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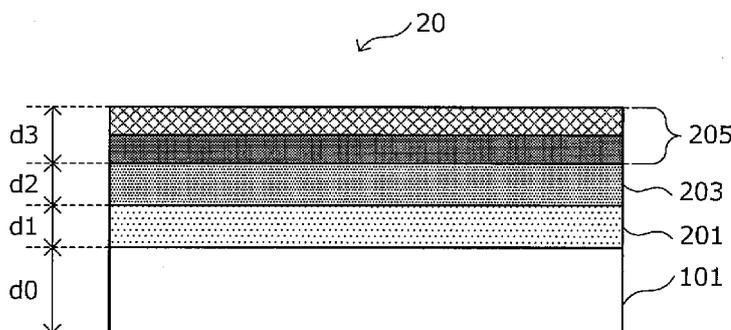
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(54) Title: PRE-COATED PLATED STEEL SHEET, AND MOULDED ARTICLE

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(57) Abstract: [Problem] To more reliably suppress the detachment of a coating film even in the case of drawing processing using a Zn-Al-Mg alloy plated steel sheet as a base sheet. [Solution] This pre-coated plated steel sheet comprises: a plating layer comprising Zn-Al-Mg alloy plating located on one side or both sides of a steel sheet; a chemical conversion coating film layer located on the plating layer; and a coating film layer located on the chemical conversion coating film layer. The coating film layer includes: a primer coating film layer; and an upper layer coating film layer located on the primer coating film layer. The coating film layer satisfies at least any one of: condition (a-1) and condition (a-2); condition (b); and condition (c).

(57) 要約: 【課題】 Zn-Al-Mg系合金めっき鋼板を原板とし、絞り加工を行った場合であっても、塗膜浮きの発生をより確実に抑制すること。【解決手段】本発明に係るプレコートめっき鋼板は、鋼板の片面又は両面に位置する、Zn-Al-Mg系合金めっきからなるめっき層と、前記めっき層上に位置する化成処理皮膜層と、前記化成処理皮膜上に位置する塗膜層と、を備え、前記塗膜層は、プライマー塗膜層と、前記プライマー塗膜層上に位置する上層塗膜層と、を有しており、条件(a-1)かつ条件(a-2)、又は、条件(b)、又は、条件(c)の少なくとも何れかを満足する。

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[Name of Document] DESCRIPTION

[Title of the Invention] PRE-COATED PLATED STEEL SHEET AND MOLDED PRODUCT

[Technical Field]

5 [0001]

The present invention relates to a pre-coated plated steel sheet and a molded product.

[Background Art]

[0002]

10 For the use of home electric appliances, building materials, and automobiles, a pre-coated plated steel sheet becomes to be used in place of a conventional post-painted product obtained by performing painting after molding. This pre-coated plated steel sheet is one obtained by coating a plated steel sheet after being subjected to rust prevention treatment with a
15 colored organic film, and has a characteristic that it has sufficient workability and good corrosion resistance while exhibiting a beautiful appearance.

[0003]

The pre-coated plated steel sheet is often used for applications of air conditioner outdoor units and the like, of which quite severe workability in
20 deep drawing, bending of elongated portion, or the like is required. Accordingly, many techniques have been conventionally studied as a method for improving the adhesion between the plated steel sheet and the paint film at a severely worked portion.

[0004]

25 For example, Patent Document 1 below discloses a technique in which a thermosetting paint film having a minimum value of a dynamic storage

elastic modulus in a rubbery elastic region of 2×10^7 Pa or less is used for any layer of a paint film of a pre-coated plated steel sheet, to thereby secure excellent drawability.

[0005]

5 Further, Patent Document 2 below discloses a technique in which a paint film of a pre-coated plated steel sheet has one layer or more of a paint film having a flow region further on a high-temperature side of a rubber elastic region of a viscoelastic curve, to thereby secure excellent drawability.

[0006]

10 Further, Patent Document 3 below discloses a high-gloss pre-coated plated steel sheet having one or two or more of paint film layers, in which the uppermost surface layer has Tg of 5 to 30°C, a universal hardness under a load of 5 mN at 23°C of 2.5 N/mm² or more, and a fracture elongation at 23°C of 100% or more, which makes it difficult to cause gloss degradation of
15 the paint film at a worked portion even when deep drawing is performed.

[0007]

Further, Patent Document 4 below discloses a technique in which a resin paint film having a proportional elastic limit in a tensile test, and having a tensile elastic modulus of 300 kg/mm² or less is coated as a paint film of a
20 pre-coated plated steel sheet, to thereby secure excellent drawability. Further, it is disclosed that such a paint film preferably has an elastic limit elongation of 15% or less, a total elongation of 15% or more, and a yield point elongation in the tensile test.

[0008]

25 Further, Patent Document 5 below discloses a paint component for under painting for a non-chromate pre-coated metal sheet excellent for an

application of deep drawing, containing (A) a polyester and/or epoxy modified polyester resin having Tg of 60°C or more, Mn of 15000 or more, and OH valence of 5 mgKOH/g or less, and (B) a curing agent of an amino resin, a blocked polyisocyanate compound and/or an epoxy resin, in which, in
5 100 parts by mass in total of (A) + (B), a ratio of (A) is 70 to 95 parts by mass, and a ratio of the curing agent (B) is 5 to 30 parts by mass.

[0009]

Further, Patent Document 6 below discloses a pre-coated metal sheet that is difficult to cause damage such as cracks and peeling in a paint film
10 when being subjected to drawing, since a polyester resin in the paint film has Mn of 10000 or more and 50000 or less, OH valence of 10 mg-KOH/g or less, and Tg of 20°C or more and 67°C or less, a melamine resin is composed of imino group-type methylated melamine or butylated melamine and complete alkyl-type methylated melamine, a solid content ratio of the melamine resin is
15 0.5 to 30 parts by mass with respect to 100 parts by mass of a solid content of the resin other than the melamine resin, and melamine resin particles having a maximum particle size of greater than 50 nm and 1000 nm or less are dispersed in the film.

[Prior Art Document]

20 [Patent Document]

[0010]

Patent Document 1: Japanese Laid-open Patent Publication No. 2001-323389

Patent Document 2: Japanese Laid-open Patent Publication No.
25 2003-103697

Patent Document 3: Japanese Laid-open Patent Publication No.

2007-44922

Patent Document 4: Japanese Laid-open Patent Publication No. 09-193286

Patent Document 5: Japanese Laid-open Patent Publication No. 2005-82623

Patent Document 6: Japanese Laid-open Patent Publication No. 2005-52997

[0011]

In recent years, a pre-coated plated steel sheet is often used for the application designed for a heavy salt damage area, and is required to have a corrosion resistance greater than that of a conventional pre-coated plated steel sheet. When a hot-dip galvanized steel sheet (GI) or an electrogalvanized steel sheet (EG) is used as a base sheet of the pre-coated plated steel sheet, like the way it used to be, a sufficient corrosion resistance performance cannot be satisfied, so that a Zn-Al-Mg-based alloy plated steel sheet excellent in corrosion resistance becomes to be used as the base sheet.

[0012]

Here, the Zn-Al-Mg-based alloy plating is hard and a plating configuration is non-uniform, when compared to conventional zinc plating such as GI and EG. Accordingly, when a plated steel sheet is worked, cracks occur locally in the plating at an elongated portion. Further, at a compressed portion, a plating thickness increases locally and a stress concentrates on an interface between a paint film and the plating, which becomes a cause of an occurrence of peeling of the paint film. Specifically, when the

Zn-Al-Mg-based alloy plated steel sheet is used as the base sheet of the pre-coated plated steel sheet, the corrosion resistance is improved, but the paint film peeling at the worked portion becomes likely to occur, and thus there arises a problem that it is not possible to use the means for solving the problems regarding the paint film peeling at the worked portion, which has been effective for the conventional galvanized steel sheets.

[0013]

As a form of the paint film peeling to be a problem in particular, there can be cited paint film floating at a drawn molded portion. When the pre-coated plated steel sheet is used to be subjected to drawing for a top plate of an air conditioner outdoor unit, or the like, a phenomenon called paint film floating (a phenomenon in which the paint film becomes rough due to aggregates of minute point-like blisters) occurs at a drawn portion. Hereinafter, the portion where these phenomena occur is referred to as a “paint film floating portion.” From a cross-sectional observation of the paint film floating portion, it can be understood that the paint film floating is a phenomenon in which the paint film is detached upward in portions where the paint film fails to follow deformation (compression) of the plated steel sheet during draw molding of the pre-coated plated steel sheet and becomes redundant, resulting in that the stress of the paint film exceeds the paint film-plating adhesion.

[0014]

The technique of Patent Document 1 described above aims to inhibit the buckling of the paint film due to the compressive strain of the drawn molded portion, which occurs during drawing, by specifying the paint film physical properties. Here, the base sheet supposed in Patent Document 1

described above is a galvanized steel sheet, and can be estimated to be different from the Zn-Al-Mg-based alloy. As a result of studies conducted by the present inventors, it was clarified that when the method of Patent Document 1 described above is actually applied to the Zn-Al-Mg-based alloy plated steel sheet, a cohesive force of the paint film is not sufficient, and thus the paint film fails to follow local deformation of plating and cohesive failure of the paint film occurs, which promotes the paint film floating. Besides, it was not possible to avoid a reduction in the paint film performance such as a chemical resistance also at a portion where the paint film floating does not occur. From such viewpoints, Patent Document 1 described above still has room for improvement.

[0015]

The technique of Patent Document 2 described above is the same as the technique of Patent Document 1 described above in that the paint film physical properties are specified to inhibit the buckling of the paint film due to the compressive strain during drawing. As a result of studies conducted by the present inventors, it was clarified that when the method of Patent Document 2 is actually applied to the Zn-Al-Mg-based alloy plated steel sheet, a cohesive force of the paint film is not sufficient, and thus the paint film fails to follow local deformation of plating and cohesive failure of the paint film occurs, which promotes the paint film floating. Besides, it was not possible to avoid a reduction in the paint film performance such as the chemical resistance also at a portion where the paint film floating does not occur. From such viewpoints, Patent Document 2 described above still has room for improvement.

[0016]

The technique of Patent Document 3 described above has an object to inhibit so-called scuffing of a paint film by specifying physical properties of the paint film of the uppermost surface layer of the pre-coated plated steel sheet to increase a hardness of the paint film. Accordingly, it can be estimated that such a technique does not contribute to inhibit the “paint film floating portion” focused this time.

[0017]

The technique of Patent Document 4 described above is the same as the technique of Patent Document 1 described above in that the paint film physical properties are specified to inhibit the buckling of the paint film due to the compressive strain during drawing. As a result of studies conducted by the present inventors, it was clarified that when the method of Patent Document 4 is actually applied to the Zn-Al-Mg-based alloy plated steel sheet, the molding can be performed without causing the paint film floating right after the deep drawing, but the paint film floating is caused with time or by heating. It was inferred that this is because the paint film under the yield point elongation state causes entropy elasticity with time or by heating, resulting in that the stress applied to the interface between the plating and the paint film increases. As described above, Patent Document 4 still has room for improvement.

[0018]

The technique of Patent Document 5 described above is based on the technical idea that the low cross-linked paint film with high glass transition point (T_g) is used to reduce the stress during working. This technique is the same as the technique of Patent Document 1 described above in that the paint film physical properties are specified to inhibit the buckling of the paint film

due to the compressive strain during drawing. As a result of studies conducted by the present inventors, it was clarified that when the method of Patent Document 5 is actually applied to the Zn-Al-Mg-based alloy plated steel sheet, a cohesive force of the paint film is not sufficient, and thus the paint film fails to follow local deformation of plating and cohesive failure of the paint film occurs, which promotes the paint film floating. Besides, it was not possible to avoid a reduction in the paint film performance such as the chemical resistance also at a portion where the paint film floating does not occur. From such viewpoints, Patent Document 5 still has room for improvement.

[0019]

The technique of Patent Document 6 described above is based on the technical idea that the low cross-linked paint film with high Tg is used and the self-condensation reaction of melamine is promoted to lower the cross-link density inside the paint film and reduce the stress during working. This technique is the same as the technique of Patent Document 1 described above in that the paint film physical properties are specified to inhibit the buckling of the paint film due to the compressive strain during drawing. As a result of studies conducted by the present inventors, it was clarified that when the method of Patent Document 6 is actually applied to the Zn-Al-Mg-based alloy plated steel sheet, a cohesive force of the paint film is not sufficient, and thus the paint film fails to follow local deformation of plating and cohesive failure of the paint film occurs, which promotes the paint film floating. Besides, it was not possible to avoid a reduction in the paint film performance such as the chemical resistance also at a portion where the paint film floating does not occur. From such viewpoints, Patent Document 6 still has room for

improvement.

[0019a]

Any reference to publications cited in this specification is not an admission that the disclosures constitute common general knowledge in Australia.

SUMMARY OF THE INVENTION

[0020]

Disclosed herein is a pre-coated plated steel sheet and a molded product, which may be capable of more securely inhibiting the occurrence of paint film floating even when drawing is performed by using a Zn-Al-Mg-based alloy plated steel sheet as a base sheet.

[0020a]

In a first aspect there is provided a pre-coated plated steel sheet, comprising: a plating layer composed of Zn-Al-Mg-based alloy plating, the plating layer being positioned on one side or both sides of a steel sheet;

a chemical treatment film layer positioned on the plating layer; and

a paint film layer positioned on the chemical treatment film, wherein:

the paint film layer includes a primer paint film layer, and an upper paint film layer positioned on the primer paint film layer; and

out of conditions below, at least any of the following is satisfied: both a condition (a-1) and a condition (a-2); a condition (b); and a condition (c); wherein

the chemical treatment film layer contains any one or more selected from the group consisting of a resin, a silane coupling agent, a zirconium compound, silica, phosphoric acid and salts thereof, fluoride, a vanadium compound, and tannin or tannic acid;

the plating layer is a plating layer containing aluminium of 0.5 mass% or more and 60.0 mass% or less, magnesium of 0.5 mass% or more and 15.0 mass% or less, and the balance being composed of zinc and impurities;

a thickness of the primer paint film layer is 2 to 10 μm ;

a total thickness of the primer paint film layer and the upper paint film layer is 10 to 30 μm ;

the primer paint film layer contains a first polyester-based resin having an average molecular weight of 15000 to 20000 and a glass transition point T_g of 20 to 50 $^{\circ}\text{C}$, a second polyester-based resin having an average molecular weight of 20000 to 25000 and a glass transition point T_g of less than 20 $^{\circ}\text{C}$, and a curing agent, wherein T_g is determined by differential scanning calorimetry; and

the curing agent contains blocked isocyanate;

(a-1) A cut strength measured by cutting an interface between the paint film layer and a layer positioned on the steel sheet side relative to the paint film layer by a SAICAS method is 1.00 kN/m or more on average, 5% or less of a cut area is in the form of interfacial peeling, and the remaining cut area is in the form of cohesive failure within the paint film layer;

(a-2) When a portion where a thickness of the pre-coated plated steel sheet after being subjected to deep drawing has increased by 20% or more when compared to a thickness of a non-molded portion is cut by the SAICAS method, at an interface between the paint film layer and a layer positioned on the steel sheet side relative to the paint film layer, a cut strength is 1.0 kN/m or more on average, 20% or less of a cut area is in the form of interfacial peeling, and the remaining cut area is in the form of cohesive failure within the paint film layer;

(b) An indentation load when a microhardness measuring quadrangular pyramid-shaped indenter is inserted at a rate of 2 μm per minute with respect to a position 1 μm away in a direction of the primer paint film layer from an interface between the primer paint film layer and a layer positioned on the steel sheet side relative to the primer paint film layer, at a cross section obtained by cutting the

primer paint film layer in a thickness direction, and the indenter reaches a depth of 10 μm , is less than 1000 mN;

(c) A load curve with respect to a displacement when a microhardness measuring quadrangular pyramid-shaped indenter is inserted at a rate of 10 μm per second to a depth of 10 μm with respect to a position 1 μm away from an interface between the primer paint film layer and a layer positioned on the steel sheet side relative to the primer paint film layer, at a cross section obtained by cutting the primer paint film layer in the thickness direction, and then the indenter is unloaded at a rate of 2 μm per minute is drawn, and at a plane defined by the displacement and the load, an area of a range surrounded by a straight line corresponding to the displacement of 10 μm , a straight line corresponding to the load of 0, and the load curve when performing the unloading is less than 500 μm mN.

