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DESCRIPTION

PRECOATED METAL SHEET HAVING EXCELLENT PRESS-FORMABILITY AND PRODUCTION METHOD THEREOF

5 Field of the Invention

The present invention relates to a surface-treated metal material excellent in press formability and corrosion resistance, which can exhibit a rust preventive effect and coating adhesion when press-formed, particularly without using hexavalent chromium having a problem in view of environment, for use in home appliances, building materials, construction materials, machines, automobiles, furniture or containers.

Background Art

15 In place of conventional post-coated products obtained by resin-coating after working, which are used for home appliances, construction materials and automobiles, a precoated metal applied with a colored coating has been used. This precoated metal sheet is one
20 obtained by forming a layer of a resin coating composition on a metal sheet which has been subjected to a pretreatment for metals. After covering with the resin coating composition, the precoated metal sheet is used by cutting and press-forming. Therefore, the precoated
25 metal sheet has problems in corrosion resistance on the cut end face part where the metal is exposed without being covered with the resin coating layer, and separation of the resin coating during the press-forming. However, when a chromate treatment is applied as a
30 pretreatment for metals and the resin coating containing a hexavalent chromium-base antirust pigment is used, these problems are solved. Such metal sheets are being used at present for general purposes.

35 However, the hexavalent chromium, which may dissolve out from the chromate treatment film, and the hexavalent chromium-base antirust pigment-containing resin coating layer, have a problem in view of environment. Therefore,

demands for non-chromate chemical conversion treatment and non-chromate resin coating material containing no hexavalent chromium are recently increasing. Japanese Unexamined Patent Publication (Kokai) No. 2001-89868
5 discloses a technique for providing a precoated metal sheet having excellent adhesion in the worked part and high corrosion resistance by using a chemical conversion treatment simultaneously containing tannin, a tannic acid, a silane coupling agent and fine particles of
10 silica in place of the chromate treatment. On the other hand, Japanese Unexamined Patent Publication No. 9-12931 discloses a technique for providing a precoated metal sheet having excellent corrosion resistance in the cut end face part, by using polyester-base and epoxy-base
15 coating compositions in which a phosphorus acid-base antirust pigment and an ion-exchange silica-base antirust pigment are used in combination, in place of the hexavalent chromium-base antirust pigment.

The chemical conversion technique disclosed in
20 Japanese Unexamined Patent Publication No. 2001-89868 ensures excellent adhesion in the worked part at an Erichsen test or a T-bending test but has a problem in that when press-forming, represented by deep-drawing formation, is performed, the coating is scratched by a
25 mold and readily peeled off as compared with a precoated metal sheet which has been subjected to a chromate treatment. On the other hand, the technique disclosed in Japanese Unexamined Patent Publication No. 9-12931 uses
30 zinc phosphate for the chemical conversion treatment and has a problem in that the adhesion of coating in the worked part is insufficient as compared with a precoated metal sheet which has been subjected to chromate treatment and when press-forming is performed, the
coating is scratched by a mold and is readily peeled off.

35 The object of the present invention is to solve those problems in conventional techniques and provide a precoated metal sheet having excellent corrosion

resistance, even if hexavalent chromium is not contained and, further, having excellent press formability, and to provide a production method thereof.

SUMMARY OF THE INVENTION

5 The present inventors have found that, when a chemical conversion coating layer simultaneously containing a silane coupling agent, fine particles of silica and at least either one of tannin and a tannic acid is formed and, further, a resin coating layer
10 containing an aluminum phosphate-base pigment is formed thereon, the obtained composite coating film can have not only excellent corrosion resistance but also very excellent press formability. The present invention has been accomplished based on this finding. The gist of the
15 present invention resides in the followings.

(1) A precoated metal sheet having excellent press formability, comprising a metal sheet having on one surface or both surfaces thereof a chemical conversion coating layer simultaneously containing, as solid
20 contents, a silane coupling agent, fine particles of silica and at least either one of tannin and a tannic acid, and further having thereon a resin coating layer containing from 1 to 140 parts by mass of an aluminum phosphate-base pigment per 100 parts by mass of resin
25 solid contents.

(2) The precoated metal sheet having excellent press formability as described in (1) above, wherein the chemical conversion coating layer further contains a polyester resin as a solid content.

30 (3) The precoated metal sheet having excellent press formability as described in (1) or (2) above, wherein the aluminum phosphate-base pigment contained in the resin coating layer is aluminum dihydrogen triphosphate.

35 (4) The precoated metal sheet having excellent press formability as described in any one of (1) to (3) above, wherein the resin coating layer further contains

an antirust pigment and the total content of the antirust pigment and aluminum phosphate-base pigment is 140 parts by mass or less per 100 parts by mass of resin solid contents.

5 (5) The precoated metal sheet having excellent press formability as described in (4) above, wherein the antirust pigment contained in the resin coating layer is a calcium ion-exchanging silica.

10 (6) The precoated metal sheet having excellent press formability as described in any one of (1) to (5) above, wherein the metal sheet is a metal sheet having a plated layer on one surface or both surfaces thereof.

15 (7) A method for producing a precoated metal sheet having excellent press formability, comprising coating a treating solution simultaneously containing a silane coupling agent, fine particles of silica and at least either one of tannin and a tannic acid on one surface or both surfaces of a metal sheet, drying the treating solution to form a chemical conversion coating layer, 20 further coating a resin coating composition containing from 1 to 140 parts by mass of an aluminum phosphate-base pigment per 100 parts by mass of resin solid contents on the chemical conversion coating layer, and drying and curing the coating material.

25 (8) The method for producing a precoated metal sheet having excellent press formability as described in (7) above, wherein the treating solution further contains a polyester resin.

30 (9) The method for producing a precoated metal sheet having excellent press formability as described in (7) or (8) above, wherein the coating composition further contains an antirust pigment and the total content of the antirust pigment and aluminum phosphate-base pigment is 140 parts by mass or less per 100 parts by mass of resin 35 solid contents.

