

DESCRIPTION

TITLE

5 PRECOATED STEEL SHEET EXCELLENT IN SCRATCH RESISTANCE AND MOISTURE
ABSORPTION RESISTANCE OF COATING AND EXCELLENT IN
END FACE RED RUST CORROSION RESISTANCE

FIELD

10

[0001]

The present invention relates to precoated steel sheet excellent in end face red rust corrosion resistance and excellent in scratch resistance and moisture absorption resistance of the coating. More particularly speaking, the present invention relates to a chromate-free type precoated steel sheet used in environments where it is wet by water, in particular in outdoor environments where it is exposed to rainwater etc., in the fields of for example electrical products, buildings, etc., more particularly a chromate-free type precoated steel sheet excellent in moisture absorption resistance of the coating and also excellent in scratch resistance.

20

BACKGROUND

[0002]

If a precoated steel sheet set outdoors is exposed to a high temperature and rain-prone environment such as during a rainy season, it is known that there is a problem of red rust forming on the cut uncoated end face in a short period of time. To solve this problem, a precoated steel sheet provided with end face red rust corrosion resistance has been proposed.

[0003]

As one example, PTL 1 describes an end face red rust inhibiting type precoated steel sheet comprised of a plated steel sheet having on at least one surface a coating in which an antirust pigment exhibiting a red rust inhibiting effect is added. This is so that when an end face of the precoated steel sheet is immersed in water, the antirust pigment is eluted from the coating and the constituents of the same protect the end face to thereby inhibit the formation of red rust. As an example greatly effective as an antirust pigment and in commercial use, sodium tungstate may be mentioned. In addition, various antirust pigments exhibiting red rust inhibiting effects have been discovered. Various precoated steel sheets introducing these into the coatings have been proposed. PTL 2, which describes a chrome-free coated steel sheet excellent in end face red

rust corrosion resistance in the same manner, describes that a phosphate and chloride of an alkali metal and a hypophosphite of an alkali earth metal can be used as an antirust pigment exhibiting a red rust inhibiting effect.

[0004]

5 The precoated steel sheets described in PTLs 1 and 2 are predicated on the antirust pigment being eluted from the coating due to wetting by water, so these antirust pigments are the same on the point of being substances high in water solubility and having deliquescence at a high humidity. The problem has surfaced that a coating containing such a deliquescent antirust pigment easily absorbs moisture in a high moisture environment and becomes a state where the surface of the coating becomes wet. For example, if using a precoated steel sheet as a housing of equipment, if the surface of the coating becomes wet, when attaching warning stickers or foam members etc. for improving air-tightness to the coated surface by a tackifier, the problem arises of the tackifier not being able to be used.

[0005]

15 PTL 3 describes a precoated steel sheet comprised of a plated steel sheet on one surface of which a film-forming layer able to easily pass water (below, referred to as a “water permeable film”) is coated. This allows water to easily permeate through the film and reach the steel sheet surface of the base sheet to thereby proactively cause the formation of a galvanic couple current between the base iron and plating at the cut end face of the steel sheet and use the sacrificial corrosion prevention effect of zinc to try to suppress the formation of red rust from the end face. As the permeable film, a film designed including a predetermined amount of pigment in a relatively thin film and making at least part of that a pigment with a relatively large particle size so that moisture from the outside easily passes through the coating to reach the galvanized layer has been proposed.

[0006]

25 In the precoated steel sheet described in PTL 3, there is no problem of the film easily absorbing moisture like with the films of PTLs 1 and 2, but the effect of inhibiting red rust of the cut end face is not sufficient with just the sacrificial corrosion preventing effect of zinc, and formation of white rust from the surface of the steel sheet due to dissolution of zinc cannot be avoided.

[0007]

35 As a precoated steel sheet solving the problems in the arts of PTLs 1 to 3, the present inventors developed the precoated steel sheet described in PTL 4. This is a precoated steel sheet where the surface of the coating containing the antirust pigment effective for preventing red rust at the end face is covered with a topmost layer coating (water permeable/water vapor impermeable coating) passing liquid water for obtaining the effect of the antirust pigment, but

not passing gaseous water (water vapor) causing absorption of moisture by the deliquescence of the antirust pigment in the coating.

[0008]

A precoated steel sheet shipped out in a state with a coating formed in advance and shaped at the user side without requiring a coating step generally is required to have a good workability (bendability, press workability, etc.). As art meeting such a demand, it has been known to add wax to the coating. For example, PTL 4 describes including wax or another constituent in a water permeable/water vapor impermeable coating provided on a coating containing an antirust pigment.

