smoke, oil mists, exhaust gas and carbon black as well as other possible substances becoming attached thereto for a long period of time.

[0005]

Precoated steel sheets having an individual specific function such as an antibacterial/antifungal function or antifouling function have been developed. However, there have not been developed multifunctional precoated steel sheets that have additional functions.

[0006]

Precoated steel sheets with an antibacterial/antifungal function have a coating layer in which a compound containing silver, copper or the like is dispersed. Such a compound has an antibacterial effect and suppresses the growth of or kills fungi, bacteria and algae on the surface of the coating layer. Such antifouling precoated steel sheets prevent accumulation of attached substances by the action of a coating layer which maintains the surface as hydrophilic as possible so that contaminants that have become attached to the surface will be washed away by rainwater.

[0007]

In particular, an example of a precoated steel sheet having antibacterial and antifouling functions utilizes a photocatalyst which decomposes attached substances such as organic substances. That is, a substance having a photocatalytic activity is dispersed in a coating layer on the surface of the steel sheet, and organic substances that have become attached to the surface are decomposed by the generated active oxygen. However, the photocatalyst gradually decomposes the coating layer itself, which is a matrix, at the same time it decomposes contaminants such as organic substances that have become attached to the surface of the steel sheet. Thus, this technology utilizing photocatalysts has a problem in that chalking is caused and

the coating layer is worn away quickly.

[0008]

To remedy this problem, it has been proposed that an inorganic substance, a fluororesin or an organic-inorganic complex that is negligibly decomposed be used as the matrix of a photocatalyst layer (PTL 1 to 3). Further, a method has been proposed in which at least one surface of a metal sheet is coated with a photocatalyst layer containing a photocatalyst and a fluororesin wax, with a protective layer formed of an inorganic coating material provided therebetween (PTL 4). Furthermore, there have been proposed members that have a substrate and a photocatalytic coating layer as a surface layer on the substrate in which a fluororesin having lubricating and buffering effects is dispersed in a matrix, for example, silica (PTL 5 and 6).

[0009]

In general, a photocatalytic coating layer has a high refractive index and easily exhibits an interference color due to, for example, unevenness in the amounts of the attached photocatalytic substance. In particular, unevenness in the treatment results is more noticeable and an interference color appears as a marked streak when the surface of the base substrate to be treated has a higher gloss or is flatter with a smaller surface roughness, resulting in aesthetic damage.

[0010]

To remedy this problem, methods have been proposed in which a substrate is coated with a discontinuous photocatalyst layer that is dispersed into island-like shapes whereby the photocatalyst layer can remain stably on the substrate permanently without being cracked while ensuring excellent design and durability (PTL 7 and 8).

Citation List

Patent Literature

[0011]

PTL 1: Japanese Unexamined Patent Application
Publication No. 2007-55207

PTL 2: Japanese Unexamined Patent Application
Publication No. 2006-233073

PTL 3: Japanese Unexamined Patent Application
Publication No. 2006-192716

PTL 4: Japanese Unexamined Patent Application
Publication No. 2007-181951

PTL 5: Japanese Unexamined Patent Application
Publication No. 2001-64539

PTL 6: International Publication No. WO97/45502

PTL 7: Japanese Unexamined Patent Application
Publication No. 2000-246115

PTL 8: Japanese Unexamined Patent Application
Publication No. 2009-131987

Summary of Invention

Technical Problem

[0012]

The technology disclosed in PTL 1 achieves good weather resistance, for example resistance to discoloration or fading, due to the photocatalytic substance being dispersed in the inorganic coating layer. However, the coating layer has poor flexibility. That is, when this coating layer is directly applied to a precoated steel sheet, the coating layer is easily cracked when the sheet is bent or drawn, resulting in the separation of the coating layer.

[0013]

The technology disclosed in PTL 2 concerns a steel sheet that has a fluororesin coating layer in which a photocatalytic substance is dispersed. However, when this steel sheet is used as an exterior material placed on a south face outdoors, the photocatalyst induces slight decomposition of the matrix of the coating layer. This defect can be solved by increasing the thickness of the coating layer. However, increasing the layer thickness results in another problem in that the flexibility becomes poor and the processability is lowered as a result.

[0014]

The technology disclosed in PTL 3 is directed to a metal that has been surface-treated with a coating layer in

which a photocatalytic substance is dispersed in an organic-inorganic complex. Although this coating layer slightly surpasses the inorganic coating layer of PTL 1 in terms of processability, the layer thickness has to be small in order to satisfy the level of processability required for the precoated steel sheet. Consequently, the photocatalytic function is lowered.

[0015]

The coated metal sheet according to the disclosure of PTL 4 has a similar problem in that when the coated metal sheet is used as an exterior material, the photocatalyst induces the decomposition of the matrix of the coating layer.

[0016]

The technologies disclosed in PTL 5 and 6 are effective in preventing abrasions and scratches. However, processing involving deformation such as press shaping tends to result in flaws in the photocatalytic coating layer. Thus, it is difficult to apply these technologies to precoated steel sheets.

[0017]

The technology disclosed in PTL 7 involves a complicated method in order to form the photocatalyst coating layer in island-like shapes. Further, a special device is necessary to stably form the coating layer. According to the technologies disclosed in PTL 7 and 8,

processing such as pressing or rolling inevitably results in damage such as flaws in the photocatalyst layer. Thus, the application of these technologies to precoated steel sheets has been difficult.

[0018]

As described above, it has been difficult to apply the technologies in the art to precoated steel sheets or it has not been possible to meet the needs in terms of characteristics of precoated steel sheets such as processability, weather resistance, aesthetic durability utilizing the photocatalytic function, and resistance of the layer matrix to decomposition by the photocatalyst. Further, in the existing technologies, countermeasures against unevenness in treatment results or generation of interference colors have not been sufficiently considered.

[0019]

The present invention is aimed at solving the aforementioned problems in the art. It is therefore an object of the invention to provide precoated steel sheets and production processes therefor in which a photocatalyst layer (coating layer) as the outermost layer is formed in a discontinuous (network) configuration and thereby aesthetic deteriorations caused by unevenness in treatment results or streaks of an interference color can be prevented and the precoated steel sheets achieve required performances, for

example uniform appearance and processability, as well as other properties such as high weather resistance, aesthetic durability and resistance to decomposition caused by the photocatalyst.

Solution to Problem

[0020]

The present inventors propose a novel technology summarized below as an effective solution to the aforementioned problems in the art, thereby achieving the above object.

[0021]

An aspect of the invention is directed to a precoated steel sheet that includes a steel sheet substrate and, on at least one surface thereof, a clear coating layer (A) which contains a silicon compound as a main component and water repellent fine particles as a dispersed component and a clear coating layer (B) which is stacked on the clear coating layer (A) and contains photocatalytic titanium oxide fine particles as a main component.