 (10) A press-formed precoated metal article comprising a press-formed precoated metal sheet, said

press-formed precoated metal sheet being as set forth in (1) to (9).

BRIEF DESCRIPTION OF DRAWING

Fig. 1 is a schematical cross-section of a press-formed precoated metal sheet, in which on a surface of a metal sheet 1, a chemical conversion coating layer 2 comprising at least one of tannin or tannic acid, a silane coupling agent and fine particles of silica, a resin coating layer 3 containing aluminum phosphate-base pigment, and optionally a top coat layer 4 are formed. The layers 2 to 4 may be formed on both surfaces of the metal sheet.

Modes for Carrying Out the Invention

The present invention can be achieved by forming a chemical conversion coating layer simultaneously containing, as solid contents, a silane coupling agent, a fine particles of silica and at least either one of tannin and a tannic acid on one surface or both surfaces of a metal sheet or a plated metal sheet, and further forming thereon a resin coating layer containing from 1 to 140 parts by mass of an aluminum phosphate-base pigment. The aluminum phosphate-base pigment is preferably aluminum dihydrogen tripolyphosphate, because the coating is more resistant to scratching during press-forming. Furthermore, the chemical conversion coating layer used in the precoated metal sheet of the present invention preferably further contains a polyester resin as a solid content, because the adhesion of the coating is improved and the coating is more resistant to scratching during press-forming.

The resin coating layer formed in the precoated metal sheet of the present invention preferably contains an antirust pigment in addition to the aluminum phosphate-base pigment, because the corrosion resistance of the precoated metal sheet is enhanced. The amount of these pigments added is suitably, as a total content of the aluminum phosphate-base pigment and the antirust

pigment, 140 parts by mass or less per 100 parts by mass of resin solid contents. Furthermore, this rust pigment is preferably calcium ion-exchanging silica, because the corrosion resistance is more enhanced.

5 The chemical conversion coating layer formed in the precoated metal sheet of the present invention is preferably formed by coating a coating solution simultaneously containing a silane coupling agent, a fine particle silica and at least either one of tannin and a
10 tannic acid, or such a coating solution additionally containing a polyester resin, and drying the coated coating solution, by which the precoated metal sheet of the present invention can be more efficiently produced. Furthermore, the resin coating layer formed in the
15 precoated metal sheet of the present invention is preferably formed by coating a resin coating composition containing an aluminum phosphate-base pigment or a resin coating material containing both an aluminum phosphate-base pigment and an antirust pigment and drying and
20 curing the resin coating composition, by which the precoated metal sheet of the present invention can be more efficiently produced.

 As a result of various investigations on a non-chromate precoated metal sheet in which a coated layer is
25 hardly scratched by a mold during press-forming, the present inventors have found that when a chemical conversion coating layer simultaneously containing tannin and/or a tannic acid, a silane coupling agent and fine particles of silica is formed on a metal sheet or a
30 plated metal sheet and further a coating layer containing an aluminum-base pigment is formed thereon, the phenomenon that the coating is peeled off due to scratching by a mold during press-forming is remarkably prevented. The phenomenon that the coating is scratched
35 and peeled off by a mold during press-forming is considered to occur because the coating of the precoated metal sheet is scratched by a mold under a heavy load and

a shearing force thereby acts on the coating. Therefore, the following two methods can be considered to solve this problem. First method is to increase the adhesive strength between the coating and the metal. Second method is to make it difficult to transmit the shearing force acting on the coating to the coating peeling surface, which is the interface between the coating and the original metal sheet. The reasons why the coating of the precoated metal sheet of the present invention is resistant to scratching by a mold during press-forming are not clearly known, but are considered that a chemical conversion coating layer simultaneously containing tannin and/or a tannic acid, a silane coupling agent and fine particles of silica and having excellent adhesive property is combined with a resin coating layer containing an aluminum phosphate-base pigment, whereby the adhesion of coating is remarkably enhanced due to the synergistic effect and the shearing stress generated in the coating at the press-forming due to the intrinsic mechanical properties of the aluminum phosphate-base pigment is prevented from being easily transmitted to the interface between the coating and the metal sheet.

The metal sheet used in the precoated metal sheet of the present invention may be a generally known metal sheet or a plated metal sheet, such as cold rolled steel sheet, hot rolled steel sheet, molten zinc plated steel sheet, electric zinc plated steel sheet, fused alloyed zinc plated steel sheet, aluminum plated steel sheet, aluminum-zinc alloyed plated steel sheet, aluminum-magnesium-zinc plated steel sheet, aluminum-magnesium-silicon-zinc plated sheet, stainless steel sheet and aluminum sheet. These metal sheets may be subjected to normal treatments such as washing with warm water and degreasing with alkali, before the chemical conversion treatment.

The chemical conversion coating layer formed in the precoated metal sheet of the present invention is

characterized by containing tannin and/or a tannic acid, a silane coupling agent and fine particles of silica.

5 The tannin or tannic acid used may be a hydrolyzable tannin, a condensed tannin or a partially decomposed product thereof. The tannin and tannic acid are not particularly limited and examples thereof include hamamelitannin, Chinese gallotannin, nutgalls-tannin, myrobalan tannin, divi-divi tannin, algarobillatannin, valonia tannin and catechin. When "tannic acid: AL" 10 (produced by Fuji Kagaku Kogyo) is used, the coating is particularly improved in the working part adhesive property. The amount added of at least either one of tannin and a tannic acid is not particularly specified but the content thereof in the chemical conversion 15 solution to be coated on the metal sheet for forming the coating layer is preferably from 2 to 80 g/liter. If the amount added of at least either one of tannin and a tannic acid is less than 2 g/liter, the rust preventive effect or the coating adhesion may not be secured, 20 whereas if it exceeds 80 g/liter, the rust preventive effect or the coating adhesion may rather decrease or the tannin or tannic acid may not dissolve in the aqueous solution.