Further, PTL 5 proposes adding wax to a hydrophilic treated coating and controlling the projected area ratio of the wax on the coating surface so as to achieve the excellent formability by the wax and achieve improvement of the excellent resistance to raindrop stains by the partially hydrolyzed condensate of tetraalkoxysilane. In the coated steel sheet described in PTL 5, the end face corrosion resistance of the steel sheet is not considered.

[CITATION LIST]

[PATENT LITERATURE]

[0009]

[PTL 1] WO2011/071175

[PTL 2] Japanese Unexamined Patent Publication No. 2009-045923

[PTL 3] Japanese Unexamined Patent Publication No. 2010-083075

[PTL 4] Japanese Unexamined Patent Publication No. 2016-193593

[PTL 5] Japanese Unexamined Patent Publication No. 2013-018263

SUMMARY

[TECHNICAL PROBLEM]

[0010]

In trying to commercialize the precoated steel sheet developed and described in PTL 4, the present inventors tried to improve the workability by introducing a general low melting point type of wax in the water permeable/water vapor impermeable coating on the coating containing the antirust pigment. However, they discovered that if increasing the content of such a low melting point type of wax so as to approach the usual amount so that this effect is obtained, the end face red rust corrosion resistance of the precoated steel sheet is lost. That is, they discovered that the wax introduced into the water permeable/water vapor impermeable coating of the precoated steel sheet of PTL 4 has to be limited in amount.

[0011]

On the other hand, if limiting the amount of wax included in the water permeable/water vapor impermeable coating of the precoated steel sheet of PTL 4, a sufficient scratch resistance is not obtained. Specifically, for example, if the coating on the design side of the precoated steel sheet (side at which the coating does not contain antirust pigment for exhibiting end face red rust corrosion resistance) is thin, in precoated steel sheet stacked or coiled up for shipment to the user, due to sliding at the time of transport, the design side coating is peeled off from the substrate steel sheet or galling of the coating occurs at the time of shaping work at the user or other phenomena are observed.

[0012]

In this way, it is clearly seen that the precoated steel sheet of PTL 4 has the problem that to prevent the surface of the coating containing the antirust pigment for obtaining end face red rust corrosion resistance from becoming wet, it must be not only excellent in moisture absorption resistance, but must also be excellent in scratch resistance of the coating, in particular scratch resistance of the front and back coatings against sliding at the time of transport and resistance to galling of the coating at the time of shaping work.

[0013]

The present invention aims to solve this problem.

[SOLUTION TO PROBLEM]

[0014]

The inventors thought as follows regarding the reason why the effect of end face red rust corrosion resistance by the antirust pigment is impaired due to the addition of wax to the water permeable/water vapor impermeable topmost layer coating (below, sometimes simply referred to as the “topmost layer coating”) on the coating (below, referred to as the “lower layer coating”) containing an antirust pigment for obtaining end face red rust corrosion resistance (below, sometimes simply referred to as the “antirust pigment”).

[0015]

If the topmost layer coating is made to include low melting point general wax, the wax will melt at the time of the heating and drying for forming the topmost layer coating. Wax is hydrophobic and low in surface tension, so melted wax will end up broadly wetting the coating surface or invading the water permeation routes in the coating and clogging the same. For this reason, when the precoated steel sheet is wet with water, the water will not be able to pass through the topmost layer coating and the elution of the antirust pigment at the lower layer coating will be hindered, so expression of the end face red rust corrosion resistance will be obstructed.

[0016]

Continuing their studies based on this consideration, the inventors found that by using not wax of a type melting due to heating, but wax which takes a form scattered in an island manner protruding from the coating in particle form after forming the coating, it is possible to secure end face red rust corrosion resistance and simultaneously secure scratch resistance, so it is possible to improve the slidability. In addition to this, they discovered that the wax used is preferably one of a particle form with an average particle size of 1 to 8 μm with part present in a form protruding from the surface of the coating by a content of 1 to 10 mass% with respect to the mass of the dried coating. The present invention was completed based on these discoveries.