[0022]

The precoated steel sheet can be a more preferred solution when:

(1) at least some of the water repellent fine particles in the clear coating layer (A) are dispersed in island-like shapes that protrude from the surface of the clear coating

layer (B);

(2) the surface of the clear coating layer (B) has a water contact angle of 22 to 60°;

(3) at least some of the water repellent fine particles in the clear coating layer (A) have a larger particle diameter than the thickness of the clear coating layer (A);

(4) the water repellent fine particles in the clear coating layer (A) are fluororesin particles, fluororesin copolymer resin particles, silicone resin particles or particles whose surface is coated with any of these resins;

(5) the silicon compound in the clear coating layer (A) is an acrylic silicone resin;

(6) the titanium oxide particles in the clear coating layer (B) have been attached in an amount of 10 mg/m² to 2000 mg/m² in terms of TiO₂ per one surface;

(7) the clear coating layer (B) is formed of a mixture of anatase crystalline titanium oxide fine particles and amorphous titanium oxide, as a main component;

(8) the steel sheet substrate is a zinc-containing metal-coated steel sheet having a chemical conversion treatment layer and a resin coating layer formed thereon that are formed on at least one surface of the steel sheet, and the resin coating layer includes a primer layer that is formed of a thermosetting resin containing an antirust pigment, and a colored resin layer; and

(9) the colored resin layer is formed from an organosol-form baking fluororesin as a main component that includes polyvinylidene fluoride and an acrylic resin in a mass ratio of 85:15 to 50:50.

[0023]

Another aspect of the invention proposes a process for producing a precoated steel sheet including sequentially stacking a clear coating layer (A) which contains a silicon compound as a main component and a clear coating layer (B) which contains photocatalytic titanium oxide fine particles as a main component on at least one surface of a steel sheet substrate, wherein the clear coating layer (A) is configured to contain water repellent fine particles as a dispersed component and the amount of coating of the clear coating layer (B) is suppressed on and in the vicinities of the water repellent fine particles so as to disperse the water repellent fine particles into island-like shapes in a manner such that at least some thereof protrude from the surface of the clear coating layer (B).

[0024]

The process for producing a precoated steel sheet according to the invention can be a more preferred solution when at least some of the water repellent fine particles in the clear coating layer (A) have a larger particle diameter than the thickness of the clear coating layer (A).

Advantageous Effects of Invention

[0025]

According to the precoated steel sheets and the production processes therefor that are configured as described above, the following advantageous effects are expected.

(1) The clear coating layer (A) containing the water repellent particles is stacked as a base layer on the surface of the steel sheet substrate, and the clear coating layer (B) containing the photocatalytic titanium oxide fine particles as a dispersed component is stacked thereon.

According to this configuration, the clear coating layer (B) as the outermost layer is discontinued (to form a network shape) on the portions of the clear coating layer (A) where there are the water repellent particles. As a result, the precoated steel sheet can be processed, for example bent or drawn, with a reduced probability of cracks in the clear coating layer (B).

(2) Furthermore, the above configuration ensures that aesthetic deteriorations by unevenness in treatment results or development of an interference color on the clear coating layer (B) can be prevented. The portions of the clear coating layer (A) where there are the water repellent particles are exposed on the surface of the precoated steel sheet. According to this configuration, contaminants such

as organic substances that have attached onto the surface of the precoated steel sheet are repelled by the portions of the clear coating layer (A) (the water repellent particles) exposed on the outermost layer, as well as are decomposed by the clear coating layer (B) (the photocatalyst layer). This cleaning capability enables maintaining of the beauty of the surface permanently.

(3) As described hereinabove, the water repellent fine particles in the clear coating layer (A) that are exposed on the surface of the precoated steel sheet have lubricating and buffering effects. Accordingly, processing such as bending and drawing can be performed while suppressing the occurrence of defects such as flaws in the surface of the steel sheet.

[0026]

(4) The clear coating layer (A) based on a silicon compound is provided between the colored resin layer on the surface of the steel sheet substrate and the clear coating layer (B) that is the outermost layer. This clear coating layer effectively performs so as to give a resistance to decomposition by the photocatalyst in the clear coating layer (B). That is, the colored resin layer that lies under the clear coating layer is prevented from being decomposed and degraded by a direct contact with the photocatalyst. Thus, the precoated steel sheet achieves excellent

processability, weather resistance and aesthetic durability.

Brief Description of Drawings

[0027]

[Fig. 1] Fig. 1 is a sectional view that illustrates an embodiment of a precoated steel sheet according to the invention.

[Fig. 2(a)] Fig. 2(a) is a sectional view that illustrates another embodiment of a precoated steel sheet according to the invention.

[Fig. 2(b)] Fig. 2(b) is a plan view that illustrates another embodiment of a precoated steel sheet according to the invention.

[Fig. 3] Fig. 3 is a view that illustrates a method for evaluating bendability of a precoated steel sheet.

[Fig. 4(a)] Fig. 4(a) is a sectional view that illustrates a structure of a precoated steel sheet in COMPARATIVE EXAMPLE 3 described in EXAMPLES.

[Fig. 4(b)] Fig. 4(b) is a plan view that illustrates a structure of the precoated steel sheet in COMPARATIVE EXAMPLE 3 described in EXAMPLES.

[Fig. 5(a)] Fig. 5(a) is a sectional view that illustrates a structure of a precoated steel sheet in COMPARATIVE EXAMPLE 6 described in EXAMPLES.

[Fig. 5(b)] Fig. 5(b) is a plan view that illustrates a structure of the precoated steel sheet in COMPARATIVE

EXAMPLE 6 described in EXAMPLES.

[Fig. 6(a)] Fig. 6(a) is a sectional view that illustrates a structure of a precoated steel sheet in COMPARATIVE EXAMPLE 7 described in EXAMPLES.

[Fig. 6(b)] Fig. 6(b) is a plan view that illustrates a structure of the precoated steel sheet in COMPARATIVE EXAMPLE 7 described in EXAMPLES.

[Fig. 7(a)] Fig. 7(a) is a sectional view that illustrates a structure of a precoated steel sheet in COMPARATIVE EXAMPLE 8 described in EXAMPLES.

[Fig. 7(b)] Fig. 7(b) is a plan view that illustrates a structure of the precoated steel sheet in COMPARATIVE EXAMPLE 8 described in EXAMPLES.

Description of Embodiments

[0028]

Precoated steel sheets according to the invention have a basic structure in which, on at least one surface of a steel sheet substrate, a clear coating layer (A) which contains a silicon compound as a main component and water repellent fine particles as a dispersed component and a clear coating layer (B) which is stacked on the clear coating layer (A) and contains photocatalytic titanium oxide particles, are sequentially stacked.

[0029]

In particular, the invention is characterized in that

the clear coating layer (A) is configured to contain the water repellent fine particles that are dispersed therein. According to this configuration, the clear coating layer (B) that is formed on the clear coating layer (A) is repelled by the water repellent fine particles in the clear coating layer (A) so as to form a discontinuous (network) shape, with at least some of the water repellent fine particles protruding from the surface of the clear coating layer (B) and being dispersed in island-like shapes. As a result, the precoated steel sheet can be processed with a reduced probability of defects such as cracks in the clear coating layer (B) as the outermost layer. Furthermore, the above configuration ensures that the appearance of the clear coating layer (B) is prevented from aesthetic damage caused by unevenness in treatment results or development of an interference color.