Examples of the silane coupling agent which can be 25 used include γ -(2-aminoethyl)aminopropyltrimethoxysilane, γ -(2-aminoethyl)aminopropylmethyldimethoxysilane, γ -(2-aminoethyl)aminopropyltriethoxysilane, γ -(2-aminoethyl)aminopropylmethyldiethoxysilane, γ -(2-aminoethyl)aminopropylmethyldimethoxysilane, γ - 30 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, N- β -(N-vinylbenzylaminoethyl)- γ -aminopropylmethyldiethoxysilane, γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropylmethyldimethoxysilane, γ -glycidoxypropyltriethoxysilane, γ -glycidoxypropylmethyldiethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -mercaptopropylmethyldimethoxysilane, γ -mercaptopropyltriethoxysilane, γ -mercaptopropylmethyldiethoxysilane, methyltrimethoxysilane, dimethyldimethoxysilane, methyltriethoxysilane, dimethyldiethoxysilane, vinyltriacetoxysilane, γ -chloropropyltrimethoxysilane, γ -chloropropylmethyldimethoxysilane, γ -chloropropyltriethoxysilane, γ -chloropropylmethyldiethoxysilane, hexamethyldisilazane, γ -anilinopropyltrimethoxysilane, γ -anilinopropylmethyldimethoxysilane, γ -anilinopropyltriethoxysilane, γ -anilinopropylmethyldiethoxysilane, vinyltrimethoxysilane, vinylmethyldimethoxysilane, vinyltriethoxysilane, vinylmethyldiethoxysilane, octadecyldimethyl[3-(trimethoxysilyl)propyl]ammonium chloride, octadecyldimethyl[3-(methyldimethoxysilyl)propyl]ammonium chloride, octadecyldimethyl[3-(triethoxysilyl)propyl]ammonium chloride, octadecyldimethyl[3-(methyldiethoxysilyl)propyl]ammonium chloride, γ -chloropropylmethyldimethoxysilane, γ -mercaptopropylmethyldimethoxysilane,

methyiltrichlorosilane, dimethyldichlorosilane and trimethylchlorosilane. In particular, when γ -glycidoxypropyltrimethoxysilane having a glycidyl ether group or γ -glycidoxypropyltriethoxysilane is used, the coating is improved in the working part adhesive property. Furthermore, when a triethoxy-type silane coupling agent is used, the surface-treating agent can be improved in the storage stability. This is considered to be because the triethoxysilane is relatively stable in an aqueous solution and the polymerization proceeds at a low rate.

The amount of the silane coupling agent added is not particularly specified but the content thereof in the chemical conversion solution to be coated on a metal sheet for forming a chemical conversion coating layer is preferably from 2 to 80 g/liter. If the content is less than 2 g/liter, sufficiently high adhesion of the coating during the working may not be obtained and the corrosion resistance may be insufficient, whereas if it exceeds 80 g/liter, the coating adhesion may rather decrease.

The fine particles of silica for use in the present invention generically indicates silicas having a fine particle size and therefore, can stably maintain the water dispersion state when dispersed in water. Examples of the fine particles of silica which can be used include commercially available silica gels such as "Snowtex N", "Snowtex C", "Snowtex UP", "Snowtex PS" (all are produced by Nissan Chemicals Industries, Ltd.) and "Adelite AT-20Q" (produced by Asahi Denka Kogyo K.K.), and powder silicas such as "Aerosil #300" (produced by Nippon Aerosil). The fine particles of silica may be appropriately selected according to the performance required. When a fine particle silica capable of stably dispersing even at a pH of 4 or more like "Snowtex C" is used, the surface-treating agent can be improved in the storage stability. This is considered to result because

the pH of the chemical solution can be adjusted to 4 or more and therefore, the reaction of a silane coupling agent exhibiting high reactivity at a low pH can be suppressed.

5 The amount of the fine particle silica added is also not particularly specified but the content thereof in the chemical conversion solution to be coated on a metal sheet for forming a chemical conversion film is preferably from 1 to 40 g/liter. If the content is less
10 than 1 g/liter, the coating may have poor working part adhesive property, whereas if it exceeds 40 g/liter, the effects of working part adhesive property and corrosion resistance are saturated and this is unprofitable.

 The chemical conversion coating layer preferably
15 further contains a polyester resin as a solid content, because the working adhesive property is more improved. The content of the polyester resin is also not particularly specified but when the content thereof in the chemical conversion solution to be coated on a metal
20 sheet for forming a chemical conversion coating layer is from 1 to 60 g/liter, the working part adhesive property is more improved. If the content is less than 1 g/liter, the effect by the addition of resin is not obtained, whereas if it exceeds 60 g/liter, the working part
25 adhesive property of the coating may rather decrease. Examples of the polyester resin which can be used include "FINETEX ES-650", "FINETEX ES-611", "FINETEX ES-670", "FINETEX ES-675" (all produced by Dai-Nippon Ink & Chemicals, Inc.), "VILONAL MD-1200", "VILONAL MD-1220",
30 "VILONAL MD-1250", "VILONAL MD-1100", "VILONAL MD-1330" and "VILONAL MD-1930" (all produced by Toyobo Co., Ltd.).

 In the chemical conversion solution coated for forming the chemical conversion coating layer of the present invention, an acid, an alkali or the like may be
35 added to adjust the pH within the range of not impairing the performance.

 The chemical conversion coating layer is preferably

formed on the metal sheet by coating the above-described chemical conversion agent on a metal sheet and baking or heating/drying the chemical conversion agent, because the production efficiency is enhanced. The baking
5 temperature is preferably from 50 to 250°C. If the baking temperature is less than 50°C, the water content evaporates at a low rate and a satisfactorily good film-forming property cannot be obtained, as a result, the rust preventive force becomes insufficient, whereas if it
10 exceeds 250°C, the tannin or tannic acid as an organic material or the alkyl moiety of the silane coupling agent undertakes denaturation such as thermal decomposition and the adhesive property or corrosion resistance decreases. The baking temperature is more preferably from 70 to
15 160°C. In the hot air drying, drying for 1 second to 5 minutes is preferred, because the production efficiency is improved.