[0017]

The thus perfected precoated steel sheet of the present invention corresponds to the precoated steel sheet of PTL 4 in which the above-mentioned granular wax is added in a coating thinner than the water permeable/water vapor impermeable coating of that literature. The specific gist is as follows:

[0018]

[1] A chromate-free type precoated steel sheet comprising a galvanized steel sheet having a chromate-free type chemical conversion treatment layer on both surfaces, and pluralities of coatings formed thereon comprising a topmost layer coating and a lower layer coating adjacent thereto,

the topmost layer coating of one surface satisfies the conditions of the following conditions (1) to (5):

- (1) a contact angle of a surface of the topmost layer coating with water is 65 to 75°,
- (2) a film thickness of the topmost layer coating is 0.5 to 5 μm ,
- (3) the topmost layer coating comprises a first pigment, and a content of the pigment being 15 to 70 mass% with respect to the mass of the dried coating,
- (4) in the first pigment, a total of the pigment with an average primary particle size of 1 μm or more is 5 mass% or more with respect to the mass of the dried coating, and
- (5) the topmost layer coating contains granular wax of an average particle size of 1 to 8 μm in a content with respect to the mass of the dried coating of 1 to 10 mass%, at least part of the granular wax particles present in a state partially protruding from the coating surface, and the lower layer coating adjacent to the topmost layer coating comprises a second pigment that is one or more types of a second pigment of a deliquescent antirust pigment effective for preventing formation of red rust on the end face.

[2] The chromate-free type precoated steel sheet according to the above [1], wherein the wax is selected from a group consisting of PTFE wax, polyethylene/PTFE codispersed wax, and polymeric polyethylene wax.

[3] The chromate-free type precoated steel sheet according to the above [1] or [2], wherein the second pigment is selected from a group consisting of tungstates and silicates, phosphates and chlorides of alkali metals, and hypophosphites of alkali earth metals.

[4] The chromate-free type precoated steel sheet according to the above [3], wherein the tungstate is sodium tungstate, calcium tungstate, ammonium tungstate, lithium tungstate, magnesium tungstate, or a mixture thereof.

[5] The chromate-free type precoated steel sheet according to the above [3], wherein the silicate is sodium silicate, potassium silicate, lithium silicate, or a mixture thereof.

[6] The chromate-free type precoated steel sheet according to the above [3], wherein the alkali metal phosphate is sodium dihydrogen phosphate, potassium dihydrogen phosphate, dipotassium hydrogen phosphate, sodium tripolyphosphate, sodium dihydrogen phosphate monohydrate, sodium dihydrogen phosphate dihydrate, or a mixture thereof.

[7] The chromate-free type precoated steel sheet according to the above [3], wherein the alkali metal chloride is sodium chloride.

[8] The chromate-free steel sheet according to the above [3], wherein the hypophosphite is calcium hypophosphite.

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0019]

According to the present invention, it becomes possible to utilize a chromate-free type precoated steel sheet free of formation of white rust from the steel sheet surface and able to exhibit the effect of inhibiting red rust at the end face while avoiding wetting of the coating in a high humidity environment and also provided with galling resistance of the coating at the time of shaping work and scratch resistance of the front and back coatings against the sliding action at the time of transport and other sufficient scratch resistance.

BRIEF DESCRIPTION OF DRAWINGS

[0020]

FIGS. 1A to 1C are views showing evaluation of wetting due to moisture absorption at a back surface coating in an example.

DESCRIPTION OF EMBODIMENTS

[0021]

The precoated steel sheet of the present invention aiming at improvement of the scratch

resistance of the coating is comprised of a galvanized steel sheet on the surface of which is formed a chromate-free chemically converted layer, a coating (below, referred to as the “lower layer coating”) containing an antirust pigment for obtaining end face red rust corrosion resistance (below, also referred to as the “second pigment”) formed on the chromate-free type chemically converted layer, and a water permeable/water vapor impermeable topmost layer coating formed on the lower layer coating to touch the top surface of the lower layer coating.

In the present invention, it is important that the topmost layer coating satisfy the conditions of the following conditions (1) to (5), in particular (5):

- (1) a contact angle of a surface of the topmost layer coating with water is 65 to 75°,
- (2) a film thickness of the topmost layer coating is 0.5 to 5 μm ,
- (3) the topmost layer coating includes a first pigment, a content of the first pigment being 15 to 70 mass% with respect to the mass of the dried coating,
- (4) in the first pigment, a total of the pigment with an average primary particle size of 1 μm or more is 5 mass% or more with respect to the mass of the dried coating, and
- (5) the topmost layer coating contains granular wax of an average particle size of 1 to 8 μm in a content with respect to the mass of the dried coating of 1 to 10 mass%, at least part of the granular wax particles present in a state partially protruding from the coating surface, and the lower layer coating adjacent to the topmost layer coating comprises a second pigment that is one or more types of a deliquescent antirust pigment effective for preventing formation of red rust on the end face.