[0020b]

In a second aspect there is provided a molded product being a molded product comprising a pre-coated plated steel sheet including: a plating layer composed of Zn-Al-Mg-based alloy plating, the plating layer being positioned on one side or both sides of a steel sheet; a chemical treatment film layer positioned on the plating layer; and a paint film layer positioned on the chemical treatment film, the paint film layer including a primer paint film layer, and an upper paint film layer positioned on the primer paint film layer, wherein:

the chemical treatment film layer contains any one or more selected from the group consisting of a resin, a silane coupling agent, a zirconium compound, silica, phosphoric acid and salts thereof, fluoride, a vanadium compound, and tannin or tannic acid;

the plating layer is a plating layer containing aluminium of 0.5 mass% or more and 60.0 mass% or less, magnesium of 0.5 mass% or more and 15.0 mass% or less, and the balance being composed of zinc and impurities;

a thickness of the primer paint film layer is 2 to 10 μm ;

a total thickness of the primer paint film layer and the upper paint film layer

is 10 to 30 μm ;

the primer paint film layer contains a first polyester-based resin having an average molecular weight of 15000 to 20000 and a glass transition point T_g of 20 to 50 $^{\circ}\text{C}$, a second polyester-based resin having an average molecular weight of 20000 to 25000 and a glass transition point T_g of less than 20 $^{\circ}\text{C}$, and a curing agent, wherein the curing agent contains blocked isocyanate; and

at a portion where a thickness of a plated steel sheet in the molded product has increased by 20% or more when compared to a thickness of a non-molded portion, a cut strength measured by cutting an interface between the paint film layer and a layer positioned on the steel sheet side relative to the paint film layer by a SAICAS method is 1.00 kN/m or more on average, 20% or less of a cut area is in the form of interfacial peeling, and the remaining cut area is in the form of cohesive failure within the paint film layer.

[0021]

As a result of earnest studies conducted by the present inventors in order to solve the above-described problems, they came up with conditions that should be satisfied by the paint film. Further, as a result of performing additional studies regarding the configuration of the paint film capable of more easily realizing such conditions, the present inventors found out that when the base sheet is the Zn-Al-Mg-based alloy plated steel sheet, appropriate paint film physical properties differ from those of the conventional galvanized steel sheet as the base sheet.

Specifically, they reached a conclusion that the method of reducing the stress of the paint film during working by setting T_g of the resin to a rather high value (namely, by designing the paint film to be rather hard so that the paint film is easily subjected to plastic deformation with respect to a strain), and by decreasing an added amount of a cross-linking agent to reduce a cross-link density, like a conventional way of thinking, is not effective.

[0022]

Specifically, the present inventors found out that the paint film

floating can be more easily improved without deteriorating the paint film performance, by making the resin that has low Tg and high molecular weight and spreads well to be sufficiently hardened without lowering the added amount of the cross-linking agent (specifically, without lowering the cross-link density), to form the paint film capable of dispersing the stress
5 caused by the deformation thereof.

The gist of the present invention, which has been completed based on these findings, is as follows.

[0023]

10 (1) A pre-coated plated steel sheet includes: a plating layer composed of Zn-Al-Mg-based alloy plating, the plating layer being positioned on one side or both sides of a steel sheet; a chemical treatment film layer positioned on the plating layer; and a paint film layer positioned on the chemical treatment film, in which the paint film layer includes a primer paint film layer,
15 and an upper paint film layer positioned on the primer paint film layer, and out of conditions below, at least any of the following is satisfied: both a condition (a-1) and a condition (a-2); a condition (b); and a condition (c).

(a-1) A cut strength measured by cutting an interface between the paint film layer and a layer positioned on the steel sheet side relative to the paint
20 film layer by a SAICAS method is 1.00 kN/m or more on average, 5% or less of a cut area is in the form of interfacial peeling, and the remaining cut area is in the form of cohesive failure within the paint film layer.

(a-2) When a portion where a thickness of the pre-coated plated steel sheet after being subjected to deep drawing has increased by 20% or more
25 when compared to a thickness of a non-molded portion is cut by the SAICAS method, at an interface between the paint film layer and a layer positioned on

the steel sheet side relative to the paint film layer, a cut strength is 1.0 kN/m or more on average, 20% or less of a cut area is in the form of interfacial peeling, and the remaining cut area is in the form of cohesive failure within the paint film layer.

5 (b) An indentation load when a microhardness measuring quadrangular pyramid-shaped indenter is inserted at a rate of 2 μm per minute with respect to a position 1 μm away in a direction of the primer paint film layer from an interface between the primer paint film layer and a layer positioned on the steel sheet side relative to the primer paint film layer, at a
10 cross section obtained by cutting the primer paint film layer in a thickness direction, and the indenter reaches a depth of 10 μm , is less than 1000 mN.

 (c) A load curve with respect to a displacement when a microhardness measuring quadrangular pyramid-shaped indenter is inserted at a rate of 10 μm per second to a depth of 10 μm with respect to a position 1 μm away from
15 an interface between the primer paint film layer and a layer positioned on the steel sheet side relative to the primer paint film layer, at a cross section obtained by cutting the primer paint film layer in the thickness direction, and then the indenter is unloaded at a rate of 2 μm per minute is drawn, and at a plane defined by the displacement and the load, an area of a range surrounded
20 by a straight line corresponding to the displacement of 10 μm , a straight line corresponding to the load of 0, and the load curve when performing the unloading is less than 500 $\mu\text{m} \cdot \text{mN}$.

 (2) In the pre-coated plated steel sheet described in (1), the plating layer contains aluminum of 0.5 mass% or more and 60.0 mass% or less,
25 magnesium of 0.5 mass% or more and 15.0 mass% or less, and the balance being composed of zinc and impurities, a thickness of the primer paint film

layer is 2 to 10 μm , a total thickness of the primer paint film layer and the upper paint film layer is 10 to 30 μm , and the primer paint film layer contains a first polyester-based resin having an average molecular weight of 15000 to 20000 and a glass transition point T_g of 20 to 50°C, a second polyester-based resin having an average molecular weight of 20000 to 25000 and a glass transition point T_g of less than 20°C, and a curing agent, in which the curing agent contains blocked isocyanate.

(3) In the pre-coated plated steel sheet described in (2), the primer paint film layer further contains a pigment, and a concentration in paint film of the pigment (PWC) is 20 to 60 mass%.

(4) In the pre-coated plated steel sheet described in (2) or (3), a content of the first polyester-based resin with respect to a total content of the first polyester-based resin and the second polyester-based resin is 30 to 70% in terms of mass%.

(5) In the pre-coated plated steel sheet described in any one of (2) to (4), a content of the curing agent with respect to a total content of the first polyester-based resin, the second polyester-based resin, and the curing agent is 5 to 15% in terms of mass%.

(6) In the pre-coated plated steel sheet described in any one of (2) to (5), the curing agent further contains melamine or melamine derivative.

(7) In the pre-coated plated steel sheet described in (6), a content of the melamine resin with respect to a total content of the blocked isocyanate and the melamine or melamine derivative is 20 to 50% in terms of mass%.

(8) In the pre-coated plated steel sheet described in any one of (2) to (7), the average molecular weight of the second polyester-based resin is 21000 to 24500.

(9) In the pre-coated plated steel sheet described in any one of (2) to (8), the glass transition point T_g of the second polyester-based resin is 5 to 15°C.

(10) In the pre-coated plated steel sheet described in any one of (2) to 5 (9), the average molecular weight of the first polyester-based resin is 16000 to 19000.

(11) In the pre-coated plated steel sheet described in any one of (2) to (10), the glass transition point T_g of the first polyester-based resin is 30 to 48°C.

10 (12) In the pre-coated plated steel sheet described in any one of (2) to (11), the plating layer is composed of Zn-11%Al-3%Mg-0.2%Si alloy plating that further contains Si in place of a part of Zn being the balance.

(13) A molded product being a molded product that includes a pre-coated plated steel sheet including: a plating layer composed of 15 Zn-Al-Mg-based alloy plating, the plating layer being positioned on one side or both sides of a steel sheet; a chemical treatment film layer positioned on the plating layer; and a paint film layer positioned on the chemical treatment film, the paint film layer including a primer paint film layer, and an upper paint film layer positioned on the primer paint film layer, in which at a portion 20 where a thickness of a plated steel sheet in the molded product has increased by 20% or more when compared to a thickness of a non-molded portion, a cut strength measured by cutting an interface between the paint film layer and a layer positioned on the steel sheet side relative to the paint film layer by a SAICAS method is 1.00 kN/m or more on average, 20% or less of a cut area 25 is in the form of interfacial peeling, and the remaining cut area is in the form of cohesive failure within the paint film layer.

(14) In the molded product described in (13), the plating layer in the molded product contains aluminum of 5 mass% or more and 15 mass% or less, and magnesium of 2 mass% or more and 4 mass% or less.

[Effect of the Invention]

5 [0024]

As described above, according to the present invention, it becomes possible to more securely inhibit the occurrence of paint film floating even when drawing is performed by using the Zn-Al-Mg-based alloy plated steel sheet as the base sheet.

10 [Brief Description of the Drawings]

[0025]

[FIG. 1A] FIG. 1A is an explanatory view schematically illustrating a configuration of a plated steel sheet according to an embodiment of the present invention.

15 [FIG. 1B] FIG. 1B is an explanatory view schematically illustrating a configuration of a plated steel sheet according to the same embodiment.

[FIG. 2A] FIG. 2A is an explanatory view schematically illustrating a configuration of a pre-coated plated steel sheet according to the same embodiment.

20 [FIG. 2B] FIG. 2B is an explanatory view schematically illustrating a configuration of a pre-coated plated steel sheet according to the same embodiment.

[FIG. 3] FIG. 3 is an explanatory view for explaining a measuring method using a microhardness measuring quadrangular pyramid-shaped indenter.

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[FIG. 4] FIG. 4 is an explanatory view for explaining the measuring

method using the microhardness measuring quadrangular pyramid-shaped indenter.

[FIG. 5] FIG. 5 is an explanatory view for explaining a molded product according to the same embodiment.

5 [Embodiments for Carrying out the Invention]

[0026]

Hereinafter, preferred embodiments of the present invention will be explained in detail while referring to the attached drawings. Note that in this description and the drawings, components having substantially the same functional configuration are denoted by the same reference numerals, thereby
10 omitting their redundant explanations.

[0027]

When the present inventors observed the cross section of the portion where the paint film floating occurred (namely, the paint film floating portion) of a molded product obtained by drawing the pre-coated plated steel sheet, it
15 was observed that the paint film was compressed due to deformation (compression) of the plated steel sheet, and the redundant paint film was detached upward. When the sheet thickness of the plated steel sheet of this portion was measured, the sheet thickness increased from the sheet thickness
20 before molding. From this result, it was clarified that the paint film floating portion that the present inventors focused on is the portion where the plated steel sheet was compressed.

[0028]

On the other hand, in the portion where the paint film was peeled off
25 due to rubbing against a mold during drawing, the sheet thickness of the plated steel sheet decreased from the sheet thickness before molding. This

result revealed that the portion where the paint film was peeled off is a portion where the plated steel sheet was elongated.

[0029]

However, in the drawing, compression and elongation of the plated steel sheet do not occur independently of each other, but occur simultaneously, and the degree of compression and elongation only differs depending on the worked portion. The thickness of the plated steel sheet is greater than that before molding at the portion where compression exceeds elongation. On the other contrary, the thickness of the plated steel sheet is smaller than that before molding at the portion where elongation exceeds compression.

[0030]

Generally, when the adhesion strength (cut strength) between the paint film and the plating interface decreases with deformation of the plated steel sheet during molding, paint film floating or paint film peeling occurs.

[0031]

As a result of studies conducted by the present inventors, they came to the conclusion that the following three influencing factors (1) to (3) should be considered as factors that determine the presence or absence of the occurrence of paint film floating or paint film peeling. If these influencing factors are in a good state overall, it is believed that paint film floating and paint film peeling will be inhibited.

[0032]

(1) Soundness of plated surface after working with compression and elongation (presence or absence of irregularities or cracks)

(2) Adhesion between plating and primer paint film through chemical treatment film after working with compression and elongation

(3) State of entire paint film including top paint film deformed by working with compression and elongation (presence or absence of cracks and internal stress)

[0033]

5 Since the phenomenon of paint film floating as described above is likely to occur in pre-coated plated steel sheets that use Zn-Al-Mg-based alloy plated steel sheets as the base sheet, and further, the likeliness of the occurrence of paint film floating differs depending on the types of paint film, the present inventors focused on paint film physical properties that exert
10 influences on (3) above, and conducted further studies.

[0034]

 As a result of this, the present inventors came up with an idea that a resin paint film (primer paint film) that is brought into contact with the base sheet of the pre-coated plated steel sheet that uses the Zn-Al-Mg-based alloy
15 plated steel sheet as the base sheet, is required to satisfy at least any of the following two points.

[0035]

 The first point is that a fracture due to cohesive failure does not occur due to the working as described above, and the fracture of paint film due to
20 working means that an expansion and contraction property of the paint film is insufficient. The paint film is required to have an expansion and contraction property that is sufficient enough to cause no cracks in the paint film even at a portion subjected to a large amount of working with deformation of the steel sheet.

25 [0036]

 The second point is that a stress of the paint film is sufficiently small

in a state of receiving the deformation due to the working as described above. When the stress of the paint film in the state of receiving the deformation is large, the stress concentrates on an interface between the paint film and the plating. When the concentrated stress exceeds an interface adhesion force at
5 the worked portion, the peeling of the paint film occurs.

[0037]

The present inventors conducted studies regarding the means capable of determining the above first point, and consequently, they reached a conclusion that observation of peel form and measurement of cut strength by
10 cutting the paint film by a SAICAS method (Surface and Interfacial Cutting Analysis System) are effective. It is possible to determine whether or not the above first point is satisfied, based on whether the peel form of the primer paint film to be a measuring object is the cohesive failure of the primer paint film layer or not, and whether the cut strength has a sufficiently high value or
15 not.

[0038]

The SAICAS method is a method in which a sharp blade is used to perform cutting from the surface of a sample to the adhesive interface between a base and an adherend at an ultra-low speed to measure the cut
20 strength. Therefore, it is possible to observe the cut strength and the peel state at the interface between specific layers of a laminated multilayer film, which has been difficult to be measured by the conventional method.

[0039]

Concretely, the satisfaction of both the following two conditions (i)
25 and (ii) corresponds to the condition regarding the above first point. (i) When a plane portion of a pre-coated plated steel sheet is cut by the SAICAS

method, a cut strength at an interface between a paint film layer and a layer positioned on a steel sheet side relative to the paint film layer (more specifically, an interface between a primer paint film layer and a chemical treatment film layer or a plating layer positioned on the steel sheet side relative to the primer paint film layer) is 1.00 kN/m or more on average, 5% or less of a cut area is in the form of interfacial peeling, and the remaining cut area is in the form of cohesive failure within the paint film layer (more specifically, within the primer paint film layer). (ii) When a portion where a thickness of the pre-coated plated steel sheet after being subjected to deep drawing has increased by 20% or more when compared to a thickness of a non-molded portion is cut by the SAICAS method, at an interface between the paint film layer and a layer positioned on the steel sheet side relative to the paint film layer (more specifically, an interface between the primer paint film layer and the chemical treatment film layer or the plating layer positioned on the steel sheet side relative to the primer paint film layer), a cut strength is 1.0 kN/m or more on average, 20% or less of a cut area is in the form of interfacial peeling, and the remaining cut area is in the form of cohesive failure within the paint film layer (more specifically, within the primer paint film layer).

20 [0040]

Further, the present inventors conducted studies regarding the means capable of determining the above second point, and consequently, they reached a conclusion that a method of microhardness measurement performed by indentation of a quadrangular pyramid-shaped indenter, the method being typified by the Vickers hardness measuring method, is effective. It is possible to determine whether or not the above second point is satisfied based

on at least any one of the following. (iii) A displacement-load curve when the indenter is pushed into the paint film at a sufficiently low speed is drawn, and a value of load at a predetermined displacement (a push-back force of the paint film at that time) is measured, and (iv) elastic strain energy is
5 determined from a load curve when the indenter is pushed into the paint film to a predetermined depth at a high speed and then the indenter is unloaded, and a displacement of recovery of the paint film.