The coating method of the chemical conversion solution is not particularly limited and a generally
20 known coating method such as roll coating, ringer roll coating, air spraying, airless spraying or dipping may be employed. The chemical conversion solution is preferably coated by a general continuous coating line fully furnished with these coating devices, called a coil
25 coating line or a sheet coating line, because the coating work can be performed with good efficiency and mass production can be achieved.

The amount of the chemical conversion coating film layer formed is preferably from 10 to 500 mg/m² as solid
30 contents. If the amount formed is less than 10 mg/m², a sufficiently high working part adhesive property cannot be ensured, whereas if it exceeds 500 mg/m², the working part adhesive property rather deteriorates.

In the precoated metal sheet of the present
35 invention, the resin for the coating layer to be formed on the chemical conversion coating layer may be in any form of aqueous-type, solvent-type, powder-type and the

like. As for the kind of resin, generally known resins such as polyacryl-base resins, polyolefin-base resins, polyurethane-base resins, epoxy-base resins, polyester-base resins, polybutyral-base resins and melamine-base resins may be used as it is or in combination.

The resin coating layer of the precoated metal sheet of the present invention must contain from 1 to 140 parts by mass of an aluminum phosphate-base pigment per 100 parts by mass of resin solid contents. If the amount of the aluminum phosphate-base pigment added is less than 1 part by mass, there is no effect against scratching of the coating by a during the press-forming and this is improper. As the amount of the aluminum phosphate-base pigment added becomes larger, the effect against scratching of the coating during the press-forming is advantageously higher, however, if the amount added exceeds 140 parts by mass, the workability as the precoated metal sheet greatly deteriorates and this is improper.

Examples of the aluminum phosphate-base pigment which can be used include generally known pigments such as aluminum dihydrogen tripolyphosphate and aluminum metaphosphate. Among these, aluminum dihydrogen tripolyphosphate is easily available and preferred. Examples of the aluminum dihydrogen tripolyphosphate which can be used include commercially available products such as "K-WHITE" produced by Tayca Corporation.

In the coating layer of the precoated metal sheet of the present invention, an antirust pigment capable of exerting a rust preventive effect is preferably added in addition to the aluminum phosphate-base pigment, because the corrosion resistance is improved. As the amount of the antirust pigment added becomes larger, the effect exerted is advantageously higher, however, the total content of the aluminum phosphate-base pigment and the antirust pigment is suitably 140 parts by mass or less per 100 parts by mass of resin solid contents. If the

total amount of the aluminum phosphate-base pigment and antirust pigment added exceeds 140 parts by mass, troubles are generated and, for example, the workability greatly deteriorates when the precoated metal sheet is bent, and this is not preferred.

The antirust pigment added to the resin coating layer of the precoated metal sheet of the present invention may be a generally known antirust pigment. Examples thereof include (1) phosphoric acid-base antirust pigments such as zinc phosphate and iron phosphate, (2) molybdic acid-base antirust pigments such as calcium molybdate, aluminum molybdate and barium molybdate, (3) vanadium-base antirust pigments such as vanadium oxide, (4) chromate-base antirust pigments such as strontium chromate, zinc chromate, calcium chromate, potassium chromate and barium chromate, and (5) fine particle silicas such as water-dispersible silica, fumed silica and calcium ion-exchanging silica. However, the chromate antirust pigments of (4) are preferably not used because these have a problem in view of environment. Among the silica-based pigments of (5), calcium ion-exchanging silica is preferred, because this silica is harmless, in view of the environment, and has a great rust preventive effect and when this is added as the antirust pigment, a higher rust preventive effect is exerted. Examples of the calcium ion-exchanging silica which can be used include "Shieldex" produced by Grace. These antirust pigments may be added as a combination of a plurality of the pigments.

In the coating layer of the precoated metal sheet of the present invention, a known pigment generally called a extender pigment, or a coloring pigment for the purpose of coloring, may be used and added in combination with those aluminum phosphate-base pigment and antirust pigment. The extender pigment is a generic term for pigments added so as to improve various performances which the coating is required to have, such as

brittleness of the coating or masking property after the coating. Examples thereof include talc capable of playing a role of filling or matting the coating, titanium white (titanium oxide) for improving the masking property of the coating, and silica for matting the coating or improving the scratch property of the coating. When this extender pigment is added, various performances described above are advantageously improved. Examples of the coloring pigment which can be used include generally known coloring pigments including inorganic pigments such as titanium oxide (TiO_2), zinc oxide (ZnO), zirconium oxide (ZrO_2), calcium carbonate (CaCO_3), barium sulfate (BaSO_4), alumina (Al_2O_3), kaolin clay, carbon black and iron oxide (Fe_2O_3 , Fe_3O_4), and organic pigments. A plurality of the extender pigments and coloring pigments having different effects are preferably used in combination, because respective effects can be exerted. In the case of adding the extender pigment and coloring pigment, the amount added of all pigments as a total of aluminum phosphate-base pigment, antirust pigment, extender pigment and coloring pigment is suitably 140 parts by mass or less per 100 parts by mass of resin solid contents in the coating composition. If the amount added of all pigments exceeds 140 parts by mass, troubles may be caused, for example, the working property greatly deteriorates when the precoated metal sheet is bent.

In the precoated metal sheet of the present invention, the layer thickness of the coating containing the aluminum phosphate-base pigment is not particularly specified, however, various performances of the coating vary according to the layer thickness and therefore, the layer thickness must be appropriately selected depending on the case.