For this reason, in the precoated steel sheet of the present invention, in accordance with these conditions, in the topmost layer coating, at least part of the wax particles are dispersed at scattered points in island forms in states partially protruding from the coating surface. Due to this, the majority of the topmost layer coating surface does not lose its water permeability. For this reason, when the precoated steel sheet is wet with water, the antirust agent can pass through the topmost layer coating to be eluted and sufficient end face red rust corrosion resistance is secured.

[0022]

On the other hand, when the coating is rubbed by some object, the wax protruding from the coating is partially crushed whereby slidability is obtained. Due to this, it is possible to prevent the problem such as the design side coating being peeled off from the substrate steel sheet due to sliding at the time of transport of stacked or coiled precoated steel sheets or galling of the coating occurring at the time of shaping work at the user.

[0023]

At least part of the granular wax used in the topmost layer coating of the precoated steel

sheet of the present invention partially protrudes from the coating and is scattered at points in an island form in the granular state after formation of the coating. To satisfy this requirement, as the granular wax, use is made of one with a melting point over the temperature of the heating and drying for forming the coating or one with a melt viscosity high enough that even after melting at the time of heating and drying the coating, a granular state of an extent enabling the wax to protrude from the coating and be scattered at points in an island form after film formation is not lost. The heating and drying temperature at the time of formation of the coating is generally 200°C or so, therefore the melting point of the wax is preferably over 200°C, more preferably over 250°C, still more preferably over 300°C. On the other hand, wax having a melt viscosity of an extent where even if melted at the time of heating and drying the coating, the granular form is not lost exhibits a viscosity of 2000 mPa·s or more, preferably 2500 mPa·s or more, more preferably 3000 mPa·s or more, at the temperature of the time of heating and drying the coating.

[0024]

As wax matching these conditions, polytetrafluoroethylene (PTFE) wax, polyethylene/PTFE codispersed wax, polymeric polyethylene wax, etc. may be mentioned. As one example, the SST series wax supplied by Shamrock Technologies (U.S.) etc. may be mentioned.

[0025]

The granular wax used in the present invention is preferably one having an average particle size of 1 to 8 μm. Granular wax with an average particle size of less than 1 μm is difficult to obtain. On top of this, it is difficult to obtain a sufficient protruding height from the coating surface. With an average particle size over 8 μm, the wax greatly protrudes from the surface of the coating after film formation and the wax easily detaches when the coating is rubbed against, so this is not preferable. The more preferable average particle size of the granular wax is 3 to 5 μm.

[0026]

The height of the granular wax protruding from the surface of the topmost layer coating (distance from surface of coating to end part of wax particle most separate from surface of coating) is preferably 0.1 to 3 μm or so. If less than 0.1 μm, it is difficult to obtain the slidability due to crushing of the protruding parts, while if over 3 μm, wax is transferred to the dies when press-forming the steel sheet and the dies have to be frequently cleaned up. The more preferable protruding height is 0.5 to 2 μm.

[0027]

The state of presence of the granular wax at the topmost layer coating and the film thicknesses of the coatings of the different layers can be confirmed by burying a test piece of the precoated steel sheet in a resin, polishing the cross-section, and examining the cross-section of

the coating. Here, the film thickness of the topmost layer coating is made the average value of the film thickness of parts where there is no granular wax present.

[0028]

The content of the granular wax in the topmost layer coating is preferably 1 to 10 mass% with respect to the mass of the dried coating. If less than 1 mass%, the effect of addition of the wax is not sufficiently expressed, while if over 10 mass%, the cohesion of the coating falls and formation of a film becomes difficult. The topmost layer coating in the present invention contains a larger amount of the first pigment than usual so as to acquire water permeability and water vapor impermeability, so the cohesion is inherently small. Addition of a large amount of wax causes a further drop in the cohesion of the coating and is particularly inconvenient. The more preferable content of the granular wax is about 1 to 5 mass% with respect to the mass of the dried coating.

[0029]

If further explaining the precoated steel sheet of the present invention, this is comprised of a at least a galvanized steel sheet on each of the two surfaces of which are formed a chromate-free type chemically converted layer, a lower layer coating formed on top of that, and a topmost layer coating formed adjacent to the lower layer coating. These coatings are not limited in configuration so long as the chromate-free type chemically converted layer, lower layer coating, and topmost layer coating are successively formed in the order from the surface side of the galvanized steel sheet and so long as the topmost layer coating is provided adjacent to the lower layer coating, that is, touching the top surface of the lower layer coating. For this reason, another coating may also be provided between the chromate-free type chemically converted layer and the lower layer coating. Specifically, it is also possible to provide a primer coating on the chromate-free type chemically converted layer and provide one or more top layer coatings etc. or other plurality of coatings on top of that.