[0030]

Further, portions of the clear coating layer (A) where there are the water repellent fine particles are exposed on the surface of the steel sheet. Because the water repellent fine particles have lubricating and buffering effects, the precoated steel sheet can be processed, for example bent or drawn, while suppressing the occurrence of defects such as flaws in the surface of the steel sheet.

[0031]

Hereinbelow, the precoated steel sheets of the invention will be described in detail with reference to the drawings.

The precoated steel sheet of the invention has a preferred embodiment as illustrated in Fig. 1 in which, in sectional view, a chemical conversion treatment layer 2, a resin coating layer (a primer layer 3 and a colored resin layer 4), and two clear coating layers (a clear coating layer (A) 5 and a clear coating layer (B) 6) are sequentially stacked on at least one surface of a zinc-containing metal-coated steel sheet 1.

[0032]

Preferred examples of the zinc-containing metal-coated steel sheet 1 in the invention include processable steel sheets such as electro-galvanized steel sheets, hot-dip galvanized steel sheets, hot-dip zinc-5 mass% aluminum alloy coated steel sheets, and hot-dip zinc-55 mass% aluminum alloy coated steel sheets. The thickness of these coated steel sheets is not particularly limited, but is preferably about 0.2 to 1.6 mm from the viewpoint of processability.

[0033]

Prior to the formation of the primer layer 3, the chemical conversion treatment layer 2 is formed on one or both surfaces of the zinc-containing metal-coated steel sheet 1. The chemical conversion treatment layer 2 is

formed in order to increase the adhesion between the zinc-containing metal-coated steel sheet 1 and the primer layer 3 and to add corrosion resistance.

[0034]

Preferred examples of the chemical conversion treatment layer 2 include phosphate layers, chromate layers, silica-containing chromate layers, and thin layers which contain a chromate-free metal oxide antirust agent and an organic resin as individual compounds or a complex, in particular which contain an organic resin, a metal oxide, and a phosphoric compound and/or chromic acid in order to achieve improvements in adhesion and corrosion resistance. In this case, the organic resin is desirably a water-dispersible resin, for example an acrylic resin or a urethane resin dispersed with an emulsifier.

[0035]

Of the components for the chemical conversion treatment layer, chromic acid works as a binder which provides adhesion between the chemical conversion treatment layer and the zinc-containing coated layer. The organic resin works to increase the adhesion of the chemical conversion treatment layer to the primer layer described later. The chromium content in the chemical conversion treatment layer is preferably not less than 20 mg/m^2 in terms of metallic chromium. If the chromium content is less than 20 mg/m^2 , the

precoated steel sheet does not exhibit sufficient corrosion resistance.

[0036]

The chromate-free antirust agent, which is a component used in the chemical conversion treatment layer, preferably includes one or more compounds selected from silicic acid and/or silicic acid compounds, calcium or calcium compounds, zirconic acid and/or zirconic acid compounds, vanadic acid and/or vanadic acid compounds, molybdic acid compounds, and phosphoric acid and/or phosphoric acid compounds, and the content thereof is preferably 0.3 to 3.0 g/m². The content of the chromate-free antirust agent is specified to be in the range of 0.3 to 3.0 g/m² because any content less than 0.3 g/m² will not provide the corrosion resistance and adhesion required for the precoated steel sheet, and any content in excess of 3.0 g/m² will result in deteriorated processability. A binder, for example, a water-dispersible acrylic resin or urethane resin, may be used.

[0037]

In the precoated steel sheet of the invention, the primer layer 3 serving as the first coating layer is formed on the surface of the chemical conversion treatment layer 2 formed on at least one surface of the zinc-containing metal-coated steel sheet 1. This primer layer 3 is formed of a thermosetting resin containing an antirust pigment, and

provides corrosion resistance and adhesion between the chemical conversion treatment layer 2 and the upper coating layers (the colored resin layer 4, the clear coating layer (A) 5 and the clear coating layer (B) 6) described later.

[0038]

The thickness of the primer layer 3 is preferably not less than 2 μm and not more than 10 μm . If the thickness is less than 2 μm , sufficient antirust properties will not be obtained. Any thickness in excess of 10 μm is not preferable because it will result in deteriorated processability.

[0039]

The thermosetting resin as a main material for forming the primer layer 3 is not particularly limited. Preferably, one, or two or more resins such as polyester resins and epoxy resins may be used. Examples of the polyester resins include bisphenol A polyester resins. The epoxy resins may be partially substituted with other resins such as urethane resins, phenolic resins and amino resins. For example, epoxy compounds formed of a bisphenol such as bisphenol A, bisphenol F or bisphenol AD and epihalohydrin or β -methylepihalohydrin, and copolymers of such epoxy compounds may be used. Further, the epoxy compounds may be modified with monocarboxylic acids or dicarboxylic acids, mono-, di- or poly-alcohols, mono- or diamines, or mono-, di- or

polyphenols. Such modified products are also usable as the epoxy resins.

[0040]

The main material for the primer layer 3 is limited to the thermosetting resin because a room temperature drying resin or a thermoplastic resin is deformed or degraded by being softened at a baking temperature when the upper coating layers (the colored resin layer and the clear coating layers) are formed thereon, thus failing to achieve high adhesion with the upper coating layers.

[0041]

The curing agent for curing the primer layer 3 may be a polyisocyanate compound and/or an amino resin. Examples of the polyisocyanate compounds include compounds obtainable by common methods such as hexamethylene diisocyanate (hereinafter, HDI) and derivatives thereof, tolylene diisocyanate (hereinafter, TDI) and derivatives thereof, 4,4'-diphenylmethane diisocyanate (hereinafter, MDI) and compounds derived therefrom, xylylene diisocyanate (hereinafter, XDI) and derivatives thereof, isophorone diisocyanate (hereinafter, IPDI) and derivatives thereof, trimethylhexamethylene diisocyanate (hereinafter, TMDI) and derivatives thereof, hydrogenated TDI and derivatives thereof, hydrogenated MDI and derivatives thereof, and hydrogenated XDI and derivatives thereof. In particular, it

is preferable to use a polyisocyanate compound that has been blocked by a blocking agent such as phenol, cresol, aromatic secondary amine, tertiary alcohol, lactam or oxime. This compound is advantageous in that the system can be used as a one-pack coating agent. Because the blocked polyisocyanate compound allows the system to be stored as a one-pack coating agent, the use of the coating agent can be facilitated.

[0042]

Examples of the amino resins for use as the curing agents include resins obtained by reaction of, for example, urea, benzoguanamine or melamine with formaldehyde, and products obtained by alkyletherifying these resins with alcohols such as methanol and butanol. Specific examples include methylated urea resins, n-butylated benzoguanamine resins, methylated melamine resins, n-butylated melamine resins and iso-butylated melamine resins.

[0043]

The blending ratio for the curing agent in the primer layer 3 is preferably 9 to 50% by mass in terms of solid resin. If the ratio is less than 9% by mass, the hardness of the obtainable layer is insufficient. Any ratio in excess of 50% by mass results in insufficient processability.