In the precoated metal sheet of the present invention, the resin coating layer containing the aluminum phosphate-base pigment is preferably formed by previously preparing a coating composition containing the

pigment in an amount prescribed in the present invention based on resin solid contents, and coating, drying and curing the coated composition, whereby the production efficiency is more enhanced. The coating composition may
5 be used in any form of a solvent-type coating composition, an aqueous coating composition, a melting-type coating composition, a powder coating composition, an electrodeposition coating composition, an ultraviolet-curable coating composition and an electron beam-curable
10 coating composition. The coating composition can be coated by a generally known coating method, for example, roll coating, curtain flow coating, roller curtain coating, die coating, air spraying, airless spraying, electrodeposition coating, powder coating, dipping, bar
15 coating or brush coating. The coating composition is preferably coated by a general continuous coating line called a coil coating line or sheet coating line, furnished with roll coating, curtain flow coating or roller curtain coating, since the coating work can be
20 then performed with good efficiency and mass production can be attained. The coating composition can be dried, baked and cured by a generally known dry curing method such as hot air oven, direct fire-type oven, far infrared oven or induction heating-type oven. When the coating
25 composition is an ultraviolet-curable coating composition, a generally known ultraviolet irradiation device may be used, and in the case of an electron beam-curable coating composition, a generally known electron beam irradiation device may be used.

30 In the precoated metal sheet of the present invention, a topcoat layer may be further provided on the resin coating layer containing the aluminum phosphate-base pigment. By providing the topcoat layer, the coating appearance, color appearance, design appearance
35 and other coating performances of the precoated metal sheet are advantageously more enhanced. The topcoat layer can be formed by coating a generally known top

coating composition and drying, baking and curing the coating composition. Examples of the generally known top coating composition include a polyester-base top coating composition, an epoxy-base top coating composition, a urethane-base top coating composition, an acryl-base top coating composition and a melamine-base top coating composition. The top coating composition may be used in any form of a solvent-type coating composition, an aqueous coating composition, a powder coating composition, an electrodeposition coating composition, an ultraviolet-curable coating composition and an electron beam-curable coating composition. The top coating composition may contain a generally known coloring pigment or extender pigment such as titanium oxide (TiO_2), zinc oxide (ZnO), zirconium oxide (ZrO_2), calcium carbonate (CaCO_3), barium sulfate (BaSO_4), alumina (Al_2O_3), kaolin clay, carbon black, iron oxide (Fe_2O_3 , Fe_3O_4), talc and silica. For the top coating composition, a generally known design coating composition such as orange peel tone coating composition, crepe tone coating composition, hammer tone coating composition, matted tone coating composition, metallic tone coating composition, pearl tone coating composition or texture coating composition may also be used. The top coating composition may be coated by a generally known coating method such as roll coating, curtain flow coating, roller curtain coating, die coating, air spraying, airless spraying, electrodeposition coating, powder coating, dipping, bar coating or brush coating. The top coating material is preferably coated by a general continuous coating line called as coil coating line or sheet coating line, furnished with roll coating, curtain flow coating and roller curtain coating, because the coating work can be then performed with good efficiency and mass production can be attained. The top coating composition can be dried, baked and cured by a generally known dry and baking methods such as hot air oven, direct fire-type

oven, far infrared oven or induction heating-type oven. When the top coating composition is an ultraviolet-curable coating composition, a generally known ultraviolet irradiation device may be used, and in the case of an electron beam-curable coating composition, a generally known electron beam irradiation device may be used.

Examples

The materials used in experiments are described in detail below.

1. Metal Sheet

The following metal sheets were used as the material tested in experiments.

Molten Zinc Plated Steel Sheet (GI)

Thickness of sheet: 0.6 mm, amount of zinc applied: 60 g/m² per one surface (both surfaces were plated).

Electrical Zinc Plated Steel Sheet (EG)

Thickness of sheet: 0.6 mm, amount of zinc applied: 20 g/m² per one surface (both surfaces were plated).

55% Alloyed Aluminum Zinc Plated Steel Sheet (GL)

Thickness of sheet: 0.6 mm, amount applied in terms of zinc: 90 g/m² per one surface (both surfaces were plated).

Zn-11% Aluminum-3% Magnesium-0.2% Silicon Plated Steel Sheet (SD)

Thickness of sheet: 0.6 mm, amount applied in terms of zinc: 60 g/m² per one surface (both surfaces were plated).

Cold Rolled Steel Sheet (CR)

Thickness of sheet: 0.6 mm.

2. Chemical Conversion Solution

The following solutions were prepared as the chemical conversion solution used for the material tested in experiments.

Chemical Conversion Solution (A):

An aqueous solution containing 20 g/liter of tannic acid, 40 g/liter of a silane coupling agent and 20

g/liter of fine particles of silica was prepared and used as a pre-treatment agent for metal. The tannic acid used was "Tannic Acid AL" produced by Fuji Kagaku Kogyo, the silane coupling agent was γ -

5 glycidoxypropyltrimethoxysilane and the fine particle silica was "Snowtec-N" produced by Nissan Chemicals Industries, Ltd.

Chemical Conversion Solution (B):

10 An aqueous solution containing 20 g/liter of tannic acid, 40 g/liter of a silane coupling agent, 20 g/liter of fine particles of silica and 20 g/liter of a polyester resin was prepared and used as a pre-treatment agent for metal. The tannic acid used was "Tannic Acid AL" produced by Fuji Kagaku Kogyo, the silane coupling agent
15 was γ -glycidoxypropyltrimethoxysilane, the fine particles of silica were "Snowtec-N" produced by Nissan Chemicals Industries, Ltd., and the polyester resin was "FINETEX ES-650" produced by Dai-Nippon Ink & Chemicals, Inc.

Chemical Conversion Solution (C):

20 For comparison, a commercially available chromate treatment solution, "ZM-1300AN" produced by Nihon Parkerizing Co., Ltd., was used.

Chemical Conversion Solution (D):

25 For comparison, a commercially available zinc phosphate treatment solution, "PALBOND" produced by Nihon Parkerizing Co., Ltd., was used.