[0030]

In the precoated steel sheet of the present invention, the topmost layer coating on one surface satisfies the conditions of the above conditions (1) to (5). The lower layer coating adjacent to the topmost layer coating on the galvanized steel sheet side contains a second pigment comprised of one or more types of deliquescent antirust pigment effective for end face red rust corrosion resistance. In the present invention, the lower layer coating has to contain a deliquescent antirust pigment, but so long as this requirement is met, any other coating positioned below the topmost layer coating may also contain the above-mentioned antirust pigment.

[0031]

As the second pigment comprised of the deliquescent antirust pigment effective for end

face rust corrosion resistance, one or more selected from a group consisting of tungstates and silicates, phosphates and chlorides of alkali metals, and hypophosphites of alkali earth metals may be mentioned.

[0032]

As the tungstates, for example, sodium tungstate, calcium tungstate, ammonium tungstate, lithium tungstate, or magnesium tungstate may be used. Mixtures of these may also be used. The tungstate may be mixed into the coating in about 6 to 50 wt% or so. If less than 6 wt%, the end face red rust corrosion resistance is insufficiently expressed while if becoming greater than 50 wt%, when the coating after film formation is exposed to a wet environment, the tungstate is excessively eluted and the coating may be made to swell or peel. The tungstate content in the coating is more preferably 7 to 40 wt%, most preferably 10 to 30 wt%.

[0033]

As the silicates, for example, sodium silicate, potassium silicate, or lithium silicate may be used. Mixtures of these may also be used. The silicate may be mixed into the coating in about 5 to 50 wt% or so. If less than 5 wt%, the end face red rust corrosion resistance is insufficiently expressed while if becoming greater than 50 wt%, when the coating after film formation is exposed to a wet environment, the silicate is excessively eluted and the coating may be made to swell or peel. The silicate content in the coating is more preferably 7 to 40 wt%, most preferably 10 to 30 wt%.

[0034]

The tungstate or silicate used in the present invention is a powder at ordinary temperature. Considering the thickness of the coating in which it is mixed, the salt is preferably used dispersed in the coating material to give a maximum particle size of 5 to 20 μm , more preferably 5 to 10 μm or so.

[0035]

In the present invention, as another antirust pigment for expressing end face red rust corrosion resistance, a phosphate and chloride of an alkali metal or a hypophosphite of an alkali earth metal can also be used. As the alkali metal phosphate, for example, sodium dihydrogen phosphate, potassium dihydrogen phosphate, dipotassium hydrogen phosphate, sodium tripolyphosphate, sodium dihydrogen phosphate monohydrate, or sodium dihydrogen phosphate dehydrate can be used. Mixtures of these may also be used. As the alkali metal chloride, for example, sodium chloride can be used. As the hypophosphite, for example, calcium hypophosphite can be used. The suitable content of these antirust pigments in the coating is 0.5 to 30 wt%. 1 to 20 wt% is more preferable.

[0036]

The antirust pigment used in the present invention may also be any combination of the

above substances.

[0037]

The component constituents other than the antirust pigment effective for expression of the end face red rust corrosion resistance in the lower layer coating adjacent to the topmost layer film may be ones used in the usual coating layer of a precoated steel sheet.

[0038]

The lower layer coating preferably has a film thickness of 2 to 20 μm . If less than 2 μm , the absolute amount of the added antirust pigment becomes insufficient and a sufficient end face red rust corrosion resistance cannot be obtained. If over 20 μm , the effect of the end face red rust corrosion resistance becomes saturated and the result becomes uneconomical. Simultaneously, the adhesion at the time of working falls. The more preferable film thickness is 3 to 15 μm , more preferably 5 to 10 μm . The “film thickness” referred to here is the average film thickness of the coating layer, that is, the average of the distance between the interface of the coating layer with the top layer and the interface with the bottom layer. The film thickness can be measured by the following method. The precoated steel sheet is buried in an epoxy resin which is then cured. It is then polished from the cross-sectional direction, then the cross-section of the coating is examined under a microscope to measure the distance between the top and bottom interfaces. Considering the fact that the distance between the top and bottom interfaces fluctuates depending on the measurement location, the range of observation of the cross-section under the microscope is preferably at least 10 mm. If the particle size of the antirust pigment added is large and the pigment protrudes from the resin of the coating, the surface of the pigment protruding is deemed the interfaces of the coating layer with the top and bottom layers.