[0044]

In accordance with the purpose or application, forming

the primer layer 3 may involve a curing catalyst such as p-toluenesulfonic acid, tin octoate or dibutyl tin dilaurate. Further, various additives may be added, with examples including extender pigments such as calcium carbonate, kaolin and clay, coloring pigments such as titanium oxide, red oxide, mica, carbon black and aluminum powder, anti-foaming agents and leveling agents.

[0045]

In the invention, the primer layer 3 is configured to contain 5% by mass to 50% by mass of an antirust pigment in order to prevent swelling of the coating layer or corrosion of the coated layer which can take place at the cut edge or at flaws in the coating layer when the precoated steel sheet is shaped or used outdoors for a long term. No effects of improving the corrosion resistance are obtained if the content of the antirust pigment is less than 5% by mass. Any content in excess of 50% by mass lowers the flexibility of the primer layer, resulting in deteriorations in processability.

[0046]

The antirust pigment used in the invention is preferably one or a mixture of two or more selected from chromates, silica pigments, phosphite pigments, calcium compounds, aluminum oxides, zirconic acid and/or zirconic acid compounds, vanadic acid and/or vanadic acid compounds,

molybdcic acid compounds, and phosphoric acid and/or phosphoric acid compounds. In particular, chromates are preferable because they show higher antirust properties.

[0047]

Next, the colored resin layer 4 will be described. The colored resin layer 4 is formed on the primer layer 3. The resin for forming the colored resin layer 4 is suitably one that shows excellent adhesion with respect to the primer layer 3 and can be applied continuously in the facility for the production of precoated steel sheets. Preferred examples of such resins include polyester resins, fluororesins, acrylic resins, urethane resins and composite resins formed of these resins.

[0048]

In particular, in order to improve the processability of the precoated steel sheet and the durability thereof outdoors (the weather resistance), the main resin for forming the colored resin layer 4 is preferably an organosol-form baking fluororesin that includes polyvinylidene fluoride and an acrylic resin in a mass ratio of 85:15 to 50:50, and more preferably 85:15 to 75:25. The use of an organosol-form baking fluororesin resulting from the mixing of polyvinylidene fluoride and an acrylic resin is preferable in that the crystallization of polyvinylidene fluoride that is a crystalline resin can be suppressed while

improving the durability (the weather resistance) and the processability, as well as in that the colored resin layer 4 achieves increased adhesion with respect to the lower and upper layers thereof, namely, the primer layer 3 and the clear coating layer (A) 5.

[0049]

If the proportion of the polyvinylidene fluoride in the organosol-form baking fluororesin is in excess of 85% by mass, application properties are lowered and the crystallization of polyvinylidene fluoride proceeds, resulting in deteriorations in processability. If the proportion is less than 50% by mass, the durability, in particular weather resistance inherent to the polyvinylidene fluoride is markedly lowered.

[0050]

The acrylic resin contained in the organosol-form baking fluororesin may be a thermoplastic acrylic resin, a thermosetting acrylic resin or a composite resin formed between these resins. From the viewpoint of compatibility with polyvinylidene fluoride, examples of the thermoplastic acrylic resins include polymers of one, or two or more monomers such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate and amyl (meth)acrylate, and copolymers of these monomers with comonomers such as acrylic acid and styrene. Examples of

the thermosetting acrylic resins include those formed of acrylic resins having a crosslinkable functional group such as a hydroxyl group, a carboxyl group, a glycidyl group or an isocyanate group, with curing agents such as alkylated melamines, polyols and polyamides.

[0051]

The colored resin layer 4 dominates the color tone of the appearance of the precoated steel sheet. The colored resin layer contains a coloring pigment that can be selected from various coloring pigments such as titanium oxide, red oxide, mica, carbon black, calcined black, titanium yellow, yellow iron oxide, phthalocyanine blue and phthalocyanine green. The amount of the coloring pigment is about 15% by mass to 60% by mass because this content ensures that an opaque stable layer can be formed with the desired color hue. Where necessary, additives may be added, with examples including gloss controllers such as synthetic silica, antifoaming agents and surface conditioners for improving application workability, and flaw inhibitors.

[0052]

The thickness of the colored resin layer 4 is preferably 8 to 25 μm . Any thickness less than 8 μm results in a decrease in opacifying effects and unstable color tone, as well as insufficient durability, processability and corrosion resistance at processed portions. Any thickness

in excess of 25 μm is not preferable because it results in deteriorations in performance; for example, defects such as blisters (bubbles) are easily generated on the layer, and an internal strain at the time of processing is increased to cause cracks.

[0053]

The colored resin layer 4 may be continuously formed by a common method for producing precoated steel sheets. For example, the chemical solution that has been diluted with an organic solvent may be applied onto the primer layer 3 on the zinc-containing metal-coated steel sheet with a roll coater or a curtain coater, and the wet film may be baked at a temperature of about 230 to 270°C.

[0054]

Next, the clear coating layer (A) 5 will be described. The clear coating layer (A) 5 is formed on the colored resin layer 4 and works so as to increase the adhesion between the upper and lower layers thereof, namely, the clear coating layer (B) 6 and the colored resin layer 4. Further, the clear coating layer (A) 5 suppresses the colored resin layer 4 from being decomposed and degraded by the photocatalytic action of the titanium oxide fine particles in the clear coating layer (B) 6 with time.

[0055]

The main component for the clear coating layer (A) 5 is

a silicon compound. Examples thereof include acrylic silicone resins, trialkoxysilanes and condensates thereof, acryl silicates and condensates thereof, organohydroxysilanes and condensates thereof, compositions of these compounds, and complex compositions of these compounds with silica. In particular, an acrylic silicone resin is preferably used. Examples of the acrylic silicone resins include products formed between acrylate and silicon by complexing, copolymerization or crosslinking with a crosslinking agent or a crosslinking agent containing acrylate or silicon.

[0056]

The acrylate component in the acrylic silicone resin works so as to increase the flexibility of the clear coating layer (A) 5 as well as the adhesion with respect to the colored resin layer 4. The acrylate component may be one, or two or more compounds selected from alkyl-containing acrylic monomers such as methyl acrylate and methyl methacrylate, and oligomers and polymers of these monomers; hydroxyl group-containing acrylic monomers such as 2-hydroxyethyl acrylate, and oligomers and polymers of these monomers; ethylenically unsaturated carboxylic acid monomers such as acrylic acid, and oligomers and polymers of these monomers; and amide group- or glycidyl group-containing acrylic monomers, and oligomers and polymers of these

monomers.

[0057]

The silicone component in the acrylic silicone resin works so as to increase the adhesion with respect to the clear coating layer (B) 6 and prevent the clear coating layer (A) 5 from being decomposed and degraded by the photocatalyst contained in the clear coating layer (B) 6.

[0058]

The silicone component may be one, or two or more selected from alkoxysilane compounds such as methyltriethoxysilane, dimethyldiethoxysilane, phenylmethyldiethoxysilane and γ -glycidoxypropyltrimethoxysilane, hydrolyzates thereof and condensates of these compounds.