[0041]

Concretely, the satisfaction of at least either of the following
10 conditions corresponds to the condition under which the above second point is satisfied. (iii) An indentation load when a microhardness measuring quadrangular pyramid-shaped indenter is inserted at a rate of 2 μm per minute with respect to a position 1 μm away in a direction of the primer paint film layer from an interface between the primer paint film layer and a layer
15 positioned on the steel sheet side relative to the primer paint film layer, at a cross section obtained by cutting the primer paint film layer in a thickness direction, and the indenter reaches a depth of 10 μm is less than 1000 mN, and (iv) a load curve with respect to a displacement when a microhardness measuring quadrangular pyramid-shaped indenter is inserted at a rate of 10
20 μm per second to a depth of 10 μm with respect to a position 1 μm away in a direction of the primer paint film layer from an interface between the primer paint film layer and a layer positioned on the steel sheet side relative to the primer paint film layer, at a cross section obtained by cutting the primer paint film layer in the thickness direction, and then the indenter is unloaded at a rate
25 of 2 μm per minute is drawn, and at a plane defined by the displacement and the load, an area of a range surrounded by a straight line corresponding to the

displacement of 10 μm , a straight line corresponding to the load of 0, and the load curve when performing the unloading is less than 500 $\mu\text{m} \cdot \text{mN}$.

[0042]

Here, the reason why the “interface with the layer positioned on the steel sheet side” is set in the above three types of determination methods, is because the thickness of the chemical treatment film layer is generally about 0.1 μm , which is extremely thin, and thus there is a case where the chemical treatment film layer is integrated with the primer paint film layer, and an interface between the primer paint film layer and the chemical treatment film layer cannot be specified.

[0043]

As described above, it was clarified that the paint film floating due to deep drawing can be inhibited by applying, as the primer paint film layer of the pre-coated plated steel sheet using the Zn-Al-Mg-based alloy plated steel sheet as the base sheet, the paint film satisfying at least either of the contents described regarding the above first point and the contents described regarding the second point (most preferably, the paint film simultaneously satisfying the contents described regarding the above first point and the contents described regarding the second point).

[0044]

Further, the present inventors studied the cut strength and the peel form at the interface between the chemical treatment film layer or the paint film layer (more specifically, the primer paint film layer) and the plating layer of a molded body obtained by molding the above-described pre-coated plated steel sheet. In a conventional peel test, it was possible to measure the peel strength of the paint film of the pre-coated steel sheet, but it was not possible

to accurately measure the peel strength and the peel form of a compressed portion of the plated steel sheet forming the molded body. The present inventors evaluated the cut strength and the peel form using the SAICAS method as a method capable of simultaneously measuring these portions.

5 [0045]

The present inventors performed cylindrical cup drawing using the pre-coated steel sheet in order to prepare a sample of the compressed portion of the plated steel sheet of the molded body. The present inventors focused on the portion where the thickness has increased when compared to the
10 thickness of the plated steel sheet before molding as a compression-dominant molded portion, and measured this portion by using the SAICAS method, to thereby obtain the following findings.

[0046]

Specifically, it was found out that in the molded body formed of the
15 pre-coated plated steel sheet that does not cause the paint film floating as described above, the peel form of the paint film is not in the form of interfacial peeling at the interface between the chemical treatment film layer or the paint film layer (more specifically, the primer paint film layer) and the plating layer, but in the form of cohesive failure of the paint film layer (more
20 specifically, the primer paint film layer), and the cut strength of certain level or more is obtained.

[0047]

Consequently, it became clear that when the cut strength of the elongated portion of the plated steel sheet by the SAICAS method (that is, the
25 portion where the thickness of the plated steel sheet of the molded product has decreased by 20% or more when compared to that before molding (which can

also be considered as a non-molded portion)) is 1.00 kN/m or more on average, 20% or less of a cut area is in the form of interfacial peeling, and the remaining cut area is in the form of cohesive failure within the paint film (for example, within the primer paint film when the paint film is composed of a plurality of layers), it is possible to obtain the molded product formed of the pre-coated plated steel sheet excellent in the cracking resistance of the paint film, the paint film adhesion, and the corrosion resistance at the elongated portion.

[0048]

10 Here, the form of interfacial peeling refers to any of cohesive failure of the chemical treatment film layer, interfacial peeling between the chemical treatment film layer and the paint film layer (more specifically, the primer paint film layer), and interfacial peeling between the chemical treatment film layer and the plating layer, or a combined form of these states. However, since the film thickness of the chemical treatment film is extremely thin as described above, it is often the case where the chemical treatment film is integrated with the plating layer or the paint film layer (more specifically, the primer paint film layer), and thus the above peel form cannot be visually distinguished.

20 [0049]

As a result of further studies regarding the primer paint film layer satisfying the above conditions, based on the findings as described above, the present inventors could further obtain the following findings. Specifically, they came up with an idea that it is preferable to adopt, as the primer paint film layer that is brought into contact with the base sheet of the pre-coated plated steel sheet using the Zn-Al-Mg-based alloy plated steel sheet as the

base sheet, a paint film formed by making a resin that has low glass transition point (T_g) and high molecular weight and spreads well to be sufficiently hardened without lowering an added amount of a cross-linking agent (specifically, without lowering a cross-link density), and in which a stress is dispersed during the deformation thereof to prevent an excessive stress from being applied to the adhesive interface with the base sheet. By using such a paint film, it can be expected that it is possible to improve the paint film floating without lowering the paint film performance such as the chemical resistance.

10 [0050]

When the base sheet is the Zn-Al-Mg-based alloy plated steel sheet, it can be considered that the conventional design concept of the paint film such that the stress of the paint film during working is reduced by setting T_g of the resin to a rather high value (namely, by designing the paint film to be rather hard so that the paint film is easily subjected to plastic deformation with respect to a strain), and by reducing an added amount of the cross-linking agent to reduce the cross-link density, is not effective based on two reasons, unlike the case where the galvanized steel sheet is the base sheet.

[0051]

20 The first reason is that a barrier effect of the paint film is lowered by reducing the cross-link density, which makes it easy for a corrosion factor to permeate and infiltrate the paint film, resulting in that the chemical resistance and the corrosion resistance cannot be maintained. The Zn-Al-Mg-based alloy plating is excellent in corrosion resistance when compared to pure zinc plating, but since it contains chemically-unstable Mg, it is likely to be corroded by chemicals. A case where chemicals permeate the paint film to

25

reach the plating layer of the base sheet, becomes a cause of bringing about a paint film blister due to poor chemical resistance. Regarding the corrosion resistance as well, since the corrosion resistance is lowered by the infiltration of the corrosion factor, it is not possible to exhibit excellent corrosion resistance inherent in the Zn-Al-Mg-based alloy plating.

[0052]

The second reason is that the cohesive force of the paint film cannot be maintained by the reduction in cross-link density. When the galvanized steel sheet is the base sheet, as in the conventional case, the plating is uniformly elongated and compressed by working, and thus the paint film can also deform uniformly to follow the elongation and the compression. However, the Zn-Al-Mg-based alloy plating is hard and non-uniform, so that great deformation (cracks or compressive strain) occurs locally due to working. The paint film also deforms greatly in accordance with such a great deformation of plating, so that if the cohesive force of the paint film is not sufficient, the cohesive failure occurs within the paint film layer, which, if anything, causes the paint film peeling.

[0053]

As described above, when the base sheet is the Zn-Al-Mg-based alloy plated steel sheet, it is necessary to design the paint film in a manner different from that of the conventional galvanized steel sheet.

[0054]

As a result of studies conducted by the present inventors regarding a new design of the primer paint film layer, it was clarified that it is possible to realize the conditions as described above by combining two types of resin having appropriate Tg and average molecular weight and by using blocked

isocyanate as a curing agent to realize an appropriate cross-linked state, although details thereof will be explained again below.

[0055]

With respect to the paint film as described above and the steel sheet
5 provided with the paint film, it is required that when the paint film is deformed by following the deformation of the base sheet due to pressing, the stress due to the deformation of the paint film is not large, and the stress is dispersed to prevent the stress from concentrating on the interface between the base sheet and the paint film. In order to realize that, it is effective to use
10 the paint film based on the design manual as described above as the primer paint film layer, and to use the primer paint film layer as a lower layer of the upper paint film.

[0056]

Hereinafter, there will be explained in detail the pre-coated plated steel
15 sheet and the molded product according to the embodiments of the present invention, which have been completed based on the above findings.

[0057]

(Regarding Zn-Al-Mg-based alloy plated steel sheet to be base sheet)

First, the Zn-Al-Mg-based alloy plated steel sheet being the base sheet
20 of the pre-coated plated steel sheet according to an embodiment of the present invention will be explained in detail while referring to FIG. 1A and FIG. 1B.

FIG. 1A is an explanatory view schematically illustrating an example
of a structure of the Zn-Al-Mg-based alloy plated steel sheet according to the present embodiment, and FIG. 1B is an explanatory view schematically
25 illustrating another example of the structure of the Zn-Al-Mg-based alloy plated steel sheet according to the present embodiment.

[0058]

As schematically illustrated in FIG. 1A, a Zn-Al-Mg-based alloy plated steel sheet 10 according to the present embodiment includes a steel sheet 101 serving as a base material, and a Zn-Al-Mg-based alloy plating layer 103 as an example of the plating layer and positioned on one side of the steel sheet. Further, in the Zn-Al-Mg-based alloy plated steel sheet 10 according to the present embodiment, the Zn-Al-Mg-based alloy plating layers 103 may be positioned on both sides of the steel sheet 101 serving as the base material, as schematically illustrated in FIG. 1B.

10 [0059]

<Regarding steel sheet 101>

Various steel sheets can be used for the steel sheet 101 used as the base material of the Zn-Al-Mg-based alloy plated steel sheet 10 according to the present embodiment, depending on the mechanical strength, or the like required of the Zn-Al-Mg-based alloy plated steel sheet 10. As such a steel sheet 101, there can be cited various steel sheets such as, for example, Al-killed steel, ultralow carbon steel containing Ti, Nb, and the like, and high-strength steel obtained by making the ultralow carbon steel further contain strengthening elements such as P, Si, and Mn.

20 [0060]

Further, a thickness of the steel sheet 101 according to the present embodiment (a thickness d_0 in FIG. 1A and FIG. 1B) may be appropriately set according to the mechanical strength, or the like required of the Zn-Al-Mg-based alloy plated steel sheet 10, and can be set to about 0.2 mm to 2.0 mm, for example.

[0061]

<Regarding Zn-Al-Mg-based alloy plating layer 103>

The Zn-Al-Mg-based alloy plating layer 103 (which will be sometimes abbreviated to a “plating layer 103” hereinbelow) according to the present embodiment is a layer to be formed on at least one surface of the steel sheet 101, as schematically illustrated in FIG. 1A and FIG. 1B, and is provided to improve the corrosion resistance of the Zn-Al-Mg-based alloy plated steel sheet 10. First, the chemical composition of the Zn-Al-Mg-based alloy plating layer 103 according to the present embodiment will be explained below.

10 [0062]

The Zn-Al-Mg-based alloy plating layer 103 according to the present embodiment is, for example, a plating layer containing: in terms of mass%, aluminum (Al): 0.5% or more and 60.0% or less; magnesium (Mg): 0.5% or more and 15.0% or less; and the balance being composed of zinc (Zn) and impurities.

[0063]

[Al: 0.5 to 60.0 mass%]

The Zn-Al-Mg-based alloy plating layer 103 according to the present embodiment preferably contains Al of 0.5 mass% or more and 60.0 mass% or less. By setting the content of Al to 0.5 mass% or more and 60.0 mass% or less, the corrosion resistance of the Zn-Al-Mg-based alloy plated steel sheet 10 according to the present embodiment improves, and the adhesion of the Zn-Al-Mg-based alloy plating layer 103 (more specifically, the adhesion to the steel sheet 101) can be secured. When the content of Al is less than 0.5 mass%, the Zn-Al-Mg-based alloy plating layer 103 becomes brittle, and the adhesion of the Zn-Al-Mg-based alloy plating layer 103 decreases in some

cases. The content of Al is more preferably 5.0 mass% or more. On the other hand, when the content of Al exceeds 60.0 mass%, the effect of improving the corrosion resistance of the Zn-Al-Mg-based alloy plated steel sheet 10 is saturated in some cases. The content of Al is more preferably
5 15.0 mass% or less.

[0064]

[Mg: 0.5 to 15.0 mass%]

The Zn-Al-Mg-based alloy plating layer 103 according to the present embodiment preferably contains Mg of 0.5 mass% or more and 15.0 mass%
10 or less. By setting the content of Mg to 0.5 mass% or more and 15.0 mass% or less, the corrosion resistance of the Zn-Al-Mg-based alloy plated steel sheet 10 according to the present embodiment improves, and the adhesion of the Zn-Al-Mg-based alloy plating layer 103 (more specifically, the adhesion to the steel sheet 101) can be secured. When the content of Mg is less than
15 0.5 mass%, the effect of improving the corrosion resistance of the Zn-Al-Mg-based alloy plated steel sheet 10 becomes insufficient in some cases. The content of Mg is more preferably 2.0 mass% or more. On the other hand, when the content of Mg exceeds 15.0 mass%, the Zn-Al-Mg-based alloy plating layer 103 becomes brittle, and the adhesion of
20 the Zn-Al-Mg-based alloy plating layer 103 decreases in some cases. The content of Mg is more preferably 4.0 mass% or less.

[0065]

[Balance: Zn and impurities]

In the Zn-Al-Mg-based alloy plating layer 103 according to the
25 present embodiment, the balance other than the above components is Zn and impurities. Further, the Zn-Al-Mg-based alloy plating layer 103 according

to the present embodiment may contain silicon (Si) in a content of 0 mass% or more and 2.0 mass% or less in place of a part of Zn being the balance.

[0066]

[Si: 0 to 2.0 mass%]

5 The Zn-Al-Mg-based alloy plating layer 103 according to the present embodiment may contain Si of 0 mass% or more and 2.0 mass% or less in place of a part of Zn being the balance. By setting the content of Si to 0 mass% or more and 2.0 mass% or less, the adhesion of the Zn-Al-Mg-based alloy plating layer 103 can be further improved. When the content of Si
10 exceeds 2.0 mass%, the effect of improving the adhesion of the Zn-Al-Mg-based alloy plating layer 103 is saturated in some cases. The content of Si is more preferably 1.6 mass% or less.

[0067]

Further, in the Zn-Al-Mg-based alloy plating layer 103 according to
15 the present embodiment, 1 mass% or less of elements such as Fe, Sb, and Pb may be contained alone or in combination in place of a part of Zn being the balance.

[0068]

As the plated steel sheet 10 provided with the Zn-Al-Mg-based alloy
20 plating layer 103 having the chemical composition as described above, there can be cited, for example, such a hot-dip zinc-aluminum-magnesium-silicon alloy plated steel sheet as a plated steel sheet including a Zn-11%Al-3%Mg-0.2%Si alloy plating layer (for example, “SuperDyma (registered trademark)” and “ZAM (registered trademark)” manufactured by
25 Nippon Steel Corporation), and so on.

[0069]

[Regarding average film thickness of plating layer 103]

In the Zn-Al-Mg-based alloy plated steel sheet 10 according to the present embodiment, an average film thickness (a thickness d1 in FIG. 1A and FIG. 1B) of the Zn-Al-Mg-based alloy plating layer 103 is preferably 6 μm or more, and more preferably 9 μm or more, for example. Since the
5 Zn-Al-Mg-based alloy plating layer 103 has such an average film thickness, the corrosion resistance of the Zn-Al-Mg-based alloy plated steel sheet 10 can be further improved. Note that when the average film thickness d1 of the Zn-Al-Mg-based alloy plating layer 103 exceeds 45 μm , the influence of the
10 increase in plating cost is greater than the improvement in corrosion resistance. Therefore, from an economic point of view, the average film thickness d1 of the Zn-Al-Mg-based alloy plating layer 103 is preferably 45 μm or less.

[0070]

15 Note that the average film thickness d1 of the Zn-Al-Mg-based alloy plating layer 103 can be calculated by the following gravimetric method, for example. That is, a Zn-Al-Mg-based alloy plated steel sheet having a predetermined area (for example, 50 mm \times 50 mm) is dissolved in hydrochloric acid containing an inhibitor, and the dissolved weight is
20 calculated by the difference in weight before and after dissolution. The weight ratio of elements such as Al, Zn, and Fe contained in a solution is separately measured and calculated by high-frequency inductively coupled plasma (Inductively Coupled Plasma: ICP) emission spectrometry, and the average specific gravity of the Zn-Al-Mg-based alloy plating layer is
25 calculated from the ratio. The average film thickness d1 of the Zn-Al-Mg-based alloy plating layer 103 is calculated by dividing the

dissolved weight by the average specific gravity and then dividing the resultant by the area (or the area $\times 2$ in the case of double-sided plating).

[0071]

The Zn-Al-Mg-based alloy plated steel sheet 10 according to the present embodiment has been explained above in detail with reference to FIG. 1A and FIG. 1B.