[0039]

As explained above, the topmost layer coating adjacent to the lower layer coating containing the second pigment has to satisfy the following conditions in addition to the condition of (5) of the above [1]:

- (1) a contact angle of a surface of the coating with water is 65 to 75°,
- (2) a film thickness of the coating is 0.5 to 5 μm ,
- (3) the coating includes a first pigment, a content of the first pigment being 15 to 70 mass% with respect to the mass of the dried coating, and
- (4) in the first pigment, a total of the pigment with an average primary particle size of 1 μm or more is 5 mass% or more with respect to the mass of the dried coating.

The “first pigment” here means the pigment intended for coloring or rust prevention as a whole, but the deliquescent antirust pigment present at the lower layer is not included. Further, as the constituents forming the mass of the dried coating (the mass of the coating in the dried state), the binder, pigment, beads, and other constituents may be mentioned. The “film

thickness” referred to here is the average film thickness of the coating layer, that is, the average of the distance between the surface of the topmost layer coating layer minus the parts where the granular wax protrudes and the lower layer coating. The film thickness can be measured together when measuring the film thickness of the lower layer coating explained above. Note that if the particle size of the antirust pigment of the second pigment added to the lower layer coating is large and the pigment protrudes out from the resin of the lower layer coating into the topmost layer coating, the surface of the pigment protruding is deemed the interface with the lower layer coating layer.

[0040]

The contact angle of the surface of the coating with water has to be 65 to 75°. If less than 65°, the effect as a barrier layer to water vapor is insufficient and the absorption of moisture by the deliquescent action of the antirust pigment in the adjacent to lower layer coating cannot be sufficiently suppressed, while if over 75°, elution of the antirust pigment from the lower layer coating when immersed in water is blocked and sufficient end face red rust corrosion resistance cannot be obtained.

[0041]

The contact angle is measured by preparing a coated steel sheet, cutting out a test piece in size of 30 mm×60 mm by shears, allowing it to stand under wet test conditions (temperature 49°C, relative humidity 90 to 95%) for 15 hours, then sufficiently drying it by a blower, then measuring the contact angle with water of the topmost layer coating at the surface provided with the coating containing the antirust pigment effective for end face red rust corrosion resistance (water permeable/water vapor impermeable coating). The contact angle with water after 30 seconds after dropping water from a microsyringe on to the topmost layer coating is measured using a general purpose contact angle measuring device (for example, a CA-A Type contact angle measuring device made by Kyowa Interface Science Co., Ltd. etc.).

[0042]

Along with satisfying the conditions of the above (1) to (4) to make the surface of the topmost layer coating hydrophilic, a predetermined amount of the first pigment is included in the relatively thin topmost layer coating. At least part of the first pigment is made a pigment of a relatively large particle size. By this, the topmost layer coating becomes a barrier layer against gaseous water (water vapor) touching the topmost layer coating and the absorption of moisture by the deliquescent action of the second antirust pigment in the adjacent to lower layer coating is suppressed. The liquid water touching the topmost layer coating can reach the surface of the lower layer coating by the capillary action of the coating and thereby enable expression of the effect of prevention of red rust of the end face by elution of the antirust pigment. Simultaneously, the liquid water reaching the surface of the lower layer coating containing the

antirust pigment never contacts the galvanized layer of the surface of the steel sheet, so formation of white rust from the surface of the steel sheet by dissolution of zinc is avoided.

[0043]

In this way, the water permeable/water vapor impermeable topmost layer coating is mainly comprised of a binder, first pigment, and above granular wax and contains other constituents according to need.

[0044]

The binder is comprised of the main constituents of a binder resin and curing agent and other constituents.

[0045]

The type of the binder resin is suitably selected in accordance with the performance demanded as a coated steel sheet in practice. An epoxy resin, polyurethane resin, polyester resin, and other various resins which have been used for coated steel sheets in the past can be used. This being said, in the present invention, the contact angle of the surface of the topmost layer coating with the water has to be made 65 to 75°. Therefore, use of a resin enabling the contact angle to be kept within this range when adding other constituents to form the topmost layer coating is sought. As such a resin, one having an epoxy resin, polyurethane resin, or polyester resin as a base resin and, for example, including a partially hydrolyzed condensate of tetraalkoxysilane may be illustrated.