3. Coating Composition Containing Aluminum Phosphate

30 An aluminum phosphate-base pigment and if desired, an antirust pigment were added to each of commercially available polyester-base, urethane-base and epoxy-base clear coating compositions, all completely free of a pigment, and they were stirred to prepare coating compositions. The aluminum phosphate-base pigment used was "K-G105" produced by Tayca Corporation. The antirust
35 pigment used was "NP-530" produced by Toho Ganryo as a zinc phosphate-base antirust pigment (shown as "Zn

phosphate" in Table), "Shieldex-C303" produced by Grace as a calcium ion-exchanging silica (shown as "Ca-Si" in Table) or a commercially available strontium chromate as a chromium-base antirust pigment (shown as "Sr-Cr" in Table). The amount added of each of these pigments is shown in Table 1. Additionally, if desired, an extender pigment was used and the extender pigment used was "Aerosil 300" produced by Nippon Aerosil as a commercially available fine particle silica (shown as "silica" in Table) or a titanium oxide "CR-95" produced by Ishihara Sangyo Kaisha Ltd. as a white pigment (shown as "titanium white" in Table). The amount of each of these pigments is shown in Table.

4. Top Coating Composition

A commercially available polyester-base top coating composition "FL100HQ" produced by Nippon Paint Co., Ltd. was used. The color was white.

5. Back Coating Composition

A commercially available polyester-base top coating composition "FL100HQ" produced by Nippon Paint Co., Ltd. was used. The color was gray.

6. Preparation of Precoated Metal Sheet

Each metal sheet was degreased by dipping it in an aqueous solution of FC-364S (produced by Nihon Parkerizing Co., Ltd.) at a concentration of 2 mass% and a temperature of 60°C for 10 seconds, then washed with water and dried. Chemical Conversion Solution (A), (B), (C) or (D) was coated on both surfaces of each metal sheet by a roll coater and dried in a hot air drying furnace to obtain a chemical conversion coating layer. As for the amount of the chemical conversion solution applied, the amount of the entire dried film applied became 200 mg/m² in the cases of Chemical Conversion Solution (A), (B) or (D). Chemical Conversion Solution (C) was coated to give an applied amount of 50 mg/m² in terms of metallic chromium. In the specimen using Chemical Conversion Solution (E), the chemical conversion

coating layer was obtained by dipping the degreased metal sheet in Chemical Conversion Solution (E) for 2 minutes and drying it in a hot air drying furnace. Chemical Conversion Solution (E) was coated such that the amount of zinc phosphate applied became 2 g/m^2 . The ultimate sheet temperature at the chemical conversion and drying was set to 60°C . Thereafter, a resin coating solution containing an aluminum phosphate-base pigment was coated on one surface of the metal sheet by a roll coater to have a dry thickness of $5 \text{ }\mu\text{m}$ and a back resin coating composition was coated on another surface of the metal sheet by a roll coater to have a dry thickness of $5 \text{ }\mu\text{m}$. These resin coating compositions were dried and cured in an induction heating furnace while blowing hot air thereinto under the conditions such that the ultimate sheet temperature of the metal sheet was 210°C , thereby obtaining a coating layer. The coated metal sheet after drying and baking was cooled with water by spraying water thereon. Subsequently, a top coating composition was coated on the resin coating layer containing an aluminum phosphate-base pigment by a roll coater to have a dry thickness of $15 \text{ }\mu\text{m}$ and then, dried and baked in an induction heating furnace while blowing hot air thereinto under the conditions such that the ultimate sheet temperature of the metal sheet was 230°C . The metal sheet after drying and baking was cooled with water by spraying water thereon. In this manner, a precoated metal sheet was obtained as a material for use in tests.

The thus-obtained precoated metal sheets were subjected to the following evaluation tests. In any of these tests, the surface of the resin coating layer formed by a resin coating composition containing an aluminum phosphate-base pigment was used as the surface for evaluation.

1. Test of Working Part Adhesive Property of Coating

Each precoated metal sheet was worked to bend at

180° and the coating in the worked part was observed through a magnifier at 20 magnification to examine the presence or absence of cracks of the coating. At the bending test, the bending was performed such that the surface coated with a resin coating composition containing an aluminum phosphate-base pigment came outside. Furthermore, a pressure-sensitive adhesive tape was fixed to the worked part and powerfully peeled off and the residual state of the coating was observed with an eye. In this test, the tape-peeling was performed twice. The bending was performed by OT working (ECCA-T7) in an atmosphere of 20°C.

In the evaluation of cracks of the coating, the case where the coating was completely free of cracks was rated ◎, the case where the coating had about 1 to 3 very small cracks was rated ○, the case where very small cracks were present throughout the coating was rated △, and the case where large cracks clearly observable even with an eye were present throughout the worked part of the coating was rated X.

In the evaluation of the residual state of coating after tape-peeling, the case where the coating was not peeled off and remained on the steel sheet was rated ◎, the case where a part of the coating was slightly peeled off was rated ○, the case where a part of the coating was seriously peeled off was rated △, and the case where peeling off of the coating was observed almost throughout the worked part was rated X.

Each precoated metal sheet after the OT working was dipped in boiling water for 1 hour, then taken out, left standing for 24 hours and subjected to tape-peeling. In the evaluation of residual state of the coating, the case where the coating was not peeled off at all and remained on the plated steel sheet was rated ◎, the case where a part of the coating was slightly peeled off was rated ○, the case where a part of the coating was seriously peeled

off was rated Δ , and the case where peeling off of the coating was observed almost throughout the worked part was rated X.