[0059]

The thickness of the clear coating layer (A) 5 is preferably not less than 0.2 μm , and more preferably not less than 0.5 μm . The upper limit of the thickness of the clear coating layer (A) 5 is not particularly limited. In the case where the composition is poor in flexibility, however, a smaller thickness is more preferable in order to suppress a decrease in processability. In particular, good processability can be obtained irrespective of the kind of composition by forming the layer in a thickness of not more than 1 μm .

[0060]

As described hereinabove, the present invention is characterized in that the water repellent fine particles 7 are dispersed in the clear coating layer (A) 5. That is, the clear coating layer (B) 6 which is the upper layer is repelled by the water repellent fine particles 7 in the clear coating layer (A) 5 and is consequently suppressed from coating the fine particles 7 and the vicinities thereof. As a result, the clear coating layer (B) 6 does not form a continuous film. When such a precoated steel sheet is processed, the clear coating layer (B) 6 is prevented from the occurrence of defects such as cracks. Further, aesthetic deteriorations by, for example, unevenness in treatment results or streaks of an interference color can be prevented.

[0061]

Examples of the water repellent fine particles 7 that suitably exert the above effects include particles of fluororesins such as polytetrafluoroethylene, polychlorotrifluoroethylene and perfluoroalkoxyfluororesin, particles of fluororesin copolymers such as tetrafluoroethylene/hexafluoropropylene copolymer and ethylene/tetrafluoroethylene copolymer, silicone resin particles, and particles that are surface-coated with these resins. In particular, fluororesin fine particles are

preferable.

[0062]

An embodiment will be discussed in which the water repellent fine particles 7 are formed of polytetrafluoroethylene and the clear coating layer (A) 5 contains the fine particles 7 that have a larger particle diameter than the layer thickness as illustrated in Fig. 1. In such an embodiment, the fine particles 7 are exposed on the surface of the clear coating layer (A) 5, namely, on the surface of the precoated steel sheet. When the precoated steel sheet is processed, for example bent, the fine particles 7 serve more effectively as a lubricant and a buffer so as to suppress the occurrence of defects such as flaws. An example of the fluoro-resin fine particles 7 is Dyneon TF micropowder manufactured by Sumitomo 3M Limited.

[0063]

The water repellent fine particles 7 preferably have an (average) particle diameter of 0.3 to 10 μm . If the particle diameter is less than 0.3 μm , the water repellent effects are lowered and the clear coating layer (B) 6 is allowed to form a continuous film, resulting in unevenness in appearance (development of an interference color) and a decrease in processability. If the particle diameter is in excess of 10 μm , the clear coating layer (A) 5 has to be formed in a sufficiently large thickness in order to

disperse the particles in the clear coating layer (A) 5, causing cost disadvantages and difficulties in forming the clear coating layer (A) 5 stably.

[0064]

The content of the water repellent fine particles 7 in the clear coating layer (A) 5 is preferably about 0.5 to 20% by mass, and more preferably 1 to 10% by mass in terms of solid content. The aforementioned effects are not obtained at a content of less than 0.5% by mass. Any content in excess of 20% by mass is not preferable because the coating layer is clouded or the application process becomes difficult.

[0065]

The clear coating layer (A) 5 may contain various additives as long as the color tone is not changed. Exemplary additives are silica fine particles, dispersants, coupling agents and UV absorbers. For example, the clear coating layer (A) 5 may be formed in a continuous coating line in which the solution that has been diluted with an organic solvent is applied by a curtain coater, a roll coater or a die coater and the wet film is baked. When the main component for the clear coating layer (A) 5 is an acrylic silicone resin, the wet film formed by the application is preferably baked at a temperature of about 150 to 200°C.

[0066]

Next, the clear coating layer (B) 6 that is the outermost layer of the inventive precoated steel sheet will be described. The clear coating layer (B) 6 is formed on the clear coating layer (A) 5. In the invention, the clear coating layer (A) 5 that lies under the clear coating layer (B) 6 contains the water repellent fine particles 7. When an aqueous dispersion for forming the clear coating layer (B) 6 is applied by a roll coating method in the continuous coating line, the clear coating layer (B) 6 becomes a discontinuous (network) layer exposing the water repellent fine particles 7 and the vicinities thereof. According to this configuration, the precoated steel sheet can be processed with a reduced probability of defects such as cracks in the outermost clear coating layer (B) 6. Further, the above configuration suppresses the development of streaks of an interference color that is encountered when the clear coating layer (B) 6 forms a continuous film. Thus, aesthetic deteriorations on the surface can be prevented.

[0067]

As described hereinabove, the clear coating layer (B) is not formed on the water repellent fine particles 7 dispersed in the clear coating layer (A) and the vicinities of the particles, and the water repellent fine particles are exposed on the surface of the clear coating layer (B). The

contact angle between the surface of the clear coating layer (B) and water is not more than 60° , and preferably 22 to 50° . If the water contact angle is in excess of 60° , the self cleaning effects (by which stains like rain streaks attached outdoors are automatically cleaned by rainfall) are not obtained. In particular, marked effects are achieved when the contact angle is not more than 50° . Any water contact angle less than 22° is not preferable because it can cause a decrease in the effects that are produced by the water repellent fine particles dispersed in the clear coating layer (A) (namely, improved shaping processability of the precoated steel sheet, and clean wiping off of the attached stains).

[0068]

The clear coating layer (B) 6 adds a new function to the precoated steel sheet. That is, this layer is effective in maintaining the surface beautiful permanently by decomposing contaminants such as organic substances that have attached to the surface of the precoated steel sheet used as an interior or exterior material, thereby cleaning the surface. This function is exerted by the photocatalytic titanium oxide fine particles contained in the coating layer (B) 6.

[0069]

In the invention, the titanium oxide fine particles

that have a high level of photocatalytic activity are preferably anatase crystalline titanium oxide. From the viewpoints of application properties and photocatalytic properties, the particle diameter of the anatase crystalline titanium oxide is optimally about 0.001 to 0.2 μm . Examples of such anatase crystalline titanium oxides include ST-01, ST-21 and ST-30L manufactured by ISHIHARA SANGYO KAISHA, LTD. [0070]

In general, the anatase crystalline titanium oxide is activated by short-wavelength lights in the ultraviolet region. Thus, when the precoated steel sheet is used as an exterior member, the photocatalytic properties can be induced by ultraviolet rays in the sunlight. When the precoated steel sheet is used as an interior member, visible light responsive anatase crystalline titanium oxide is preferably used. Examples of the visible light responsive titanium oxides include titanium oxides doped with nitrogen, sulfur or carbon, oxygen-deficient titanium oxides, dye-sensitized titanium oxides and metal-supported titanium oxides.

[0071]

The clear coating layer (B) 6 may contain amorphous titanium oxide together with the anatase crystalline titanium oxide. In this case, the mixing ratio between the anatase crystalline titanium oxide and the amorphous

titanium oxide is preferably 10:90 to 80:20 by mass. The amorphous titanium oxide works so as to improve the stability of the coating solution, to serve as a binder in the coating layer, and to improve the processability and the durability of the coating layer.