[0072]

The Zn-Al-Mg-based alloy plated steel sheet 10 according to the present embodiment as explained above can be manufactured as follows, for example. First, pretreatments such as washing and degreasing are performed on the surface of the prepared steel sheet 101 as necessary. Thereafter, an ordinary non-oxidizing furnace type hot-dip plating method is applied to the steel sheet 101 after being subjected to the pretreatments as necessary, to thereby form a plating layer.

[0073]

Here, a hot-dip galvanizing bath containing desired chemical composition (that is, a hot-dip galvanizing bath containing at least Al: 0.5 to 60.0 mass% and Mg: 0.5 to 15.0 mass%, and the balance being composed of Zn and impurities) is prepared, and the bath temperature of such a plating bath is controlled to about 450°C. After that, the obtained steel sheet 101 is immersed in the plating bath to apply hot-dip galvanization to the surface of the steel sheet so as to obtain a desired average film thickness. Thereafter, a cooling rate after plating is controlled to 10°C/second or more. Thereby, the Zn-Al-Mg-based alloy plating layer can be formed.

[0074]

(Regarding pre-coated plated steel sheet)

Next, a pre-coated plated steel sheet 20 using the Zn-Al-Mg-based alloy plated steel sheet 10 as explained above will be explained in detail with reference to FIG. 2A and FIG. 2B.

FIG. 2A is an explanatory view schematically illustrating an example of a structure of a pre-coated plated steel sheet according to the present embodiment, and FIG. 2B is an explanatory view schematically illustrating another example of the structure of the pre-coated plated steel sheet according to the present embodiment.

[0075]

As schematically illustrated in FIG. 2A, the pre-coated plated steel sheet 20 according to the present embodiment is one using the Zn-Al-Mg-based alloy plated steel sheet 10 explained previously, for example, as the base material, and includes a steel sheet 101, a Zn-Al-Mg-based alloy plating layer 201 positioned on one side of the steel sheet 101, a chemical treatment film layer 203 positioned on the Zn-Al-Mg-based alloy plating layer 201, and a paint film layer 205 positioned on the chemical treatment film layer 203. Further, the pre-coated plated steel sheet 20 according to the present embodiment may include the Zn-Al-Mg-based alloy plating layers 201, the chemical treatment films 203, and the paint films 205 formed on both sides of the steel sheet 101, as schematically illustrated in FIG. 2B.

[0076]

Here, the steel sheet 101 in the pre-coated plated steel sheet 20 according to the present embodiment has the same configuration as the steel sheet 101 in the Zn-Al-Mg-based alloy plated steel sheet 10 explained previously, and exhibits the same effect, so that its detailed explanation will be omitted below.

[0077]

Further, regarding the Zn-Al-Mg-based alloy plating layer 201 in the pre-coated plated steel sheet 20 according to the present embodiment, along with the formation of the chemical treatment film layer 203 to be described later, interdiffusion or the like of atoms or the like contained in each layer may occur in the vicinity of an interface between the Zn-Al-Mg-based alloy plating layer 201 and the chemical treatment film layer 203. However, the average chemical composition of the Zn-Al-Mg-based alloy plating layer 201 is the same as that of the Zn-Al-Mg-based alloy plating layer 103 in the Zn-Al-Mg-based alloy plated steel sheet 10 explained previously, and the same effect is exhibited, so that its detailed explanation will be omitted below.

[0078]

<Regarding chemical treatment film layer 203>

The chemical treatment film layer 203 according to the present embodiment is a film layer positioned on the Zn-Al-Mg-based alloy plating layer 201, and is a layer formed by a chemical treatment after removing impurities such as oil and surface oxides adhering to the surface of the Zn-Al-Mg-based alloy plated steel sheet 10 by well-known degreasing step and washing step.

[0079]

The chemical treatment film layer 203 according to the present embodiment may contain any one or more selected from a group consisting of a resin, a silane coupling agent, a zirconium compound, silica, phosphoric acid and its salt, fluoride, a vanadium compound, and tannin or tannic acid, for example. These substances are contained, to thereby further improve the film formability obtained after applying a chemical treatment solution, the

barrier property (denseness) of the film against corrosion factors such as moisture and corrosive ions, the film adhesion to the Zn-Al-Mg-based alloy plated surface, and the like, resulting in contribution to the improvement in the corrosion resistance of the film.

5 [0080]

In particular, when the chemical treatment film layer 203 contains any one or more of a silane coupling agent and a zirconium compound, a cross-linked structure is formed within the film layer 203, which strengthens bonding with the Zn-Al-Mg-based alloy plated surface as well, resulting in
10 that it becomes possible to further improve the adhesion and the barrier property of the film.

[0081]

Further, when the chemical treatment film layer 203 contains any one or more of silica, phosphoric acid and its salt, fluoride, and a vanadium
15 compound, these substances function as inhibitors and form a precipitation film or passive film on the Zn-Al-Mg-based alloy plating or steel surface, resulting in that it becomes possible to further improve the corrosion resistance.

[0082]

20 In the following, each component that can be contained in the chemical treatment film layer 203 as described above will be described in detail while citing examples.

[0083]

[Resin]

25 The resin is not particularly limited, and well-known organic resins such as a polyester resin, a polyurethane resin, an epoxy resin, a phenol resin,

an acrylic resin, and a polyolefin resin, for example, can be used. To further improve the adhesion to the plated steel sheet for pre-coated steel sheet, it is preferable to use at least one of the resins (polyester resin, urethane resin, epoxy resin, acrylic resin, and so on) having a forced site or polar functional group in a molecular chain. The resins may be used alone or in combination of two or more.

[0084]

The content of the resin in the chemical treatment film layer 203 is preferably, for example, 0 mass% or more and 85 mass% or less with respect to the solid content of the film. The content of the resin is more preferably 0 mass% or more and 60 mass% or less, and still more preferably 1 mass% or more and 40 mass% or less. When the content of the resin exceeds 85 mass%, the ratio of the other film components may decrease, and the performance required as the film other than corrosion resistance may decrease.

[0085]

[Silane coupling agent]

As the silane coupling agent, there can be cited, for example, γ -(2-aminoethyl)aminopropyltrimethoxysilane, γ -(2-aminoethyl)aminopropylmethyldimethoxysilane, γ -(2-aminoethyl)aminopropyltriethoxysilane, γ -(2-aminoethyl)aminopropylmethyldiethoxysilane, γ -(2-aminoethyl)aminopropylmethyldimethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropylmethyldimethoxysilane, γ -methacryloxypropyltriethoxysilane,

γ -methacryloxypropylmethyldiethoxysilane,
 N- β -(N-vinylbenzylaminoethyl)- γ -aminopropyltrimethoxysilane,
 N- β -(N-vinylbenzylaminoethyl)- γ -aminopropylmethyldimethoxysilane,
 N- β -(N-vinylbenzylaminoethyl)- γ -aminopropyltriethoxysilane,
 5 N- β -(N-vinylbenzylaminoethyl)- γ -aminopropylmethyldiethoxysilane,
 γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropylmethyldimethoxysilane,
 γ -glycidoxypropyltriethoxysilane, γ -glycidoxypropylmethyldiethoxysilane,
 γ -mercaptopropyltrimethoxysilane, γ -mercaptopropylmethyldimethoxysilane,
 γ -mercaptopropyltriethoxysilane, γ -mercaptopropylmethyldiethoxysilane,
 10 methyltrimethoxysilane, dimethyldimethoxysilane, methyltriethoxysilane,
 dimethyldiethoxysilane, vinyltriacetoxysilane,
 γ -chloropropyltrimethoxysilane, γ -chloropropylmethyldimethoxysilane,
 γ -chloropropyltriethoxysilane, γ -chloropropylmethyldiethoxysilane,
 hexamethyldisilazane, γ -anilinopropyltrimethoxysilane,
 15 γ -anilinopropylmethyldimethoxysilane, γ -anilinopropyltriethoxysilane,
 γ -anilinopropylmethyldiethoxysilane, vinyltrimethoxysilane,
 vinylmethyldimethoxysilane, vinyltriethoxysilane, vinylmethyldiethoxysilane,
 octadecyldimethyl[3-(trimethoxysilyl)propyl]ammonium chloride,
 octadecyldimethyl[3-(methyldimethoxysilyl)propyl]ammonium chloride,
 20 octadecyldimethyl[3-(triethoxysilyl)propyl]ammonium chloride,
 octadecyldimethyl[3-(methyldiethoxysilyl)propyl]ammonium chloride,
 γ -chloropropylmethyldimethoxysilane,
 γ -mercaptopropylmethyldimethoxysilane, methyltrichlorosilane,
 dimethyldichlorosilane, trimethylchlorosilane, and so on. The added amount
 25 of the silane coupling agent in a chemical treatment agent for forming the
 chemical treatment film layer 203 can be set to, for example, 2 to 80 g/L.

When the added amount of the silane coupling agent is less than 2 g/L, the adhesion to the plated surface may be insufficient, leading to a decrease in the work adhesion of the paint film. Further, when the added amount of the silane coupling agent exceeds 80 g/L, the cohesive force of the chemical treatment film layer may be insufficient, leading to a decrease in the work adhesion of the paint film layer. The silane coupling agents as described as examples above may be used alone or in combination of two or more.

[0086]

[Zirconium compound]

As the zirconium compound, there can be cited, for example, zirconium normal propylate, zirconium normal butyrate, zirconium tetraacetylacetonate, zirconium monoacetylacetonate, zirconium bisacetylacetonate, zirconium monoethylacetoacetate, zirconium acetylacetonate bisethylacetoacetate, zirconium acetate, zirconium monostearate, zirconium carbonate, zirconium ammonium carbonate, potassium zirconium carbonate, sodium zirconium carbonate, and so on. The added amount of the zirconium compound in the chemical treatment agent for forming the chemical treatment film layer 203 can be set to, for example, 2 to 80 g/L. When the added amount of the zirconium compound is less than 2 g/L, the adhesion to the plated surface may be insufficient, leading to a decrease in the work adhesion of the paint film. Further, when the added amount of the zirconium compound exceeds 80 g/L, the cohesive force of the chemical treatment film layer may be insufficient, leading to a decrease in the work adhesion of the paint film layer. Such zirconium compounds may be used alone or in combination of two or more.

[0087]

[Silica]

As the silica, there can be used, for example, commercially available silica gels such as “SNOWTEX N,” “SNOWTEX C,” “SNOWTEX UP,” and “SNOWTEX PS” manufactured by Nissan Chemical Corporation, and
5 “ADELITE AT-20Q” manufactured by ADEKA CORPORATION, or powdered silica such as AEROSIL #300 manufactured by NIPPON AEROSIL CO., LTD.. Silica can be appropriately selected according to the required performance of the pre-coated plated steel sheet. The added amount of the silica in the chemical treatment agent for forming the chemical treatment film
10 layer 203 is preferably set to 1 to 40 g/L. When the added amount of the silica is less than 1 g/L, the work adhesion of the paint film layer may decrease, and when the added amount of the silica exceeds 40 g/L, the effects of work adhesion and corrosion resistance are highly likely to be saturated, which is uneconomical.

15 [0088]

[Phosphoric acid and its salt]

As the phosphoric acid and its salt, there can be cited, for example, phosphoric acids such as orthophosphoric acid, metaphosphoric acid, pyrophosphoric acid, triphosphoric acid, and tetraphosphoric acid and salts
20 thereof, ammonium salts such as triammonium phosphate and diammonium hydrogen phosphate, phosphonic acids such as aminotri(methylenephosphonic acid), 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediaminetetra(methylenephosphonic acid), and diethylenetriaminepenta(methylenephosphonic acid) and salts thereof, organic
25 phosphoric acids such as phytic acid and salts thereof, and so on. Note that as salts of phosphoric acid other than ammonium salts, there can be cited

metal salts with Na, Mg, Al, K, Ca, Mn, Ni, Zn, Fe, and so on. The phosphoric acid and its salt may be used alone or in combination of two or more.

[0089]

5 Note that the content of the phosphoric acid and its salt is preferably 0 mass% or more and 20 mass% or less with respect to the solid content of the film. When the content of the phosphoric acid and its salt exceeds 20 mass%, the film becomes brittle, and the work adhesion of the film may decrease when the pre-coated plated steel sheet is molded. The content of
10 the phosphoric acid and its salt is more preferably 1 mass% or more and 10 mass% or less.

[0090]

[Fluoride]

As the fluoride, there can be cited, for example, ammonium zirconium
15 fluoride, ammonium silicofluoride, ammonium titanium fluoride, sodium fluoride, potassium fluoride, calcium fluoride, lithium fluoride, titanium hydrofluoride, zirconium hydrofluoride, and so on. Such fluorides may be used alone or in combination of two or more.

[0091]

20 Note that the content of the fluoride is preferably 0 mass% or more and 20 mass% or less with respect to the solid content of the film. When the content of the fluoride exceeds 20 mass%, the film becomes brittle, and the work adhesion of the film may decrease when the pre-coated plated steel sheet is molded. The content of the fluoride is more preferably 1 mass% or
25 more and 10 mass% or less.

[0092]

[Vanadium compound]

As the vanadium compound, there can be cited, for example, vanadium compounds obtained by reducing pentavalent vanadium compounds such as vanadium pentoxide, metavanadic acid, ammonium
5 metavanadate, sodium metavanadate, and vanadium oxytrichloride to 2 to 4 valences with a reducing agent, vanadium compounds with oxidation numbers of 4 to 2 valences, such as vanadium trioxide, vanadium dioxide, vanadium oxysulfate, vanadium oxyoxalate, vanadium oxyacetylacetonate, vanadium acetylacetonate, vanadium trichloride, phosphovanadomolybdic acid,
10 vanadium sulfate, vanadium dichloride, and vanadium oxide, and so on. Such vanadium compounds may be used alone or in combination of two or more.

[0093]

Note that the content of the vanadium compound is preferably 0
15 mass% or more and 20 mass% or less with respect to the solid content of the film. When the content of the vanadium compound exceeds 20 mass%, the film becomes brittle, and the work adhesion of the film may decrease when the pre-coated plated steel sheet is molded. The content of the vanadium compound is more preferably 1 mass% or more and 10 mass% or less.

20 [0094]

[Tannin or tannic acid]

As tannin or tannic acid, it is possible to use either of hydrolyzable tannin and condensed tannin. As examples of tannin and tannic acid, there can be cited hamamelitannin, gall tannin, gallnut tannin, myrobalan tannin,
25 divi-divi tannin, algarovilla tannin, valonia tannin, catechin, and so on. The added amount of the tannin or tannic acid in the chemical treatment agent for

forming the chemical treatment film 203 can be set to 2 to 80 g/L. When the added amount of the tannin or tannic acid is less than 2 g/L, the adhesion to the plated surface may be insufficient, leading to a decrease in the work adhesion of the paint film. Further, when the added amount of the tannin or tannic acid exceeds 80 g/L, the cohesive force of the chemical treatment film may be insufficient, leading to a decrease in the work adhesion of the paint film.

[0095]

Further, an acid, an alkali, or the like may be added to the chemical treatment agent for forming the chemical treatment film 203 in order to adjust pH within a range that does not impair the performance.

[0096]

The chemical treatment agent containing various components as described above is applied to one side or both sides of the Zn-Al-Mg-based alloy plated steel sheet 10, and then dried to form the chemical treatment film layer 203. In the pre-coated steel sheet according to the present embodiment, it is preferable to form the chemical treatment film layer 203 of 10 to 1000 mg/m² per side on the Zn-Al-Mg-based alloy plated steel sheet. The weight of the chemical treatment film layer 203 is more preferably 20 to 800 mg/m², and most preferably 50 to 600 mg/m². Note that a film thickness (a thickness d2 in FIG. 2A and FIG. 2B) of the chemical treatment film layer 203 corresponding to such a weight is approximately 0.01 to 1 μm, depending on the components contained in the chemical treatment agent.

[0097]

<Regarding paint film layer 205>

The paint film layer 205 according to the present embodiment is a

layer formed on the chemical treatment film layer 203 as described above. Such a paint film layer 205 is composed of a plurality of layers of the primer paint film layer and the upper paint film layer, as schematically illustrated in FIG. 2A and FIG. 2B.

5 [0098]

Here, a paint film layer that is brought into contact with the chemical treatment film layer 203 in the paint film layer 205 is called a primer paint film layer. This primer paint film layer secures the adhesion between the entire paint film layer 205 and the chemical treatment film layer 203 and the corrosion resistance, and is placed as the most important factor that exerts an influence on the paint film floating. On the other hand, the upper paint film layer being a paint film positioned above such a primer paint film layer is also called a top paint film, and is often provided to secure design through coloring, barrier properties, and other surface functionality. This upper paint film layer is placed as a factor related to physical properties as the entire paint film layer 205 exerting an influence on the paint film floating.