2. Test of Coating Scratching by Bead

5 A "Test Method of Coating Scratching by Bead" (see, Technical Disclosure Publication (Kokai-Giho) No. 95-1078) was performed, which is a test method of reproducing the peeling of a coating of a precoated metal sheet generated due to scratching of the coating by a
10 mold during press-forming the precoated metal sheet. First, the precoated metal sheet prepared was cut into a specimen of 30 mm (width) $\times$ 300 mm (length). This specimen was sandwiched by a flat metal mold and a metal mold having provided thereon beads having a radius of 3
15 mmR. At this time, the specimen was sandwiched such that the beads of the metal mold was pressed against the surface of the resin coating layer containing an aluminum phosphate-base pigment (surface for evaluation) of the specimen, and a load of 1 ton was applied so as to press
20 the bead part of the mold to the evaluation surface of the precoated metal sheet. In this state, the precoated metal sheet was drawn out at a rate of 200 mm/min and the peeled state of the coating on the evaluation surface of the precoated metal sheet rubbed by the beads was
25 observed with an eye and evaluated.

 In the evaluation, the case where the coating was not peeled off at all was rated $\odot$, the case where the coating was very partially peeled off was rated $\bigcirc$, the case where the coating corresponding to about 20% or more
30 as an area ratio to the portion rubbed by the beads was peeled off was rated Δ , and the case where the coating was entirely peeled off was rated X.

3. Test of Corrosion Resistance

35 On the surface coated with a coating composition containing an aluminum phosphate-base pigment of the precoated metal sheet prepared, cuts were made by a

cutter passing through the coating and reaching the metal sheet. Furthermore, the edge part of the sheet was cut to allow the burr formed by the cutting to come to the surface coated with the back resin coating layer (lower burr). Thus, a sample for corrosion resistance test was prepared. The sample was then subjected to a salt spray test in accordance with the method described in JIS K 5400-9.1. The salt water was sprayed on the surface coated with a resin coating composition containing an aluminum phosphate-base pigment of the sheet. The test time was 120 hours when the blank of the precoated metal sheet was a cold rolled steel sheet, 240 hours when the blank was an electrical zinc plated steel sheet, and 360 hours when the blank was a fused zinc plated steel sheet, a 55% alloyed aluminum zinc plated steel sheet or a Zn-11% aluminum-3% magnesium-0.2% silicon plated steel sheet.

In the evaluation of the coating at the cut part, the case where the maximum blister width at one side of the cut was less than 1 mm was rated ◎, the case where it was from 2 to less than 3 mm was rated ○, the case where it was from 3 to less than 5 mm was rated △, and the case where it was 5 mm or more was rated ×.

In the evaluation of the cut end face part, the case where the blister width from the end face was 2 mm or less was rated ◎, the case where from 2 to less than 3 mm was rated ○, the case where from 3 to less than 5 mm was rated △, and the case where 5 mm or more was rated ×.

Table

	No.	Metal Sheet	Pretreat- ment for Metal	Coating Composition Containing Aluminum Phosphate-Base Pigment						
				Kind of Resin	Amount Added of Aluminum Phosphate- Base Pigment (parts by mass per 100 parts by mass of resin solid contents)	Antirust Pigment		Extender Pigment		Total Amount Added of All Pigments (parts by mass per 100 parts by mass of resin)
						Kind	Amount Added (parts by mass per 100 parts by mass of resin)	Kind	Amount Added (parts by mass per 100 parts by mass of resin)	
Example of Invention	1	GI	A	polyester	20	Ca-Si	50	not added	-	80
	2	GI	B	polyester	1	not added	-	not added	-	1
	3	GI	B	polyester	10	not added	-	not added	-	10
	4	GI	B	polyester	20	not added	-	not added	-	20
	5	GI	B	polyester	50	not added	-	not added	-	50
	6	GI	B	polyester	100	not added	-	not added	-	100
	7	GI	B	polyester	140	not added	-	not added	-	140
	8	GI	B	polyester	20	Ca-Si	10	not added	-	30
	9	GI	B	polyester	20	Ca-Si	20	not added	-	40
	10	GI	B	polyester	20	Ca-Si	50	not added	-	70
	11	GI	B	polyester	20	Ca-Si	100	not added	-	120
	12	GI	B	polyester	20	Ca-Si	50	silica	10	80
	13	GI	B	polyester	20	Ca-Si	100	silica	40	160
	14	GI	B	polyester	20	Ca-Si	50	titanium white	10	80
Comparative Example	15	GI	B	polyester	20	Zn phosphate	50	not added	-	70
	16	GI	B	polyester	20	Sr-Cr	50	not added	-	70
	17	GI	B	urethane	20	Ca-Si	50	not added	-	70
	18	GI	B	epoxy	20	Ca-Si	50	not added	-	70
	19	EG	B	polyester	20	Ca-Si	50	not added	-	70
	20	GL	B	polyester	20	Ca-Si	50	not added	-	70
	21	SD	B	polyester	20	Ca-Si	50	not added	-	70
	22	CR	B	polyester	20	Ca-Si	50	not added	-	70
	23	GI	B	polyester	not added	not added	-	not added	-	0
	24	GI	B	polyester	0.5	not added	-	not added	-	0.5
	25	GI	B	polyester	150	not added	-	not added	-	150
	26	GI	C	polyester	20	Ca-Si	50	not added	-	70
	27	GI	C	polyester	20	Sr-Cr	50	not added	-	70
	28	GI	D	polyester	20	Ca-Si	50	not added	-	70
	29	GI	E	polyester	20	Ca-Si	50	not added	-	70

Table (continued)