[0072]

The clear coating layer (B) 6 is formed such that the amount of the titanium oxide particles attached per one surface of the zinc-containing metal-coated steel sheet is 10 mg/m² to 2000 mg/m², and more preferably 50 mg/m² to 2000 mg/m² in terms of TiO₂. If the attached amount is less than 10 mg/m², the photocatalytic properties are markedly lowered and the uniform coating layer cannot be formed. If the amount is in excess of 2000 mg/m², the coating layer will be cracked or separated when the precoated steel sheet is subjected to various processing, and the cracks can extend to such a depth as to reach the colored resin layer 4.

[0073]

The clear coating layer (B) 6 may contain, in addition to the titanium oxide fine particles, one, or two or more film-forming binders and additives, with examples including inorganic compounds such as oxides and compounds of metals such as silicon, aluminum and zirconium, and phosphoric acid compounds.

[0074]

The clear coating layer (B) 6 may contain antibacterial agents such as silver compounds, and adsorbents such as activated carbons and zeolites while maintaining the color tone. These compounds increase aesthetic durability by exerting, for example, antibacterial properties.

[0075]

The clear coating layer (B) 6 may be formed on the clear coating layer (A) 5 in a continuous coating line in which the chemical solution that has been diluted with water or an organic solvent is applied onto the surface of the clear coating layer (A) 5 formed on the zinc-containing metal-coated steel sheet, by a roll coater or a die coater and the wet film is baked at a temperature of about 180 to 250°C.

[0076]

As described hereinabove, the invention is characterized in that the clear coating layer (A) 5 containing the water repellent substance and the clear coating layer (B) 6 containing the photocatalytic particles are provided on one or both surfaces of the steel sheet substrate. According to this configuration, as illustrated in the sectional view in Fig. 2(a) and the plan view in Fig. 2(b), the clear coating layer (B) 6 that is the upper layer is repelled by the water repellent fine particles 7 in the clear coating layer (A) 5 and is consequently suppressed

from coating the fine particles 7 and the vicinities of the particles. That is, the water repellent fine particles 7 are exposed on the surface of the precoated steel sheet (the clear coating layer (B) 6) and are present astride the clear coating layer (A) 5 and the clear coating layer (B) 6. With this configuration, the precoated steel sheet of the invention achieves aesthetic durability by the action of the photocatalyst, resistance to decomposition by the photocatalyst, and excellent appearance uniformity and processability.

Further, the steel sheet substrate has the primer layer 3 and the colored resin layer 4 stacked on the chemical conversion treatment layer 2. According to this configuration, the layers produce mutual effects so as to achieve the above various properties required for the precoated steel sheet.

[0077]

The coating layers are formed on at least one surface of the steel sheet substrate. The identical coating layers may be formed on the other surface (the back surface). Alternatively, the back surface may be chemical conversion treated and thereafter service coated with a so-called one-coat one-bake coating system commonly used for precoated steel sheets.

EXAMPLES

[0078]

The present invention will be described by the following examples.

(INVENTIVE EXAMPLE 1)

The steel sheet substrate used in INVENTIVE EXAMPLE 1 was a hot-dip 55% aluminum-zinc alloy coated steel sheet (the amount of the deposit was 80 g/m² per one side) which had a thickness of 0.5 mm and which had been coated with silica-containing chromate in an amount of 40 mg/m² in terms of metallic chromium. The hot-dip zinc-coated steel sheet was coated with melamine-curable polyester resin coating agent "PRECOLOR PRIMER FX-2 (manufactured by BASF Coatings Japan Ltd.)" containing approximately 20% by mass of strontium chromate as an antirust pigment with use of a bar coater such that the dry thickness would be 5 μm. The wet film was baked at about 230°C for 60 seconds to give a primer layer (a-1).

[0079]

Next, the primer layer was coated with a coating agent (b-1) that was a mixture of organosol-form baking fluororesin "PRECOLOR No. 8800 (manufactured by BASF Coatings Japan Ltd.)" containing polyvinylidene fluoride and an acrylic resin in a mass ratio of 80:20, with titanium oxide and calcined black as coloring pigments and calcined silica as a surface conditioner. The coating agent was

applied with a bar coater such that the dry thickness would be 22 μm . The wet film was baked at about 240°C for 60 seconds to give a colored resin layer (which had a gloss value of 10 at 60 degrees).

[0080]

Next, the colored resin layer was coated with a coating agent (c-1) which contained a solution of an acrylic silicone resin that had a weight average molecular weight of about 20,000 and that included n-butyl acrylate and methyl methacrylate as acrylic components and γ -methacryloxypropyltriethoxysilane as a silicone component, as well as 5% by mass of polytetrafluoroethylene fine particles having an average particle diameter of 4 μm (Dyneon TF 9207 manufactured by Sumitomo 3M Limited). The coating agent was applied with a bar coater such that the dry thickness would be 2 μm . The wet film was baked at about 150°C for 30 seconds to give a clear coating layer (A).

[0081]

On the clear coating layer (A), an aqueous dispersion (d-1) was applied which had been prepared by mixing 20% by mass in terms of solid of anatase titanium oxide ST-21 manufactured by ISHIHARA SANGYO KAISHA, LTD., with amorphous titanium oxide dispersion "PTI-5600" manufactured by Nihon Parkerizing Co., Ltd. The aqueous dispersion was applied with a roll coater such that the attached amount would be

150 mg/m² in terms of TiO₂. The wet film was dried at about 200°C for 20 seconds to give a clear coating layer (B).

Thus, a precoated steel sheet according to the invention (INVENTIVE EXAMPLE 1) was manufactured.

[0082]

(INVENTIVE EXAMPLES 2 to 8, and COMPARATIVE EXAMPLES 1 to 8)

Inventive precoated steel sheets (INVENTIVE EXAMPLES 2 to 8) and comparative precoated steel sheets (COMPARATIVE EXAMPLES 1 to 8) were manufactured in the same manner as in INVENTIVE EXAMPLE 1, except that the primer layer, the colored resin layer, the clear coating layer (A) and the clear coating layer (B) in INVENTIVE EXAMPLE 1 were changed in accordance with the conditions described in Table 1. In COMPARATIVE EXAMPLE 7, the aqueous dispersion (d-1) was sprayed onto the clear coating layer (A) such that the photocatalyst would be dispersed into island-like shapes.

[0083]

In Table 1, the coating agent (b-2) for the colored resin layer was a melamine-curable polyester resin ("PRECOLOR No. 3800" (manufactured by BASF Coatings Japan Ltd.)) containing titanium oxide and carbon black as coloring pigments. This layer had a thickness of 15 μ m and a gloss value of 60.