[0099]

Such a paint film layer 205 contains at least a resin. Moreover, it is preferable that such a paint film layer 205 further contains a pigment. In addition to these components, the paint film layer 205 may contain various additives such as a leveling agent, an antifoaming agent, a coloring agent, a viscosity modifier, and an ultraviolet absorber. Note that a painting solution for forming the paint film layer 205 is preferably obtained by dispersing or dissolving each of the above components in a solvent.

25 [0100]

Hereinafter, preferred forms of the primer paint film layer and the

upper paint film layer included in the paint film layer 205 according to the present embodiment will be explained in more detail.

[0101]

[Primer paint film layer]

5 The primer paint film layer according to the present embodiment is realized based on the design manual as explained previously. Such a primer paint film layer preferably contains a first polyester-based resin having an average molecular weight of 15000 to 20000 and a glass transition point Tg of 20 to 50°C, a second polyester-based resin having an average molecular
10 weight of 20000 to 25000 and a glass transition point Tg of less than 20°C, and a curing agent.

[0102]

 When the average molecular weight (more specifically, a number average molecular weight) of the first polyester-based resin is less than 15000,
15 the workability of the formed primer paint film layer becomes insufficient. As a result of this, when the paint film layer 205 is deformed, it is not possible to follow the deformation, and a large stress occurs in the paint film layer 205. By setting the average molecular weight of the first polyester-based resin to 15000 or more, it becomes possible to follow the
20 deformation occurred in the paint film layer 205, and thus it becomes possible to suppress the stress occurred in the paint film layer 205 to a small value. The average molecular weight of the first polyester-based resin is more preferably 16000 or more, and still more preferably 17000 or more.

[0103]

25 On the other hand, when the average molecular weight of the first polyester-based resin exceeds 20000, it is not possible to make the cross-link

density to be sufficiently high, resulting in that scuffing of the paint film is likely to occur. Accordingly, the average molecular weight of the first polyester-based resin is set to 20000 or less. The average molecular weight of the first polyester-based resin is more preferably 19000 or less, and still more preferably 18000 or less.

[0104]

Further, when the glass transition point T_g of the first polyester-based resin is less than 20°C , the corrosion resistance is sometimes lowered due to the insufficient cohesive force of the paint film. Accordingly, the glass transition point T_g of the first polyester-based resin is set to 20°C or more. The glass transition point T_g of the first polyester-based resin is more preferably 30°C or more, and still more preferably 40°C or more. On the other hand, when the glass transition point T_g of the first polyester-based resin exceeds 50°C , even when the resin is combined with the second polyester-based resin, the formed primer paint film layer becomes excessively hard, resulting in that a plastic deformation is likely to occur with respect to a strain. The glass transition point T_g of the first polyester-based resin is set to 50°C or less, and besides, the first polyester-based resin is combined with the second polyester-based resin, which makes it possible to more easily realize the primer paint film layer with appropriate hardness. The glass transition point T_g of the first polyester-based resin is more preferably 48°C or less, and still more preferably 45°C or less.

[0105]

When the average molecular weight (more specifically, a number average molecular weight) of the second polyester-based resin is less than 20000, the ductility of the formed primer paint film layer becomes insufficient.

As a result of this, when the paint film layer 205 is deformed, it is not possible to follow the deformation, and a large stress occurs in the paint film layer 205. By setting the average molecular weight of the second polyester-based resin to 20000 or more, it becomes possible to follow the deformation occurred in the paint film layer 205, and thus it becomes possible to suppress the stress occurred in the paint film layer 205 to a small value. The average molecular weight of the second polyester-based resin is more preferably 21000 or more, and still more preferably 23000 or more.

[0106]

On the other hand, when the average molecular weight of the second polyester-based resin exceeds 25000, it is not possible to make the cross-link density to be sufficiently high, resulting in that scuffing of the paint film is likely to occur. Accordingly, the average molecular weight of the second polyester-based resin is set to 25000 or less. The average molecular weight of the second polyester-based resin is more preferably 24500 or less, and still more preferably 24000 or less.

[0107]

Further, when the glass transition point T_g of the second polyester-based resin is less than 20°C , the formed primer paint film layer becomes excessively hard, resulting in that a plastic deformation is likely to occur with respect to a strain. The glass transition point T_g of the second polyester-based resin is set to less than 20°C , and besides, the second polyester-based resin is combined with the first polyester-based resin, which makes it possible to more easily realize the primer paint film layer with appropriate hardness. The glass transition point T_g of the second polyester-based resin is more preferably 15°C or less, and still more

preferably 10°C or less. On the other hand, when the glass transition point Tg of the second polyester-based resin is less than 0°C, the corrosion resistance is sometimes lowered due to the insufficient cohesive force of the paint film. Therefore, the glass transition point Tg of the second
5 polyester-based resin is preferably 5°C or more.

[0108]

Note that the average molecular weights of the first and second polyester-based resins can be measured by GPC (Gel Permeation Chromatography).

10 [0109]

Further, the glass transition points Tg of the first and second polyester-based resins can be specified from a DTA curve obtained by executing a differential thermal analysis regarding a focused resin by using a differential scanning calorimeter.

15 [0110]

Further, the primer paint film layer according to the present embodiment contains blocked isocyanate as the curing agent. Since the primer paint film layer contains the blocked isocyanate as the curing agent, the polyester-based resins can be cross-linked in an appropriate state,
20 resulting in that high level of film ductility can be realized, and at the same time, it becomes possible to balance the film ductility with the adhesion and the hardness performance of the primer paint film layer.

[0111]

As the above blocked isocyanate, there can be cited, for example, TDI
25 (toluene diisocyanate), MDI (diphenylmethane diisocyanate), XDI (xylene diisocyanate), NDI (naphthylene diisocyanate), HDI (hexamethylene

diisocyanate), IPDI (isophorone diisocyanate), hydrogenated MDI, hydrogenated XDI, and so on. It is possible to use any of the blocked isocyanates, but the use of at least any of the HDI, the IPDI, the hydrogenated MDI, and the hydrogenated XDI being an aliphatic compound or alicyclic compound is particularly preferable for the above-described purpose, since
5 the cross-linking with relatively moderate and uniform reaction proceeds.

[0112]

Further, as a blocking agent of the blocked isocyanate, it is possible to use ϵ caprolactam, MEK oxime, benzotriazole, and the like, but the use of
10 MEK oxime whose dissociation temperature is relatively low, is preferable for the above-described purpose.

[0113]

Further, in the primer paint film layer according to the present embodiment, it is also possible to use, as the curing agent, one other than the
15 blocked isocyanate, as long as it satisfies at least any of the following: both conditions (a-1) and (a-2); a condition (b); and a condition (c), as will be explained below.

[0114]

The primer paint film layer according to the present embodiment has
20 the configuration as described above, and thus the formed primer paint film layer satisfies at least any of the first point and the second point as mentioned previously. As a result of this, the primer paint film layer according to the present embodiment satisfies at least any of the following: both the conditions (a-1) and (a-2); the condition (b); and the condition (c).

25 [0115]

(a-1) A cut strength measured by cutting an interface between the paint

film layer and a layer positioned on the steel sheet side relative to the paint film layer by the SAICAS method is 1.00 kN/m or more on average, 5% or less of a cut area is in the form of interfacial peeling, and the remaining cut area is in the form of cohesive failure within the paint film layer.

- 5 (a-2) When a portion where a thickness of the pre-coated plated steel sheet after being subjected to deep drawing has increased by 20% or more when compared to a thickness of a non-molded portion is cut by the SAICAS method, at an interface between the paint film layer and a layer positioned on the steel sheet side relative to the paint film layer (more specifically, an
10 interface between the primer paint film layer and the chemical treatment film layer or the plating layer positioned on the steel sheet side relative to the primer paint film layer), a cut strength is 1.00 kN/m or more on average, 20% or less of a cut area is in the form of interfacial peeling, and the remaining cut area is in the form of cohesive failure within the paint film layer (more
15 specifically, within the primer paint film layer).

[0116]

- (b) An indentation load when a microhardness measuring quadrangular pyramid-shaped indenter is inserted at a rate of 2 μm per minute with respect to a position 1 μm away in a direction of the primer paint film
20 layer from an interface between the primer paint film layer and a layer positioned on the steel sheet side relative to the primer paint film layer, at a cross section obtained by cutting the primer paint film layer in a thickness direction, and the indenter reaches a depth of 10 μm , is less than 1000 mN.

[0117]

- 25 (c) A load curve with respect to a displacement when a microhardness measuring quadrangular pyramid-shaped indenter is inserted at a rate of 10

μm per second to a depth of $10\ \mu\text{m}$ with respect to a position $1\ \mu\text{m}$ away in a direction of the primer paint film layer from an interface between the primer paint film layer and a layer positioned on the steel sheet side relative to the primer paint film layer, at a cross section obtained by cutting the primer paint
5 film layer in the thickness direction, and then the indenter is unloaded at a rate of $2\ \mu\text{m}$ per minute is drawn, and at a plane defined by the displacement and the load, an area of a range surrounded by a straight line corresponding to the displacement of $10\ \mu\text{m}$, a straight line corresponding to the load of 0, and the load curve when performing the unloading is less than $500\ \mu\text{m} \cdot \text{mN}$.

10 [0118]

Note that “a position $1\ \mu\text{m}$ away in a direction of the primer paint film layer from an interface between the primer paint film layer and a layer positioned on the steel sheet side relative to the primer paint film layer” in the above-described condition (b) and condition (c) can also be regarded as a
15 position $1\ \mu\text{m}$ away in a direction of an upper paint film layer from a lower end (an end portion on the steel sheet side) of the primer paint film layer, as schematically illustrated in FIG. 3.

[0119]

Further, as schematically illustrated in FIG. 4, the area in the condition
20 (c) corresponds to an area of a diagonally shaded region in the drawing. Here, in a case of the primer paint film layer focused in the present embodiment, a maximum load P_{MAX} generally becomes about 1000 to 2000 mN, and a displacement D_{MAX} at the maximum load generally becomes greater than $10\ \mu\text{m}$. Such an area becomes an index of strain energy that
25 remains in a focused resin when a strain is applied to the resin and then unloading is performed, and it can be considered that the larger such an area,

the larger the energy (namely, a residual stress) that remains in the resin.

[0120]

Here, the cut strength and the peel form of the primer paint film layer by the SAICAS method in the conditions (a-1) and (a-2), can be measured while performing cutting by using a measuring device that can utilize the SAICAS method (for example, DN-GS model manufactured by DAIPLA WINTES CO., LTD.).

[0121]

The cutting conditions for the SAICAS method are as follows.

10 A diamond blade (0.3 mm in width) is used as a cutting blade, and oblique cutting is performed in a constant speed mode with a horizontal velocity of 1 $\mu\text{m}/\text{sec}$. and a vertical velocity of 0.1 $\mu\text{m}/\text{sec}$. and then near the interface, the cutting is switched to only the horizontal movement to cut a length of 200 μm , and the average cut strength during the horizontal movement is measured. The depth position at which the cutting is switched to the horizontal movement is set by specifying the interface position (a position at the very limit where the plating is not cut) through a preliminary experiment. When the plated surface is cut due to the unevenness of the plating during the horizontal movement of the cutting blade, the cut strength can be discriminated because it momentarily increases abnormally. Such a case is excluded as an abnormal value, and the average cut strength is calculated. Note that the number of measurements n is set to 3, and the average value of the three values of the average cut strength is taken as the cut strength.

25 [0122]

The method of measuring the ratio of the interfacial peel form and the

cohesive failure form in the cut portion during horizontal movement is as follows.

Observation of the surface of the cut portion by the SAICAS method with an optical microscope makes it possible to clearly distinguish the difference in peel form for each portion. (A) When an extremely thin paint film remains on the cut portion, it is possible to determine that the peel form is thin-layer cohesive failure within the paint film because coloration due to the resin and pigment in the paint film is observed. (B) When the cut portion is interfacial peeling, the appearance of the plated surface of the base is observed. No strong reflection is seen even when such a portion is irradiated with light, resulting in a blackish appearance. Further, in the case of interfacial peeling, the fact that the cut strength by the SAICAS method decreases locally is also a determining factor. This is because although the moving position of the cutting blade is within the paint film immediately above the interface, interfacial peeling occurs as a result of the peeling position shifting to the interface because the adhesion force of the interface is lower than the cohesive force of the paint film. (C) When the cut portion is cohesive failure of the plating layer, a metallic luster is observed, and when such a portion is irradiated with light, the light is strongly reflected, resulting in that distinguishing from interfacial peeling is easy. Further, the fact that the cut strength by the SAICAS method increases locally is also a determining factor.

[0123]

An optical micrograph of a horizontal cut range (having a size of $300\ \mu\text{m} \times 200\ \mu\text{m}$) by the SAICAS method is taken, portions of the paint film cohesive failure, the interfacial peeling, and the plating layer cohesive failure

within the same range are specified according to the above criteria, and areas of the portions are measured using image processing software or transparent graph paper. Subsequently, the ratio of the interfacial peeling area to the area excluding the plating layer cohesive failure is calculated from the horizontal cut range by the SAICAS method.

[0124]

Here, in the primer paint film layer according to the present embodiment, the content of the first polyester-based resin with respect to the total content of the first polyester-based resin and the second polyester-based resin, is preferably 40 to 70 mass%. By setting the content of the first polyester-based resin with respect to the total content to 30 to 70 mass%, it becomes possible to realize the balance between the adhesion and the hardness of the film, and the ductility, in a more appropriate state. The content of the first polyester-based resin with respect to the total content is more preferably 40 to 60 mass%.

[0125]

Further, in the primer paint film layer according to the present embodiment, the content of the above-described curing agent is more preferably 5 to 15 mass% with respect to the total content of the first and second polyester-based resins and the curing agent. When the curing agent is contained in such a content, the cross-linked state of the polyester-based resins can be set to more appropriate one. The content of the curing agent is still more preferably 8 to 12 mass% with respect to the total content of the first and second polyester-based resins and the curing agent.

[0126]

Further, it is more preferable that the primer paint film layer according

to the present embodiment further contains, as the curing agent, melamine or melamine derivative in addition to the above-described blocked isocyanate. When the melamine or melamine derivative is further contained as the curing agent, the cross-linked state of the primer paint film layer can be made to a better one. As such melamine or melamine derivative, there can be cited, for example, a melamine compound of an imino group type, a methylol-imino group type, methylol group type, or a complete alkyl group type. Further, by using, as the melamine or melamine derivative, a complete alkyl group-type melamine compound exemplified by a methylated melamine resin, a butylated melamine resin, or the like, in particular, it becomes possible to further improve the cross-linked state of the primer paint film layer.

[0127]

Here, the content of the melamine or melamine derivative is more preferably 20 to 60 mass% with respect to the total content of the blocked isocyanate and the melamine or melamine derivative. When the melamine or melamine derivative is contained in such a content, the cross-linked state of the polyester-based resins can be set to more appropriate one. The content of the melamine or melamine derivative is still more preferably 30 to 50 mass% with respect to the total content of the blocked isocyanate and the melamine or melamine derivative.

[0128]

An appropriate base paint for the primer paint film may be selected according to the usage environment and application of the pre-coated plated steel sheet within a range that does not deviate from the range of the primer paint as described above. The base paint contains the polyester-based resins and the curing agent as described above, and can be used in any form such as

an organic solvent-based form, water-based form, or powder-based form.

[0129]

It is preferable that such a base paint further contains a pigment (a rust preventive pigment (a chromate-free rust preventive pigment, for example) in particular). As the chromate-free rust preventive pigment in the base paint, there can be used arbitrary one such as calcium ion-exchanged silica (commonly called calcium silicate in some cases), aluminum tripolyphosphate, phosphorus and vanadium pigment (PV pigment), zinc phosphate, iron phosphate, aluminum phosphate, calcium molybdate, aluminum molybdate, 10 barium molybdate, vanadium oxide, water-dispersible silica, fumed silica, orthophosphoric acid, pyrophosphoric acid, metaphosphoric acid, hypophosphoric acid, phosphorous acid, hypophosphorous acid and salts thereof. The content of such a pigment is, for example, 20 to 60 mass% with respect to the solid content of the paint film. This makes it possible to set a concentration in paint film of the pigment (PWC) in the primer paint film 15 layer to 20 to 60 mass%. When the content of the pigment is less than 20 mass%, in addition to the possibility that the effect of corrosion resistance cannot be sufficiently secured, the rigidity and cohesive force of the paint film decrease, resulting in that paint film peeling (paint film scuffing) is likely to occur in some cases when the surface of the paint film rubs against a mold 20 during pressing of the painted plated steel sheet. Further, when the content of the pigment exceeds 60 mass%, workability sometimes decreases. From the viewpoint of the balance among corrosion resistance, chemical resistance, and workability, the content of the pigment is more preferably 30 to 55 mass%, and still more preferably 35 to 50 mass%. This makes it possible to set the concentration in paint film of the pigment (PWC) in the primer paint 25

film layer to 30 to 55 mass% (still more preferably 35 to 50 mass%).