	No.	Evaluation Test Results						Remarks
		Test of Working Adhesive Property of Coating		Scratching of Coating by Head	Corrosion Resistance Test			
		Evaluation of Cracks	Evaluation of Peeling		Cut Part	End Face Part		
Example of Invention	1	⊙	⊙	○	△	X	-	
	2	⊙	⊙	△	X	X	-	
	3	⊙	⊙	○	△	X	-	
	4	⊙	⊙	⊙	△	X	-	
	5	⊙	⊙	⊙	△	X	-	
	6	⊙	⊙	⊙	△	X	-	
	7	○	⊙	⊙	△	X	-	
	8	⊙	⊙	⊙	○	△	-	
	9	⊙	⊙	⊙	⊙	○	-	
	10	⊙	⊙	⊙	⊙	⊙	-	
	11	⊙	⊙	⊙	⊙	⊙	-	
	12	⊙	⊙	⊙	⊙	⊙	Scratch property was improved.	
Comparative Example	13	△	⊙	⊙	⊙	⊙	Scratch property was improved.	
	14	⊙	⊙	⊙	⊙	⊙	Whiteness was improved.	
	15	⊙	⊙	⊙	○	△	-	
	16	⊙	⊙	⊙	⊙	⊙	-	
	17	⊙	⊙	⊙	⊙	⊙	-	
	18	⊙	⊙	⊙	⊙	⊙	-	
	19	⊙	⊙	⊙	⊙	⊙	-	
	20	⊙	⊙	⊙	⊙	⊙	-	
	21	⊙	⊙	⊙	⊙	⊙	-	
	22	⊙	⊙	⊙	⊙	⊙	-	
	23	⊙	⊙	⊙	X	X	-	
	24	⊙	⊙	⊙	X	X	-	
	25	△	⊙	⊙	△	X	-	
	26	⊙	⊙	⊙	⊙	⊙	-	
	27	⊙	⊙	⊙	⊙	⊙	-	
	28	⊙	⊙	⊙	⊙	⊙	-	
	29	○	○	○	△	△	-	

The evaluation results are described in detail below.

The evaluation test results of precoated metal sheets prepared are shown in the Table. In the precoated metal sheets of the present invention (Examples Nos. 1 to 22), the coating is less peeled off at the test of scratching of coating by beads in comparison with the metal sheet using a conventional chromate-free chemical conversion treatment such as zinc phosphate treatment (Comparative Example No. 28), revealing that the precoated metal sheets of the present invention are excellent. Also, in comparison with those where in the resin coating layer on the chemical conversion coating layer, an aluminum phosphate-base pigment is not added (Comparative Example No. 23) or an aluminum phosphate-base pigment is added in an amount of less than 1 part by mass per 100 parts by mass of resin solid contents (Comparative Example No. 24), the coating is less peeled off at the test of scratching of coating by a bead, revealing that the precoated metal sheets of the present invention are excellent. In the precoated metal sheets of the present invention, when the chemical conversion coating layer contains a polyester resin, the working part adhesive property of the coating is improved and the coating is hard to peel off at the test of coating scratching by beads (compare between Example No. 1 and Example No. 10 of the invention), therefore, it is more preferred that the chemical conversion coating layer contains a polyester resin. When an antirust pigment is added to the coating material in addition to the aluminum phosphate-base pigment (Example Nos. 8 to 22 of the invention), the corrosion resistance is improved as compared with those where an antirust pigment is not added (Example Nos. 2 to 7 of the invention), therefore, it is preferred to additionally add an antirust pigment to the coating composition. In particular, when the antirust pigment is a calcium ion-exchanging silica

(Example Nos. 1, 8 to 14 and 17 to 22 of the invention), the corrosion resistance is more improved and, moreover, the corrosion resistance is equal to that when a conventional chromate-base antirust pigment is added
5 (comparison between Example No. 16 of the invention with Comparative Example No. 26), therefore, it is preferred that the antirust pigment is a calcium ion-exchanging silica.

Industrial Applicability

10 According to the present invention, a precoated metal sheet excellent in the working part adhesive property of the coating and the corrosion resistance and very suitable for press-forming can be provided without
15 using hexavalent chromium of which the effect on the environment is feared. Accordingly, the present invention has a very high industrial value.

CLAIMS

1. (Amended) A precoated metal sheet having excellent press formability, comprising a metal sheet having on one surface or both surfaces thereof a chemical conversion coating layer simultaneously containing, as
5 solid contents, a silane coupling agent, fine particles of silica and at least either one of tannin and a tannic acid, and further having thereon a resin coating layer containing from 1 to 140 parts by mass of aluminum
10 dihydrogen tripolyphosphate per 100 parts by mass of resin solid contents.

2. The precoated metal sheet having excellent press formability as claimed in claim 1, wherein said chemical conversion coating layer further contains a
15 polyester resin as a solid content.

3. (Deleted)

4. (Amended) The precoated metal sheet having excellent press formability as claimed in claim 1 or 2, wherein said resin coating layer further contains an
20 antirust pigment and the total content of said antirust pigment and aluminum dihydrogen tripolyphosphate is 140 parts by mass or less per 100 parts by mass of resin solid contents.

5. The precoated metal sheet having excellent
25 press formability as claimed in claim 4, wherein the antirust pigment contained in said resin coating layer is a calcium ion-exchanging silica.

6. (Amended) The precoated metal sheet having excellent press formability as claimed in claim 1, 2 or
30 4, wherein the metal sheet is a metal sheet having a plated layer on one surface or both surfaces thereof.

7. (Amended) A method for producing a precoated metal sheet having excellent press formability, comprising coating a treating solution simultaneously
35 containing a silane coupling agent, fine particles of silica and at least either one of tannin and a tannic acid on one surface or both surfaces of a metal sheet,

drying the treating solution to form a chemical conversion coating layer, further coating a resin coating composition containing from 1 to 140 parts by mass of aluminum dihydrogen tripolyphosphate per 100 parts by mass of resin solid contents on the chemical conversion coating layer, and drying and curing the coating material.

8. The method for producing a precoated metal sheet having excellent press formability as claimed in claim 7, wherein said treating solution further contains a polyester resin.

9. (Amended) The method for producing a precoated metal sheet having excellent press formability as claimed in claim 7 or 8, wherein said coating composition further contains an antirust pigment and the total content of said antirust pigment and aluminum dihydrogen tripolyphosphate is 140 parts by mass or less per 100 parts by mass of resin solid contents.

10. (Amended) A press-formed precoated metal sheet article comprising a press-formed precoated metal sheet, said precoated metal sheet being as set forth in any one of claims 1, 2 and 4 to 6.