[0046]

As examples of tetraalkoxysilanes, Methyl Silicate 51, Ethyl Silicate 40, Ethyl Silicate 48 (made by Colcoat Co., Ltd.), MKC Silicate MS51 and MS56 (made by Mitsubishi Chemical Corporation), and other commercially available products etc. may be mentioned. Further, water and catalysts may be added to tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, and other monomers to cause hydrolysis and condensation.

[0047]

As the curing agent for combination with the binder resin, for example, a melamine resin, polyisocyanate compound, etc. may be mentioned. If necessary, a cross-linking catalyst may also be mixed in.

[0048]

The content of the binder constituent with respect to the mass of the dried coating is preferably 30 to 85 mass%. If the content of the binder constituent is excessively great, the content of the first pigment relatively falls and the number of pores able to be utilized for permeation of the liquid becomes insufficient and therefore the corrosion resistance falls or coloring to the desired color tone becomes difficult. On the other hand, if the content is excessively low, the hardness of the coating itself rises and the flaw resistance is improved, but

the elongation of the coating itself falls, so the workability falls. The particularly preferable range of content is 40 to 60 mass% with respect to the mass of the dried coating.

[0049]

The type of the first pigment is not particularly limited so long as not being the same as the second pigment. Any of an antirust pigment, coloring pigment, etc. may be used. As an example of the antirust pigment, aluminum tripolyphosphate, Zn, Mg, Al, Ti, Zr, and Ce salts of phosphoric acid and phosphorous acid, Ca ion exchanged silica, and amorphous silica particles with an oil absorption of 100 to 1000 ml/100 g, a specific surface area of 200 to 1000 m²/g, and an average particle size of 2 to 30 μm may be mentioned.

[0050]

As examples of coloring pigments, zinc oxide, titanium oxide, calcium carbonate, kaolin, and other inorganic pigments, copper phthalocyanine, toluidine red, and other organic pigments and further carbon black etc. may be mentioned.

[0051]

The topmost layer coating in the present invention contains a larger amount of the first pigment than usual for acquiring water permeability and water vapor impermeability. The content of the first pigment is made 15 to 70 mass% with respect to the mass of the dried coating. With a content of the pigment of less than 15 mass%, it becomes hard for liquid water to permeate through the coating, so elution of the antirust pigment in the lower layer coating is obstructed and the effect of prevention of red rust at the end face ends up being harder to realize. On the other hand, if the content of the pigment exceeds 70 mass%, the workability falls and it becomes difficult for other properties sought from the precoated steel sheet to be satisfied.

[0052]

Further, the total content of the pigment with an average primary particle size of 1 μm or more in the first pigment has to be made 5 mass% or more with respect to the mass of the dried coating. The presence of such a pigment with a relatively large particle size is important in enabling permeation of liquid water. The upper limit of the total content of the pigment with an average primary particle size of 1 μm or more with respect to the mass of the dried coating is not particularly set, but preferably is made 70 mass% or less for the reason of maintaining workability after coating. As opposed to this, the total content of the pigment with an average primary particle size of 1 μm or more with respect to the mass of the dried coating is more preferably 5 to 30 mass%, particularly preferably 5 to 15 mass%.

[0053]

The average primary particle size of the first pigment is preferably smaller than the thickness of the coating. If there is an excessively large amount of pigment with an average primary particle size larger than the thickness of the coating, there is the concern that the

corrosion resistance of the coated surface will fall.

[0054]

The topmost layer coating may contain, in addition to the above binder and first pigment constituent, as required, a leveling agent, beads for obtaining relief shapes in outside appearance, conductive powder for improving the weldability and electromagnetic shielding ability, and other constituents. However, if the contents of these constituents increase, a drop in the permeability of liquid water or the barrier effect against gaseous water or other inherent properties of the topmost layer coating will be occurred, so the total content of these constituents with respect to the mass of the dried coating is preferably 20 mass% or less, particularly preferably 10 mass% or less.

[0055]

The thickness of the topmost layer coating is made 0.5 to 5 μm . If less than 0.5 μm , the barrier effect with respect to gaseous water (water vapor) becomes smaller. On the other hand, the topmost layer coating of the present invention contains a larger amount of the first pigment than usual so as to obtain water permeability and water vapor impermeability, so inherently the cohesion is smaller. If the film thickness becomes greater, the coating will not be able to withstand the shear force due to its surface being rubbed and the coating will easily suffer cohesive failure. The pieces of the back surface coating peeled off due to being rubbed against the front surface coating will also scratch the front surface coating. As a result, both the front and back surfaces will be scratched. Further, if the film thickness of the topmost layer coating becomes greater, the water permeability falls, so elution of the deliquescent antirust agent from the bottom layer is obstructed and the end face red rust corrosion resistance falls. For the above reason, the thickness of the topmost layer coating is 1 to 5 μm . 1 to less than 2 μm is more preferable. Note that, as explained above, the thickness of the coating is preferably made the average primary particle size or more of the first pigment contained.