[0130]

The thickness of the primer paint film layer before molding is preferably 2 to 10 μm . When the thickness of the primer paint film layer is less than 2 μm , the functions such as corrosion resistance required as the pre-coated plated steel sheet may not be exhibited sufficiently. On the other hand, when the thickness of the primer paint film layer exceeds 10 μm , the workability of the paint film may decrease. The thickness of the primer paint film layer before molding is more preferably 2 to 8 μm , and still more preferably 2 to 6 μm .

[0131]

After applying a primer paint component containing the components forming the primer paint film layer as described above, the primer paint component is baked at a temperature of 150°C or more and less than 300°C to be cured and dried. When the baking temperature is less than 150°C, adhesion may not be sufficiently secured, and when the baking temperature is 300°C or more, thermal degradation of the resin component may occur, resulting in a decrease in the workability.

[0132]

Note that the application of the primer paint component as described above can be performed by generally well-known coating methods such as roll coating, curtain flow coating, air spray, airless spray, immersion, bar coating, or brush coating, for example. Among the above, from a viewpoint of industrial productivity, it is preferable to use a roll coating method, a flow coating method, a curtain flow method, or the like being a coating method used for manufacturing pre-coated steel sheets.

[0133]

[Upper paint film layer]

An appropriate base paint for the upper paint film layer may be selected according to the usage environment and application of the pre-coated
5 plated steel sheet within a range that does not deviate from the range of the paint of the upper paint film defined in the present invention. As the type of resin for the base paint, generally well-known ones can be used. As such a resin, there can be cited, for example, a polyacrylic-based resin, a polyolefin-based resin, a polyurethane-based resin, an epoxy-based resin, a
10 polyester-based resin, a polybutyral-based resin, a melamine-based resin, a silicon resin, a fluorocarbon resin, an acrylic resin, and so on, and these resins can be used as they are or in combination. Further, these resins can be cured with any curing agent. The base paint can be used in any form such as an organic solvent-based form, water-based form, or powder-based form. Note
15 that the resin contained in the base paint of the upper paint film layer may be of the same type as or different from that contained in the base paint film of the primer paint film layer, but when considering the adhesion between the primer paint film layer and the upper paint film layer, the types of used resins are preferably the same between the layers.

20 [0134]

For use applications with more demanding molding workability, the base paint preferably contains a high-molecular polyester resin and a curing agent. The high-molecular polyester resin can be selected according to the application of the pre-coated plated steel sheet, and any high-molecular
25 polyester-based resin that is usually used as a solvent-based paint can also be used. Such a high-molecular polyester-based resin is preferably a

high-molecular polyester resin in which the main resin is composed of ester bonds of two or more resin monomers.

[0135]

As a curing agent used to form a thermosetting resin paint film by
5 reaction with the above-described high-molecular polyester resin, it is
possible to use, for example, an amino resin such as a melamine resin, a urea
resin, or a benzoguanamine resin, or an isocyanate compound and its block.
Regarding the mass ratio of the curing agent and the resin in the dry paint film,
it is preferable that the amount of the curing agent is 10 to 35 parts by mass
10 with respect to 100 parts by mass of the total amount of the resin and the
curing agent. When the amount of the curing agent is less than 10 parts by
mass, adhesion, corrosion resistance, solvent resistance, or the like may not be
sufficiently secured, and when it exceeds 35 parts by mass, workability,
chemical resistance, and impact resistance may decrease.

15 [0136]

Further, the upper paint film layer can further contain additives such
as a pigment, surface-modified metal powders or glass powders, a dispersing
agent, a leveling agent, a wax, an aggregate, and fluorocarbon resin beads, a
diluting solvent, and so on as needed.

20 [0137]

Here, when the upper paint film layer further contains a pigment, a
content of such a pigment is preferably 60% or less, for example, in terms of a
pigment weight concentration (PWC).

[0138]

25 In the paint film layer 205 according to the present embodiment, a
total thickness of the primer paint film layer and the upper paint film layer

described above, is preferably 10 to 30 μm . The total thickness of less than 10 μm is not preferable since cracks due to working become large, and besides, the corrosion resistance may decrease. The total thickness is more preferably 13 μm or more, and still more preferably 20 μm or more. On the other hand, the total thickness of the primer paint film layer and the upper paint film layer exceeding 30 μm is not preferable since the residual stress during working becomes large, and deterioration of various performances at a worked portion such as occurrence of blooming phenomenon may occur. The total thickness is more preferably 28 μm or less, and still more preferably 25 μm or less.

[0139]

Here, the thickness of the primer paint film layer, and the total thickness of the primer paint film layer and the upper paint film layer according to the present embodiment, can be measured by observing a cross section of the paint film layer 205 according to the present embodiment with an optical microscope. More specifically, the pre-coated plated steel sheet including the focused paint film layer 205 is embedded in a thermosetting resin such as an epoxy resin, a cutting machine such as a precision cutter is used to cut the sample at a position to be observed, in a direction parallel to a thickness direction, and the obtained cross section is observed with the optical microscope. Shortest distances from arbitrary positions of a plurality of places (5 places, for example) on an interface between the embedded resin and the paint film layer to an interface between the paint film layer and a layer positioned on the steel sheet side relative to the paint film layer are measured (namely, the distances are measured in a direction perpendicular to the interfaces), and the obtained measured values are averaged. The average

thickness of the paint film obtained as above can be set to the total thickness of the primer paint film layer and the upper paint film layer. The thickness of the primer paint film layer can also be measured in the same manner by measuring the shortest distance from an interface between the primer paint
5 film layer and the upper paint film layer to an interface between the paint film layer and the layer positioned on the steel sheet side relative to the paint film layer.

[0140]

After applying a paint component of the upper paint film layer, the
10 paint component is baked at a temperature of 150°C or more and less than 300°C to be cured and dried. When the baking temperature is less than 150°C, adhesion of the paint film may not be sufficiently secured, and when the baking temperature is 300°C or more, thermal degradation of the resin component such as a polyester resin component may occur, resulting in a
15 decrease in the workability.

[0141]

Note that the application of the paint for forming the upper paint film layer can be performed by generally well-known coating methods such as roll coating, curtain flow coating, air spray, airless spray, immersion, bar coating,
20 or brush coating, for example. Among the above, from a viewpoint of industrial productivity, it is preferable to use a roll coating method, a flow coating method, a curtain flow method, or the like being a coating method used for manufacturing pre-coated steel sheets.

[0142]

25 (Regarding molded product)

Next, a molded product using the pre-coated plated steel sheet 20 as

explained above, will be explained in detail while referring to FIG. 5. FIG. 5 is an explanatory view schematically illustrating an example of a structure of a molded product according to the present embodiment.

[0143]

5 As schematically illustrated in FIG. 5 as an example, a molded product 30 according to the present embodiment is one formed in a manner that the pre-coated plated steel sheet 20 as explained above is subjected to various workings such as deep drawing and square cup pressing to be molded into a desired shape.

10 [0144]

Here, the average chemical composition of a plating layer included in the molded product 30 according to the present embodiment is the same as that of the plating layer 201 included in the pre-coated plated steel sheet 20 serving as a base. Accordingly, the average chemical composition of the plating layer included in the molded product 30 contains, for example, aluminum of 0.5 to 60.0 mass% and magnesium of 0.5 to 15.0 mass%. Of the plating layers, the plating layer included in the molded product 30 according to the present embodiment preferably contains aluminum of 5 mass% or more and 15 mass% or less, and magnesium of 2 mass% or more and 4 mass% or less. The plating layer of the molded product 30 contains aluminum and magnesium in the above-described contents, thereby making it possible to achieve desired corrosion resistance more securely. Note that in the plating layer in the molded product 30, the balance other than the above-described aluminum and magnesium is elements derived from the external environment, zinc, and impurities.

25

[0145]

As a concrete shape of the molded product 30 according to the present embodiment, there can be cited various shapes that various parts have, including articles mainly used outdoors such as air conditioner outdoor units and water heaters, for example.

5 [0146]

A working method used for working the pre-coated plated steel sheet 20 according to the present embodiment to form a molded product is not particularly limited, and conditions for the working may also be appropriately set according to the working method to be used, the shape of the molded
10 product, and so on.

[0147]

It can be said that working with respect to the top plate of an air conditioner outdoor unit, which is an example of the above molded product, is a severe molding work for the pre-coated plated steel sheet 20. Although the
15 degree of working differs among air conditioner companies, in each of the companies, one type of high-speed square cup pressing is performed to form the top plate of the outdoor unit. At each of four corner portions of the top plate, a compressed portion exists. When a general pre-coated plated steel sheet is used, paint film floating frequently occurs at the compressed portions.

20 [0148]

However, when the pre-coated plated steel sheet 20 according to the present embodiment is used as a material, the stress of the paint film due to working is not large because of the physical properties of the paint film, and further, the cohesive force of the primer paint film layer is also sufficient, so
25 that it becomes possible to more securely inhibit the generation of the paint film floating portion.

[0149]

[Regarding measured values by SAICAS method>

In the molded product formed of the pre-coated plated steel sheet according to the present embodiment, the cut strength obtained by measuring
5 a specific portion by the SAICAS method, and the peel state of this portion are specified.

[0150]

In the molded product according to the present embodiment, which is schematically illustrated in FIG. 5 as an example, a portion where the
10 thickness of the pre-coated plated steel sheet of the molded product has increased by 20% or more (in FIG. 5, for example, a portion surrounded by a dotted line, and a portion where the relationship of $(d' - d) / d \geq 0.20$ is satisfied when the thickness is set to d') when compared to a thickness d of the pre-coated plated steel sheet before molding (which can also be regarded
15 as a non-molded portion), is a portion where the plated steel sheet is compressed and elongated by working, and the compression exceeds the elongation. Hereinafter, such a portion where the thickness has increased by 20% or more will be referred to as a “compressed portion.” Such a compressed portion is a portion where the paint film tends to float in the
20 molded product.

[0151]

In the portion, in the molded product according to the present embodiment, where the thickness of the pre-coated plated steel sheet has increased by 20% or more when compared to that before molding (namely,
25 the compressed portion), the cut strength between the chemical treatment film layer and the paint film layer (more specifically, the primer paint film layer) is

1.00 kN/m or more on average when measured by the SAICAS method. In addition, when such a compressed portion is cut by the SAICAS method, 20% or less of a cut area is in the form of interfacial peeling, and the remaining cut area is in the form of cohesive failure within the paint film layer (more specifically, within the primer paint film layer). When the compressed portion does not satisfy all of the above-described conditions regarding the cut strength and the peeling area, the chemical treatment film layer is destroyed by working with compression, resulting in a decrease in the adhesion. In addition, an internal stress of the paint film layer concentrates on the interface between the chemical treatment film layer and the paint film layer (more specifically, the primer paint film layer) or the interface between the chemical treatment film layer and the plating layer, resulting in that the paint film adhesion during compression is insufficient at the portion with the lowest adhesion strength, causing the paint film to float. Besides, when the cut strength measured by the SAICAS method does not reach 1.00 kN/m on average, even if a sufficient area is in the form of cohesive failure within the paint film layer (more specifically, within the primer paint film layer), the cohesive force of the primer paint film layer is insufficient, resulting in that the paint film floating due to the cohesive failure of the primer paint film layer occurs.

[0152]

Note that if the thickness of the pre-coated plated steel sheet in the molded product has increased by 20% or more when compared to that before molding, no significant difference due to the difference in % is observed in the measurement results by the SAICAS method.

[0153]

In the molded product according to the present embodiment, the above-described cut strength according to the SAICAS method is preferably an average of 1.10 kN/m or more, and more preferably 1.20 kN/m or more. Note that an upper limit value of such a cut strength is preferably as high as possible, but substantially, the upper limit is about 1.30 kN/m.

[0154]

Further, regarding the cut area of the compressed portion of the molded product according to the present embodiment by the SAICAS method, the ratio of the portion that is in the form of interfacial peeling is preferably 15% or less, and more preferably 10% or less. Note that the ratio of the portion that is in the form of interfacial peeling is preferably as small as possible, and its lower limit value is 0%.

[0155]

[Method of measuring cut strength and peel form by SAICAS method]

The cut strength and the peel form by the SAICAS method for the focused molded product using the pre-coated plated steel sheet are measured as follows.

First, three or more flat portions of the focused molded product, which are considered to be non-molded portions, are specified, and the total thickness of each of the flat portions (including the plated steel sheet of the base, and the paint films on the front and back surfaces) is measured three times with a microgauge, to calculate the average value of the measured thicknesses. Such measurements are performed at a plurality of specified positions, and an average value at each of the positions is further calculated. The average value of the obtained values at the plurality of positions is set to the thickness of the pre-coated plated steel sheet before molding (for example,

the thickness d in FIG. 5) in the focused molded product.

[0156]

Further, a measurement sample (having a size of roughly 20 mm × 20 mm or more) is cut out from a portion that seems to have been subjected to various moldings such as deep drawing, and is smoothed with a steel plate straightener (leveler). Regarding the obtained measurement sample, the total thickness (including the plated steel sheet of the base, and the paint films on the front and back surfaces) is measured with a microgauge, and the increase ratio is calculated based on the obtained measured value and the thickness of the pre-coated plated steel sheet before molding, which is obtained as described above. The portion exhibiting a value of 20% or more in terms of the increase ratio obtained in this manner is defined as the compressed portion of the molded product.

[0157]

The cut strength and the peel form of the paint film at the interface between the paint film layer and the layer positioned on the steel sheet side relative to the paint film layer are measured by cutting the compressed portion specified as above while using a measuring device that can utilize the SAICAS method (for example, DN-GS model manufactured by DAIPLA WINTES CO., LTD.). Note that the cutting direction in the SAICAS method is set to be parallel to the edge line of the steel sheet after drawing.

[0158]

Further, even with an unworked pre-coated plated steel sheet, it is possible to obtain a portion whose thickness has increased by 20% or more when compared to that before molding, by performing compression. For example, the pre-coated plated steel sheet is subjected to deep drawing at a

drawing ratio of 2.0 and a pressing pressure of 1 t by using a deep drawing testing machine. The steel sheet in the vicinity of the most compressed portion is cut out in a sufficient size (roughly 20 × 20 mm or more). Of this steel sheet piece, a compressed portion whose thickness has increased by 20%
5 or more when compared to that before molding is specified (a specification method will be described later), and the cut strength and the peel form of the paint film at that portion are measured by the SAICAS method. The cutting direction is set to a direction perpendicular to the tensile direction of the steel sheet.

10 [0159]

The increase ratio when comparing the thickness of the plated steel sheet of the molded product with that before molding, is measured in the following manner. The total thickness (including the plated steel sheet of the base, and the paint films on the front and back surfaces) at each position
15 within the steel sheet piece cut out from the molded product is measured with a microgauge, to thereby calculate the increase ratio from the total thickness (including the plated steel sheet of the base, and the paint films on the front and back surfaces) of the pre-coated plated steel sheet before molding. Note that it is possible to confirm that there is no difference in the value of the ratio
20 calculated by this method, as compared to the value calculated from the thickness of the base measured in a state where paint films are removed from the front and back surfaces of the pre-coated plated steel sheets before and after molding with a paint film remover.

[0160]

25 Note that it is possible to confirm that there is no difference in the value of the increase ratio calculated by the above method, as compared to the

value calculated from the thickness of the base measured in a state where pre-coated plated steel sheets before and after molding are prepared, and paint films are removed from the front and back surfaces of the pre-coated plated steel sheets before and after molding with a paint film remover.

5 [0161]

The cut condition by the SAICAS method, and the method of measuring the ratio of the interfacial peel form and the cohesive failure form in the cut portion are as explained previously, and thus detailed explanation thereof will be omitted below.

10 [0162]

The molded product according to the present embodiment has been explained in detail above with reference to FIG. 5.

[0163]

As explained above, according to the embodiment of the present invention, by using the plated steel sheet for pre-coated steel sheet according to the embodiment of the present invention, it is possible to obtain the pre-coated plated steel sheet and the molded body formed of the pre-coated steel sheet in which the paint film floating (the phenomenon in which the paint film becomes rough due to aggregates of minute point-like blisters) or paint film peeling does not occur at the portion worked by drawing or the like.