The coating agent (c-2) for the clear coating layer (A) was prepared by mixing the acrylic silicone resin solution

used for the coating agent (c-1) with 3% by mass in terms of solid of polytetrafluoroethylene fine particles having an average particle diameter of 8 μm (Dyneon TF 9205 manufactured by Sumitomo 3M Limited). The coating agent (c-3) was the acrylic silicone resin solution used for the coating agent (c-1) without adding any water repellent fine particles. The coating agent (c-4) was an acrylic resin emulsion coating agent. The coating agent (c-5) was prepared by mixing the coating agent (c-3) with 30% by mass in terms of solid of the powder used in (d-1) and 3% by mass in terms of solid of water repellent fine particles (Dyneon TF 9207 manufactured by Sumitomo 3M Limited).

The dispersion (d-2) for the clear coating layer (B) was the same as the dispersion (d-1) except that the anatase titanium oxide was eliminated. The dispersion (d-3) was prepared by mixing the aqueous dispersion (d-1) with 3% by mass in terms of solid of water repellent fine particles (Dyneon TF 9207 manufactured by Sumitomo 3M Limited).

[0084]

The precoated steel sheets (INVENTIVE EXAMPLES 1 to 8, and COMPARATIVE EXAMPLES 1 to 8) manufactured as described above were tested by the following methods, the results being described in Table 1.

(Testing methods and evaluation methods)

(1) Appearance uniformity

The appearance of the precoated steel sheet was visually evaluated based on the following criteria:

⊙: No interference color was observed, and the appearance was good.

○: A slight interference color was observed, but the appearance was good without any defects such as unevenness and discoloration.

△: Slight unevenness and discoloration (such as development of an interference color) were observed.

×: Marked unevenness and discoloration (such as development of an interference color) were observed.

[0085]

(2) Bendability

Two identical steel sheets were stacked one on top of the other indoors (20°C) as illustrated in Fig. 3. The precoated steel sheet was folded 180° so as to clamp the upper end portion of the stacked steel sheets. The outward bent portion (the upper end) of the coating layer was visually observed to inspect for the occurrence of defects (cracks). The evaluation was made based on the following criteria:

⊙: No cracks were observed.

○: Slight cracks were observed.

△: Marked cracks were observed.

×: Heavy cracks were observed.

[0086]

(3) Resistance to flaws by processing

The precoated steel sheet was press-bent such that the coating layer side would be bent outward. Changes in appearance of the surface of the coating layer, as well as the occurrence of flaws, were evaluated. The bending was performed indoors at 20°C such that the inner radius would be 0.8 mm.

○: No flaws were caused.

△: Slight flaws and discoloration were caused on the portions that had been in contact with the press mold.

×: Marked flaws were caused on the coating layer.

[0087]

(4) Weather resistance

An accelerated weather resistance test was carried out for 1000 hours under the following conditions. The appearance was evaluated based on the following criteria:

⊙: The color tone and the gloss were not substantially changed.

○: The color tone and the gloss were slightly changed.

△: The color tone and the gloss were changed.

×: Marked changes in color tone and gloss, for example severe chalking, were observed.

(Accelerated weather resistance test conditions)

Number of sunshine carbon arc lamps: one lamp (No

filter was used.)

Power supply voltage: single phase AC 180-230 V

Turn off-on cycles: 60 minutes - 60 minutes

Conditions at light on

Temperature indicated on a black panel thermometer:
63±3°C

Relative humidity: 50±5%

Conditions at light out

Air temperature: 30°C

Relative humidity: at least 98%

Temperature of cooling water applied to the back
surface of the test piece: about 7°C

Injection of water to the surface of the test piece:
not performed

Dosage of radiations received by the surface of the
test piece: 285±50 W/m² at 300 to 700 nm

[0088]

(5) Aesthetic durability

The precoated steel sheets produced in INVENTIVE
EXAMPLES and COMPARATIVE EXAMPLES were cut to 200 mm x 300
mm rectangles and were allowed to stand vertically for 4
months on:

(A) a wall (at a height of about 1 m from the ground)
of a building adjacent to a road, and

(B) a wall (directly on the ground) of a cottage

adjacent to paddy fields.

The appearance was evaluated based on the following criteria:

O: The surface was substantially free of attached contaminants and maintained a beautiful appearance.

Δ: The surface had been slightly covered with contaminants and had substantially lost the initial beautiful appearance.

x: Contaminants (for example living organisms such as algae, and carbon) had attached severely to a level such that they would not be removed by cleaning, and the initial beautiful appearance had been lost.

[0089]

(6) Water contact angle

The surface of the precoated steel sheets produced in INVENTIVE EXAMPLES and COMPARATIVE EXAMPLES was irradiated with UV rays at an intensity of 0.2 mW/cm^2 using a 20 W black light (FL20S-BLB manufactured by TOSHIBA Lighting & Technology Corporation) for 24 hours. Thereafter, water was dropped onto the surface and the water contact angle after 3 seconds was measured with an automatic contact angle meter (DM-500 manufactured by Kyowa Interface Science Co., Ltd.). The results are described in Table 1.

[0090]

[Table 1]

	Primer layer	Colored resin layer	Clear coating layer (A)		Clear coating layer (B)		Evaluation results					
	Kind	Kind	Kind	Thickness (μm)	Kind	Content in terms of TiO ₂ (mg/m ²)	Appearance uniformity	Bendability	Resistance to flaws by processing	Weather resistance	Aesthetic durability	Contact angle of water (degrees)
Ex. 1	a-1	b-1	c-1	2	d-1	150	O	⊙	O	⊙	O	32
Ex. 2	a-1	b-1	c-1	4	d-1	150	O	⊙	O	⊙	O	30
Ex. 3	a-1	b-1	c-1	0.2	d-1	150	O	⊙	O	⊙	O	38
Ex. 4	a-1	b-1	c-1	2	d-1	20	O	⊙	O	⊙	O	41
Ex. 5	a-1	b-1	c-1	2	d-1	1200	O	O	O	⊙	O	26
Ex. 6	a-1	b-1	c-2	6	d-1	100	O	⊙	O	⊙	O	36
Ex. 7	a-1	b-2	c-1	1	d-1	150	O	⊙	O	⊙	O	31
Ex. 8	a-1	b-2	c-1	0.2	d-1	800	O	⊙	O	⊙	O	33
Comp. Ex. 1	a-1	b-2	none	-	d-1	150	O	O	x	x	x	9
Comp. Ex. 2	a-1	b-1	c-1	2	none	-	O	O	O	⊙	x	67
Comp. Ex. 3	a-1	b-1	c-3	1	d-1	150	O	Δ	x	⊙	O	21
Comp. Ex. 4	a-1	b-1	c-1	2	d-2	150	O	⊙	O	⊙	x	63
Comp. Ex. 5	a-1	b-1	c-4	2	d-1	150	O	⊙	Δ	x	Δ	8
Comp. Ex. 6	a-1	b-1	c-3	2	d-3	150	O	O	x	O	O	14
Comp. Ex. 7	a-1	b-1	c-3	2	d-1	100	O	O	x	O	O	18
Comp. Ex. 8	a-1	b-1	c-5	2	none	-	O	Δ	Δ	x	Δ	12

[0091]

The results in Table 1 show that the precoated steel sheets in INVENTIVE EXAMPLES 1 to 8 achieved excellent performances in all the evaluation tests.