[Example]

[0164]

Hereinafter, the pre-coated plated steel sheet and the molded product according to the present invention will be concretely explained while describing examples and comparative examples. Note that the examples to be described below are merely examples of the pre-coated plated steel sheet

and the molded product according to the present invention, and the pre-coated plated steel sheet and the molded product according to the present invention are not limited to the following examples.

[0165]

5 (1. Plated steel sheet used as base sheet)

As the base sheets of the pre-coated steel sheet, the following four types of zinc-based plated steel sheets were used. Plating layers of the following zinc-based plated steel sheets were subjected to spray treatment for 5 seconds with a commercially-available sodium orthosilicate-based alkali
10 washing liquid, and then subjected to water washing and drying.

[0166]

G-A: Zn-11%Al-3%Mg-0.2%Si hot-dip zinc alloy plated steel sheet (sheet thickness 0.60 mm, plating weight 40 g/m²)

G-B: Zn-0.5%Al-0.5%Mg hot-dip zinc alloy plated steel sheet (sheet
15 thickness 0.60 mm, plating weight 40 g/m²)

G-C: Zn-6%Al-3%Mg hot-dip zinc alloy plated steel sheet (sheet thickness 0.60 mm, plating weight 40 g/m²)

G-D: Zn-55%Al-2%Mg-1.6%Si hot-dip zinc alloy plated steel sheet (sheet thickness 0.35 mm, plating weight 75 g/m²)

20 [0167]

(2. Film formation of chemical treatment film layer)

As a painting component intended for forming the chemical treatment film layer, the following was used. Note that an added amount of each component in each of the painting components was adjusted to fall within the
25 range of the added amount explained previously.

[0168]

S1: Water-based painting component composed of tannic acid, silane coupling agent, fine silica particles, and polyester resin

S2: Water-based painting component composed of silane coupling agent, phosphate, and acrylic resin

5 S3: Water-based painting component composed of silane coupling agent, fluorotitanic acid, fluorozirconic acid, and urethane resin

[0169]

The above-described painting components S1 to S3 were bar-coated on the above-described plated steel sheets for pre-coated steel sheet so as to have a predetermined weight when dried, and then dried in an air-heating furnace at a metal surface reached temperature of 70°C and air-dried.

[0170]

(3-1. Film formation of primer paint film layer)

As a painting component intended for forming the primer paint film, there were prepared primer paints obtained by variously changing the types and compounding ratios of the polyester-based resin, the curing agent, and the rust preventive pigment, as described in Table 1-1 and Table 1-2.

[0171]

<Polyester-based resin>

20 Polyester resin (number average molecular weight: 6000, Tg: 55°C)

Polyester resin (number average molecular weight: 6000, Tg: 25°C)

Polyester resin (number average molecular weight: 8000, Tg: 5°C)

Polyester resin (number average molecular weight: 11000, Tg: 40°C)

Polyester resin (number average molecular weight: 15000, Tg: 5°C)

25 Polyester resin (number average molecular weight: 15000, Tg: 20°C)

Polyester resin (number average molecular weight: 17000, Tg: 45°C)

Polyester resin (number average molecular weight: 20000, Tg: 5°C)

Polyester resin (number average molecular weight: 20000, Tg: 15°C)

Polyester resin (number average molecular weight: 20000, Tg: 19°C)

Polyester resin (number average molecular weight: 20000, Tg: 35°C)

5 Polyester resin (number average molecular weight: 23000, Tg: 5°C)

Polyester resin (number average molecular weight: 25000, Tg: 5°C)

Polyester resin (number average molecular weight: 25000, Tg: 45°C)

Polyester resin (number average molecular weight: 30000, Tg: 5°C)

[0172]

10 <Curing agent>

BI-A: MEK oxime blocked HDI

BI-B: ε caprolactam blocked MDI

MF-A: Methylated melamine

MF-B: Butylated melamine

15 [0173]

<Rust preventive pigment>

Compounded product of equal mass of calcium ion-exchanged silica and aluminum tripolyphosphate

[0174]

20 The primer paints having the components as described in Table 1-1 and Table 1-2 below were used and bar-coated on the plated steel sheets after being subjected to the above-described chemical treatment so as to have a thickness when dried as described in Table 1-1 and Table 1-2, and then dried in an air-heating furnace at a metal surface reached temperature of 215°C.

25 [0175]

(3-2. Film formation of upper paint film layer)

As a painting component intended for forming the upper paint film layer, the following was used.

[0176]

T-A: High-molecular polyester/melamine resin curing system composition (FLC7000 manufactured by Nippon Paint Co., Ltd.)

T-B: Polyester/melamine resin curing system composition (FLC7100 manufactured by Nippon Paint Co., Ltd.)

T-C: Polyester/melamine resin curing system composition (containing rust preventive pigment)

10 [0177]

Each of the above-described T-A to T-C was bar-coated on the layer having the above-described primer paint film formed thereon, so as to have a total thickness when dried as described in Table 1-1 and Table 1-2, and then dried in an air-heating furnace at a metal surface reached temperature of

15 230°C.

[0178]

(4-1. State of paint film in unworked condition)

The state of the paint film of each of the pre-coated plated steel sheets manufactured by the above-described method was checked by SAICAS and indenter insertion.

20

[0179]

(1) SAICAS

The interface between the chemical treatment film layer and the primer paint film layer or the interface between the chemical treatment film layer and the plating layer of the pre-coated plated steel sheet was cut by the SAICAS method to measure the cut strength and the peel form. Note that

25

the device used for the SAICAS method is DN-GS model manufactured by DAIPLA WINTES CO., LTD..

[0180]

<Cut strength>

5 A diamond blade (0.3 mm in width) was used, and oblique cutting was performed in a constant speed mode with a horizontal velocity of 1 $\mu\text{m}/\text{second}$ and a vertical velocity of 0.1 $\mu\text{m}/\text{second}$ and then near the interface, the cutting was switched to only the horizontal movement to cut a length of 200 μm , and the average cut strength during the horizontal
10 movement was measured. The depth position at which the cutting was switched to horizontal movement was set by specifying the interface position (a position at the very limit where the plating layer is not cut) through a preliminary experiment. When the plated surface is cut due to the unevenness of the plating during the horizontal movement of the cutting blade,
15 the cut strength can be discriminated because it momentarily increases abnormally. Such a case was excluded as an abnormal value, and the average cut strength was calculated. In each case, the number of measurements was set to $n = 3$, and the average value of the three values of the average cut strength was taken as the cut strength.

20 [0181]

A case where the obtained cut strength was 1.00 kN/m or more was evaluated as a score “A”, and a case where the obtained cut strength was less than 1.00 kN/m was evaluated as a score “B”.

[0182]

25 <Peel form>

An optical micrograph of a horizontal cut range ($300 \times 200 \mu\text{m}$) by

SAICAS was taken, portions of the primer cohesive failure, the interfacial peeling, and the plating cohesive failure within the same range were specified according to the above criteria, and areas of the portions were measured using transparent graph paper. Subsequently, the ratio of the interfacial peeling area to the area excluding the plating cohesive failure was calculated from the horizontal cut range by SAICAS.

[0183]

A case where the obtained ratio was 5% or less was evaluated as a score “A”, and a case where the obtained ratio was greater than 5% was evaluated as a score “B”.

[0184]

(2) Indenter insertion

A microhardness measuring quadrangular pyramid-shaped indenter was used to perform measurement regarding the indentation load and the elastic strain energy corresponding value.

[0185]

<Indentation load and elastic strain energy corresponding value>

A load when a microhardness measuring quadrangular pyramid-shaped indenter was inserted at a rate of 2 μm per minute with respect to a position 1 μm away in a direction of the primer paint film layer from an interface between the primer paint film layer and the chemical treatment film layer or an interface between the primer paint film layer and the plating layer, at a cross section obtained by cutting the primer paint film layer in the thickness direction, and the indenter reached a depth of 10 μm was measured, and a value of the load was set to the indentation load. After that, a load curve with respect to a displacement when the indenter was

unloaded at a rate of 2 μm per minute was measured subsequently. The obtained load curve was used to calculate, at a plane defined by the displacement and the load, an area of a range surrounded by a straight line corresponding to the displacement of 10 μm , a straight line corresponding to the load of 0, and the load curve when performing the unloading, and the resultant was set to the elastic strain energy corresponding value.

[0186]

(4-2. State of paint film after molding (soundness))

As described above, an interface between the chemical treatment film layer and the primer paint film layer or an interface between the chemical treatment film layer and the plating layer of a portion of the pre-coated plated steel sheet after being subjected to molding and whose film thickness has increased by 20% or more, was cut by the SAICAS method to measure its cut strength and peel form.

[0187]

<Cut strength>

A diamond blade (0.3 mm in width) was used, and oblique cutting was performed in a constant speed mode with a horizontal velocity of 1 $\mu\text{m}/\text{second}$ and a vertical velocity of 0.1 $\mu\text{m}/\text{second}$ and then near the interface, the cutting was switched to only the horizontal movement to cut a length of 200 μm , and the average cut strength during the horizontal movement was measured. The depth position at which the cutting was switched to horizontal movement was set by specifying the interface position (a position at the very limit where the plating layer is not cut) through a preliminary experiment. When the plated surface is cut due to the unevenness of the plating during the horizontal movement of the cutting blade,

the cut strength can be discriminated because it momentarily increases abnormally. Such a case was excluded as an abnormal value, and the average cut strength was calculated. In each case, the number of measurements was set to $n = 3$, and the average value of the three values of the average cut strength was taken as the cut strength.

[0188]

A case where the obtained cut strength was 1.10 kN/m or more was evaluated as a score “A1”, a case where the obtained cut strength was 1.00 kN/m or more and less than 1.10 kN/m was evaluated as a score “A2”, and a case where the obtained cut strength was less than 1.00 kN/m was evaluated as a score “B”.

[0189]

<Peel form>

An optical micrograph of a horizontal cut range ($300 \times 200 \mu\text{m}$) by SAICAS was taken, portions of the primer cohesive failure, the interfacial peeling, and the plating cohesive failure within the same range were specified according to the above criteria, and areas of the portions were measured using transparent graph paper. Subsequently, the ratio of the interfacial peeling area to the area excluding the plating cohesive failure was calculated from the horizontal cut range by SAICAS.

[0190]

A case where the obtained ratio was 15% or less was evaluated as a score “A1”, a case where the obtained ratio was greater than 15% and 20% or less was evaluated as a score “A2”, and a case where the obtained ratio was greater than 20% was evaluated as a score “B”.

[0191]

(5. Performance evaluation)

The performance of the compressed portion of each of the pre-coated plated steel sheets manufactured by the above-described method was evaluated by the following method.

5 [0192]

<Contents of aluminum and magnesium in plating layer>

The contents of aluminum and magnesium in the plating layer were measured by (Quantum 2000 model manufactured by ULVAC-PHI, Inc.).

[0193]

10 <Cylindrical cup drawing>

The cylindrical cup drawing of the pre-coated plated steel sheet for evaluating the paint film floating was conducted by performing drawing on the steel sheet under conditions including a punch size: 50 mm ϕ , a punch shoulder R: 5 mm, a blank diameter: 100 mm ϕ , a drawing ratio: 2.0, and a pressing pressure: 1 t.

15

[0194]

<Square cup drawing>

The square cup drawing of the pre-coated plated steel sheet for evaluating the paint film floating was conducted by performing drawing on the steel sheet under conditions including a punch size: 50 mm square, a punch shoulder R: 5 mm, a blank diameter: 100 mm ϕ , a drawing ratio: 2.0, and a pressing pressure: 1 t.

20

[0195]

<Paint film abnormality evaluation>

25

Regarding the molded product obtained by the above-described cylindrical cup drawing, a crosscut was applied to a body portion of the

cylindrical cup, and the cylindrical cup was immersed in boiling water for 1 hour, to thereby perform evaluation regarding a state of the paint film floating. Note that the crosscut was applied at two locations facing each other out of positions between a rolling direction (L direction) of the steel sheet and a direction orthogonal to the rolling direction (C direction) (positions at 45°
5 from the L direction and the C direction), at the body portion of the cylindrical cup drawn portion. The crosscut was applied from a position at a height of 5 mm from a drawn end face of the body portion as a starting point, toward a bottom surface of the cylindrical cup, so that two cuts each having a
10 length of 40 mm were orthogonal to each other at 90°.

[0196]

[State of paint film floating: loupe evaluation]

At the body portion of the cylindrical cup drawn portion, a state of the paint film floating of the body portion at a position at a height of 5 mm from
15 the drawn end face of the body portion at two locations facing each other with no crosscuts applied thereto (two locations in total of the body portion corresponding to a center angle 90°) when the positions between the rolling direction (L direction) of the steel sheet and the direction orthogonal to the rolling direction (C direction) (positions at 45° from the L direction and the C
20 direction) were set as a center, was evaluated by a loupe observation. The evaluation was performed by the following scores, based on the average value of two locations. The following scores are given per compressed portion. A score “4” or “5” was set as acceptance, and a score “A” representing the acceptance was described in Tables. Scores “1” to “3” were set as failure,
25 and a score “B” representing the failure was described in Tables.

[0197]

Further, at the square cup drawn portion, the compressed corner portion was observed with a loupe at four locations per one square cup to check the presence or absence of paint film peeling, and the state of paint film floating was evaluated by the following scores based on the average value of the four locations. The following scores are given per corner. A score “4” or “5” was set as acceptance, and a score “A” representing the acceptance was described in Tables. Scores “1” to “3” were set as failure, and a score “B” representing the failure was described in Tables.

[0198]

10 ♦ Loupe observation (cylindrical cup drawn material)

5: No paint film floating portion

4: 1 to 9 paint film floating portions

3: 10 to 19 paint film floating portions

2: 20 to 49 paint film floating portions

15 1: 50 or more paint film floating portions

[0199]

♦ Loupe observation (square cup drawn material)

5: No paint film floating portion

4: 1 to 9 paint film floating portions

20 3: 10 to 19 paint film floating portions

2: 20 or more paint film floating portions

1: 20 or more paint film floating portions and the presence of peeling due to connection of paint film floating portions

[0200]

25 [Crosscut test]

Regarding the crosscuts at two locations applied to the body portion

after being subjected to the cylindrical cup drawing, peeled widths of the paint film from the cut portions were measured, and a score was given to the maximum peeled width. Note that scores “A” and “B” were set as acceptance, and a score “C” was set as failure.

- 5 A: 0.2 mm or less
 B: greater than 0.2 mm and 0.4 mm or less
 C: greater than 0.4 mm

[0201]

- The obtained results are collectively described in Table 1-1 and Table
10 1-2 below.

[0202]

[Table 1-1]

and thus no occurrence of paint film floating or paint film peeling was observed in the actual working of the top plate of the air conditioner outdoor unit.

[0205]

5 On the other hand, in each of the comparative examples, the paint film physical properties based on the method of inserting the microhardness measuring quadrangular pyramid-shaped indenter, and the cut strength and the peel form of the compressed portion of the molded product by SAICAS did not satisfy the criteria, and thus occurrences of paint film floating and
10 paint film peeling were observed in the actual working of the top plate of the air conditioner outdoor unit.

[0206]

The preferred embodiments of the present invention have been described in detail above with reference to the attached drawings, but the
15 present invention is not limited to such examples. It is apparent that a person having common knowledge in the technical field to which the present invention belongs is able to devise various variation or modification examples within the range of technical ideas described in the claims, and it should be understood that such examples belong to the technical scope of the present
20 invention as a matter of course.

[Explanation of Codes]

[0207]

10 Zn-Al-Mg-based alloy plated steel sheet
20 pre-coated plated steel sheet
25 30 molded product
101 steel sheet

103, 201 Zn-Al-Mg-based alloy plating layer

203 chemical treatment film layer

205 paint film layer

CLAIMS

1. A pre-coated plated steel sheet, comprising:
 - a plating layer composed of Zn-Al-Mg-based alloy plating, the plating layer being positioned on one side or both sides of a steel sheet;
 - a chemical treatment film layer positioned on the plating layer; and
 - a paint film layer positioned on the chemical treatment film, wherein:
 - the paint film layer includes a primer paint film layer, and an upper paint film layer positioned on the primer paint film layer; and
 - out of conditions below, at least any of the following is satisfied: both a condition (a-1) and a condition (a-2); a condition (b); and a condition (c); wherein
 - the chemical treatment film layer contains any one or more selected from the group consisting of a resin, a silane coupling agent, a zirconium compound, silica, phosphoric acid and salts thereof, fluoride, a vanadium compound, and tannin or tannic acid;
 - the plating layer is a plating layer containing aluminium of 0.5 mass% or more and 60.0 mass% or less, magnesium of 0.5 mass% or more and 15.0 mass% or less, and the balance being composed of zinc and impurities;
 - a thickness of the primer paint film layer is 2 to 10 μm ;
 - a total thickness of the primer paint film layer and the upper paint film layer is 10 to 30 μm ;
 - the primer paint film layer contains a first polyester-based resin having an average molecular weight of 15000 to 20000 and a glass transition point T_g of 20 to 50 $^{\circ}\text{C}$, a second polyester-based resin having an average molecular weight of 20000 to 25000 and a glass transition point T_g of less than 20 $^{\circ}\text{C}$, and a curing agent, wherein T_g is determined by differential scanning calorimetry; and
 - the curing agent contains blocked isocyanate;
 - (a-1) A cut strength measured by cutting an interface between the paint film layer and a layer positioned on the steel sheet side relative to the paint film layer

by a SAICAS method is 1.00 kN/m or more on average, 5% or less of a cut area is in the form of interfacial peeling, and the remaining cut area is in the form of cohesive failure within the paint film layer;

(a-2) When a portion where a thickness of the pre-coated plated steel sheet after being subjected to deep drawing has increased by 20% or more when compared to a thickness of a non-molded portion is cut by the SAICAS method, at an interface between the paint film layer and a layer positioned on the steel sheet side relative to the paint film layer, a cut strength is 1.0 kN/m or more on average, 20% or less of a cut area is in the form of interfacial peeling, and the remaining cut area is in the form of cohesive failure within the paint film layer;

(b) An indentation load when a microhardness measuring quadrangular pyramid-shaped indenter is inserted at a rate of 2 μm per minute with respect to a position 1 μm away in a direction of the primer paint film layer from an interface between the primer paint film layer and a layer positioned on the steel sheet side relative to the primer paint film layer, at a cross section obtained by cutting the primer paint film layer in a thickness direction, and the indenter reaches a depth of 10 μm , is less than 1000 mN;

(c) A load curve with respect to a displacement when a microhardness measuring quadrangular pyramid-shaped indenter is inserted at a rate of 10 μm per second to a depth of 10 μm with respect to a position 1 μm away from an interface between the primer paint film layer and a layer positioned on the steel sheet side relative to the primer paint film layer, at a cross section obtained by cutting the primer paint film layer in the thickness direction, and then the indenter is unloaded at a rate of 2 μm per minute is drawn, and at a plane defined by the displacement and the load, an area of a range surrounded by a straight line corresponding to the displacement of 10 μm , a straight line corresponding to the load of 0, and the load curve when performing the unloading is less than 500 μm mN.

2. The pre-coated plated steel sheet according to claim 1, wherein

- the primer paint film layer further contains a pigment, wherein a concentration in paint film of the pigment (PWC) is 20 to 60 mass%.
3. The pre-coated plated steel sheet according to claim 1 or 2, wherein a content of the first polyester-based resin with respect to a total content of the first polyester-based resin and the second polyester-based resin is 30 to 70% in terms of mass%.
 4. The pre-coated plated steel sheet according to any one of claims 1 to 3, wherein a content of the curing agent with respect to a total content of the first polyester-based resin, the second polyester-based resin, and the curing agent is 5 to 15% in terms of mass%.
 5. The pre-coated plated steel sheet according to any one of claims 1 to 4, wherein the curing agent further contains melamine or melamine derivative.
 6. The pre-coated plated steel sheet according to claim 5, wherein a content of the melamine resin with respect to a total content of the blocked isocyanate and the melamine or melamine derivative is 20 to 50% in terms of mass%.
 7. The pre-coated plated steel sheet according to any one of claims 1 to 6, wherein the average molecular weight of the second polyester-based resin is 21000 to 24500.
 8. The pre-coated plated steel sheet according to any one of claims 1 to 7, wherein

the glass transition point T_g of the second polyester-based resin is 5 to 15°C.

9. The pre-coated plated steel sheet according to any one of claims 1 to 8, wherein

the average molecular weight of the first polyester-based resin is 16000 to 19000.

10. The pre-coated plated steel sheet according to any one of claims 1 to 9, wherein

the glass transition point T_g of the first polyester-based resin is 30 to 48°C.

11. The pre-coated plated steel sheet according to any one of claims 1 to 10, wherein

the plating layer is composed of Zn-11%Al-3%Mg-0.2%Si alloy plating that further contains Si in place of a part of Zn being the balance.

12. A molded product being a molded product comprising a pre-coated plated steel sheet including: a plating layer composed of Zn-Al-Mg-based alloy plating, the plating layer being positioned on one side or both sides of a steel sheet; a chemical treatment film layer positioned on the plating layer; and a paint film layer positioned on the chemical treatment film, the paint film layer including a primer paint film layer, and an upper paint film layer positioned on the primer paint film layer, wherein:

the chemical treatment film layer contains any one or more selected from the group consisting of a resin, a silane coupling agent, a zirconium compound, silica, phosphoric acid and salts thereof, fluoride, a vanadium compound, and tannin or tannic acid;

the plating layer is a plating layer containing aluminium of 0.5 mass% or more and 60.0 mass% or less, magnesium of 0.5 mass% or more and 15.0 mass% or less, and the balance being composed of zinc and impurities;

a thickness of the primer paint film layer is 2 to 10 μm ;

a total thickness of the primer paint film layer and the upper paint film layer is 10 to 30 μm ;

the primer paint film layer contains a first polyester-based resin having an average molecular weight of 15000 to 20000 and a glass transition point T_g of 20 to 50 $^{\circ}\text{C}$, a second polyester-based resin having an average molecular weight of 20000 to 25000 and a glass transition point T_g of less than 20 $^{\circ}\text{C}$, and a curing agent, wherein the curing agent contains blocked isocyanate; and

at a portion where a thickness of a plated steel sheet in the molded product has increased by 20% or more when compared to a thickness of a non-molded portion, a cut strength measured by cutting an interface between the paint film layer and a layer positioned on the steel sheet side relative to the paint film layer by a SAICAS method is 1.00 kN/m or more on average, 20% or less of a cut area is in the form of interfacial peeling, and the remaining cut area is in the form of cohesive failure within the paint film layer.

13. The molded product according to claim 12, wherein

the plating layer in the molded product contains aluminum of 5 mass% or more and 15 mass% or less, and magnesium of 2 mass% or more and 4 mass% or less.

Nippon Steel Corporation
Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON

FIG. 1A

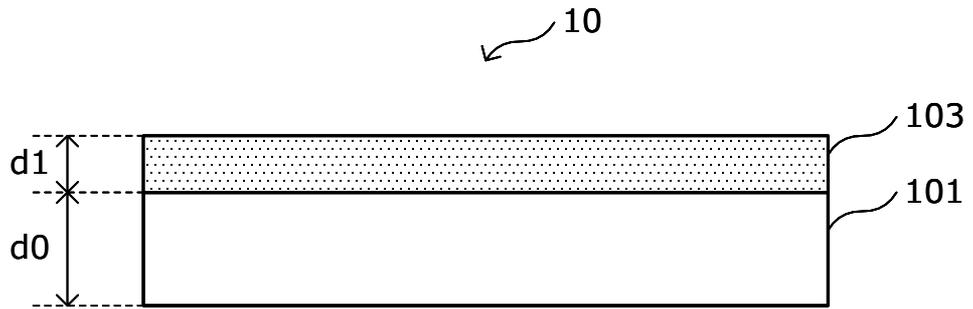


FIG. 1B

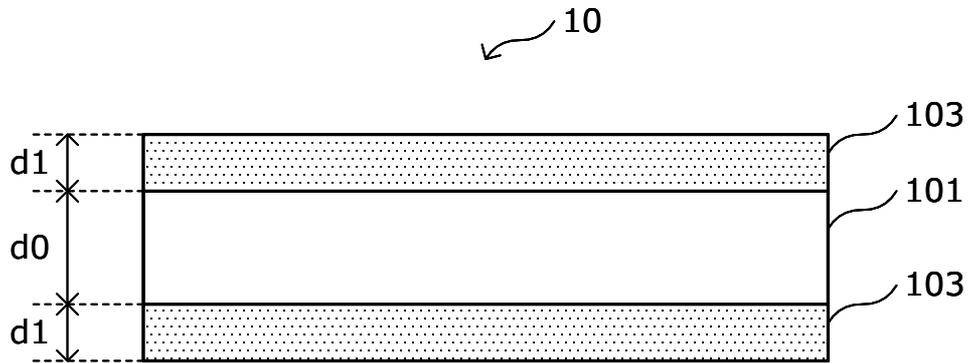


FIG. 2A

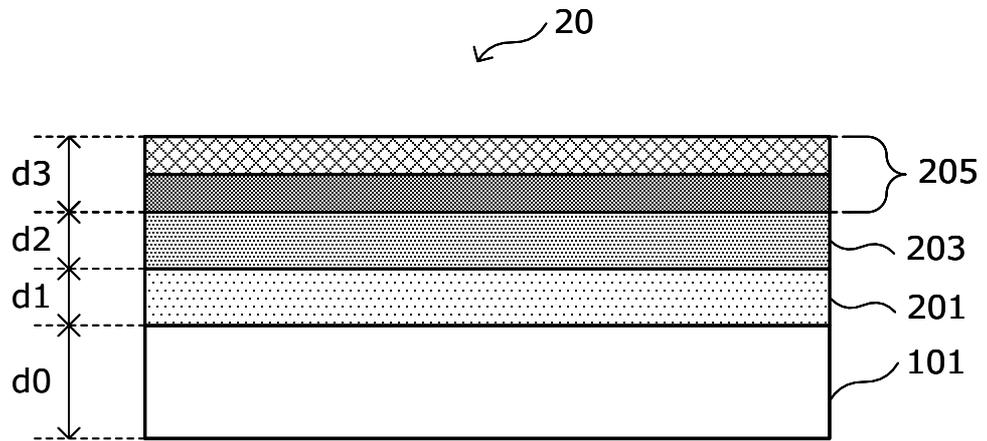


FIG. 2B

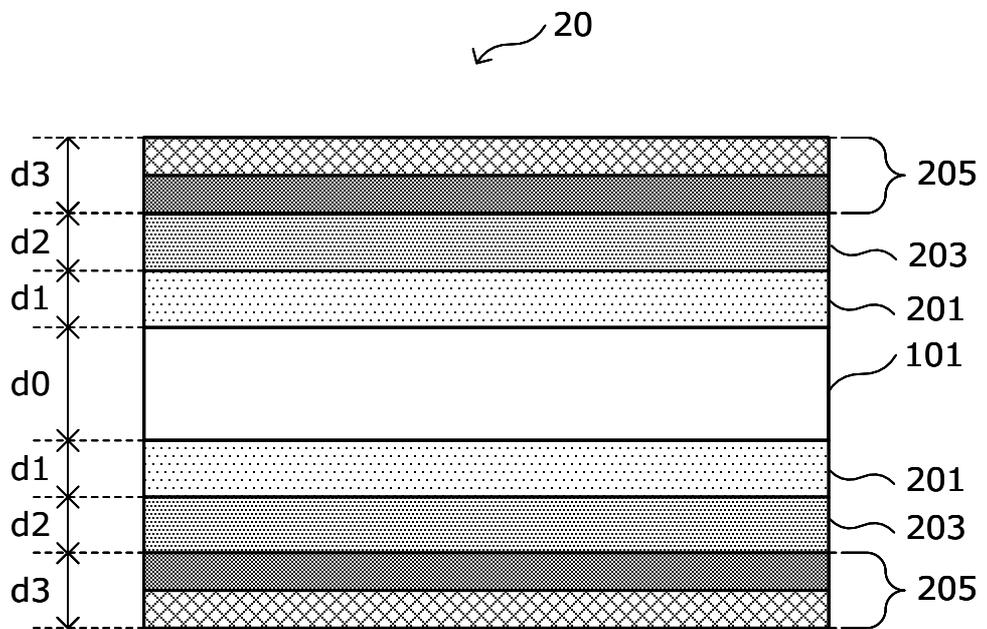


FIG. 3

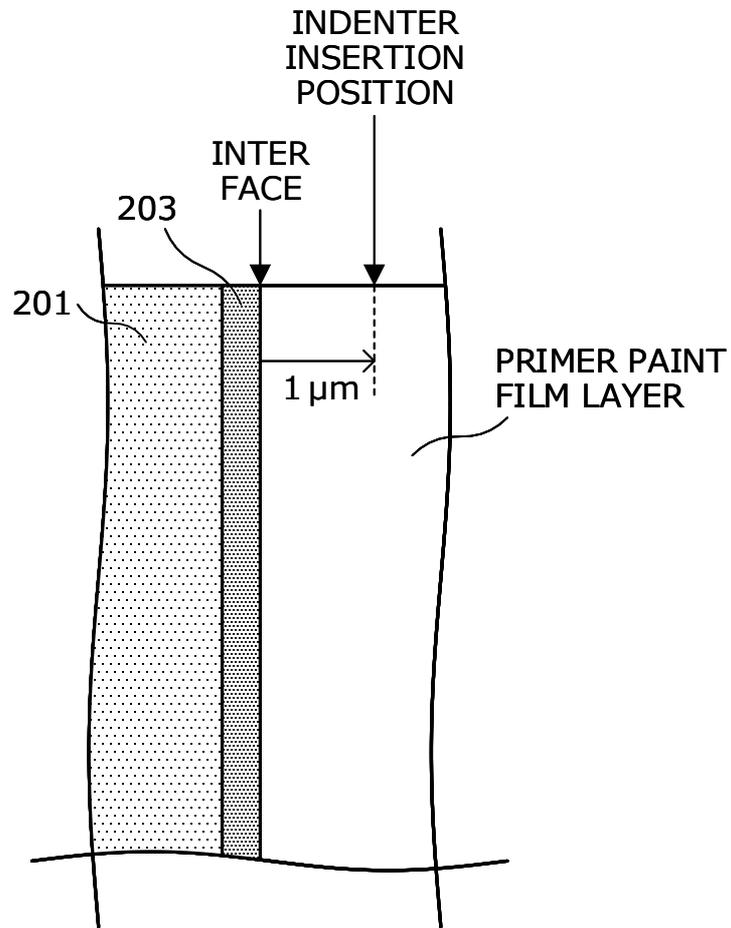


FIG. 4

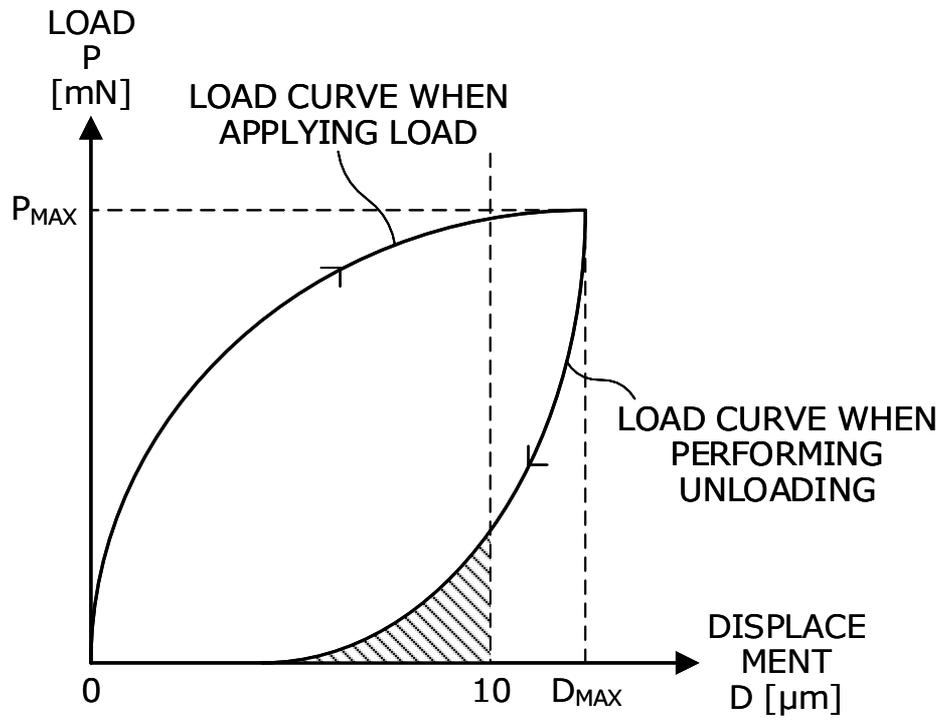


FIG. 5