In contrast, the precoated steel sheet in COMPARATIVE EXAMPLE 1 was found to be poor in the resistance to flaws by processing, the weather resistance and the aesthetic durability because this precoated steel sheet did not have the clear coating layer (A).

The precoated steel sheet in COMPARATIVE EXAMPLE 2 did not show any photocatalytic effects because this precoated steel sheet did not have the clear coating layer (B). Thus, the aesthetic durability was poor.

The precoated steel sheet in COMPARATIVE EXAMPLE 3 did not contain any water repellent fine particles in the clear coating layer (A) 5. Consequently, as illustrated in the sectional view in Fig. 4(a) and the plan view in Fig. 4(b), the clear coating layer (B) 6 provided thereon formed a continuous film and flaws were caused on the surface by processing.

In COMPARATIVE EXAMPLE 4, the clear coating layer (B) did not contain titanium oxide and thus failed to maintain the beautiful appearance by the photocatalytic action. In COMPARATIVE EXAMPLE 5, the clear coating layer (A) was formed of an acrylic resin emulsion coating agent which did

not contain any silicon compounds or water repellent fine particles. Thus, the clear coating layer (A) was decomposed and degraded by the photocatalyst, resulting in deteriorations in weather resistance and processability.

[0092]

In COMPARATIVE EXAMPLE 6, the water repellent fine particles were mixed in the coating liquid for the clear coating layer (B). Consequently, as illustrated in the sectional view in Fig. 5(a) and the plan view in Fig. 5(b), the water repellent fine particles 7 were present only in the clear coating layer (B) 6. Because of the presence of the water repellent fine particles 7, the clear coating layer (B) 6 formed a discontinuous shape and achieved excellent uniformity in appearance. However, the retention force for holding the fine particles 7 in the clear coating layer (B) 6 was so weak that flaws were easily caused during processing and most of the fine particles were detached by processing.

In COMPARATIVE EXAMPLE 7, as illustrated in the sectional view in Fig. 6(a) and the plan view in Fig. 6(b), the photocatalyst layer 8 was dispersed into island-like (discontinuous) shapes on the surface of the clear coating layer (A) 5. (The surface covering rate was 90% of the area.) However, because the layer did not contain any water repellent fine particles 7, processing such as pressing or

rolling resulted in flaws in the surface.

In COMPARATIVE EXAMPLE 8, the clear coating layer (A) was configured to contain both the water repellent fine particles and the photocatalyst particles. As illustrated in the sectional view in Fig. 7(a) and the plan view in Fig. 7(b), the water repellent fine particles 7 were exposed on the surface of the clear coating layer (A) 5. The precoated steel sheet in COMPARATIVE EXAMPLE 8 showed good bendability by the effects of the water repellent fine particles 7. However, the weather resistance was low because the photocatalyst particles 8 were buried in the clear coating layer (A) 5.

[0093]

In COMPARATIVE EXAMPLES 1 to 8, the water contact angle was outside the range of 22 to 60°.

Industrial Applicability

[0094]

According to the precoated steel sheets and the production processes therefor of the present invention, excellent properties such as processability, weather resistance and aesthetic durability are achieved. The precoated steel sheets are suited for use as exterior materials of electrical equipment, and building interior and exterior materials. Needless to mention, the precoated steel sheets may be used in other applications requiring the

aforementioned performances.

Reference Signs List

[0095]

- 1 COATED STEEL SHEET
- 2 CHEMICAL CONVERSION TREATMENT LAYER
- 3 PRIMER LAYER
- 4 COLORED RESIN LAYER
- 5 CLEAR COATING LAYER (A)
- 6 CLEAR COATING LAYER (B)
- 7 WATER REPELLENT FINE PARTICLES
- 8 PHOTOCATALYST PARTICLES, PHOTOCATALYST LAYER

CLAIMS

[Claim 1]

A precoated steel sheet comprising:

a steel sheet substrate and, on at least one surface thereof,

a clear coating layer (A) which contains a silicon compound as a main component and water repellent fine particles as a dispersed component and

a clear coating layer (B) which is stacked on the clear coating layer (A) and contains photocatalytic titanium oxide fine particles as a main component.

[Claim 2]

The precoated steel sheet according to Claim 1, wherein at least some of the water repellent fine particles in the clear coating layer (A) are dispersed in island-like shapes that protrude from the surface of the clear coating layer (B).

[Claim 3]

The precoated steel sheet according to Claim 1 or 2, wherein the surface of the clear coating layer (B) has a water contact angle of 22 to 60°.

[Claim 4]

The precoated steel sheet according to any one of Claims 1 to 3, wherein at least some of the water repellent fine particles in the clear coating layer (A) have a larger particle diameter than the thickness of the clear coating layer (A).

[Claim 5]

The precoated steel sheet according to any one of Claims 1 to 4, wherein the water repellent fine particles in the clear coating layer (A) are fluororesin particles, fluororesin copolymer resin particles, silicone resin particles or particles whose surface is coated with any of these resins.

[Claim 6]

The precoated steel sheet according to any one of Claims 1 to 5, wherein the silicon compound in the clear coating layer (A) is an acrylic silicone resin.

[Claim 7]

The precoated steel sheet according to any one of Claims 1 to 6, wherein the titanium oxide particles in the clear coating layer (B) have been attached in an amount of 10 mg/m² to 2000 mg/m² in terms of TiO₂ per one surface.

[Claim 8]

The precoated steel sheet according to any one of Claims 1 to 7, wherein the clear coating layer (B) is formed of a mixture of anatase crystalline titanium oxide fine particles and amorphous titanium oxide, as a main component.

[Claim 9]

The precoated steel sheet according to any one of Claims 1 to 8, wherein the steel sheet substrate is a zinc-containing metal-coated steel sheet having a chemical conversion treatment layer and a resin coating layer formed thereon that are formed on at least one surface of the steel sheet, and

the resin coating layer includes a primer layer that is formed of a thermosetting resin containing an antirust pigment, and a colored resin layer.

[Claim 10]

The precoated steel sheet according to Claim 9, wherein the colored resin layer is formed from an organosol-form baking fluororesin as a main component that includes polyvinylidene fluoride and an acrylic resin in a mass ratio of 85:15 to 50:50.

[Claim 11]

A process for producing a precoated steel sheet comprising sequentially stacking a clear coating layer (A) which contains a silicon compound as a main component and a clear coating layer (B) which contains photocatalytic titanium oxide fine particles as a main component on at least one surface of a steel sheet substrate, wherein

the clear coating layer (A) is configured to contain water repellent fine particles as a dispersed component and the amount of coating of the clear coating layer (B) is suppressed on and in the vicinities of the water repellent fine particles so as to disperse the water repellent fine particles into island-like shapes in a manner such that at least some thereof protrude from the surface of the clear coating layer (B).

[Claim 12]

The process for producing a precoated steel sheet according to Claim 11, wherein at least some of the water repellent fine particles in the clear coating layer (A) have a larger particle diameter than the thickness of the clear coating layer (A).