[0056]

The coating used as the topmost layer coating in the present invention is similar to the coating described in PTL 3 as one which water permeates through. The role of the water permeable coating in PTL 3 is to enable liquid water contacting the coating to freely pass through the coating at that time and fill the voids in the coating and wet the plated surface under the coating by liquid (water). In the present invention, the lower layer adjacent to the topmost layer coating is not a plated layer, but a coating layer containing a deliquescent antirust pigment. The role of the coating of enabling liquid water to permeate to the lower layer is the same as that in PTL 3. That is, to inhibit the formation of red rust from the cut end face when a precoated steel sheet product installed outdoors is wet by water by rainfall etc., deliquescent antirust pigment exhibiting an effect of prevention of red rust by elution into the water has to be made to

elute from the lower layer coating containing that deliquescent antirust pigment and act on the cut end face. For this reason, the topmost layer coating is given the role of enabling the deliquescent antirust pigment eluted from the lower layer when water impregnates the coating to freely disperse to the water wetting the surface of the precoated steel sheet product.

[0057]

On the other hand, in the present invention, in addition to the above role, the topmost layer coating is further given another role. This is the role of the topmost layer coating becoming a barrier layer and inhibiting the absorption of moisture by the deliquescent antirust pigment contained in the lower layer when gaseous water (water vapor) touches the topmost layer coating. As explained above, in the present invention, the lower layer adjacent to the topmost layer coating is not a plating layer, but is a coating layer containing a deliquescent antirust pigment. If the lower layer is a coating layer, the adhesion between the topmost layer coating and the lower layer coating layer is better than the case where the lower layer is a plated layer. By doing this, the voids enabling permeation of water in the upper layer are closed at single ends by the lower layer coating layer. The water can reach the lower layer coating layer by a capillary phenomenon, but in the case of a gas, since the bottom parts of the voids in the topmost layer coating at the portions touching the lower layer coating are closed, the gas in the voids is difficult to pass. For this reason, the new mechanism of liquid water being permeated, but gas not being permeated is believed to be exhibited. As a result, by providing the above-mentioned topmost layer coating at a layer above the deliquescent antirust pigment-containing layer, even in a high humidity environment, it is possible to prevent the surface of the precoated steel sheet product directly contacting that environment from becoming easily wet.

[0058]

In this way, in the present invention, in addition to its conventional function, the water permeable coating of PTL 3 is given a new function which may be said to have an effect in an opposite direction to the same. That is, when liquid water contacts the topmost layer coating, elution of the deliquescent antirust pigment from the lower layer is not obstructed (conventional function) and when gaseous water contacts it, elution is not easily allowed (new function).

[0059]

In the chromate-free type precoated steel sheet of the present invention, the coatings other than the topmost layer coating satisfying the conditions of (1) to (5) of the above [1] provided at one surface and the lower layer coating containing the deliquescent antirust pigment adjacent to the same (including all coating at opposite surface) can be formed from general materials used in the manufacture of chromate-free type precoated steel sheet. On the other hand, all of the coatings on the two surfaces can be easily formed by usual manufacturing facilities and manufacturing methods. There is no need to explain these in detail here.

[0060]

As the steel sheet of the substrate of the precoated steel sheet of the present invention, a galvanized steel sheet is used. As the galvanized steel sheet, for example, any of a hot dip galvanized steel sheet, electrogalvanized steel sheet, Al-Zn plated steel sheet, Al-Mg-Si-Zn plated steel sheet, etc. can be used. Among these as well, if using an Al-Mg-Si-Zn plated steel sheet, the red rust resistance is particularly notably improved, so this is preferable.

[0061]

The surface of the galvanized steel sheet is provided with a usual chromate-free chemically converted layer as a pretreatment layer for application of the coating material for the coating. As one example, the chemically converted layer may be a film containing two or more of any of silica, a silane coupling agent, tannin or tannic acid, a zirconium compound, or a titanium compound and containing a resin. The chemically converted layer may be formed by immersion in a chemical conversion treatment solution, application by a roll coater, application by a ringer roll, brushing, spray coating, etc.

EXAMPLES

[0062]

Next, examples will be used to explain the present invention. Needless to say, the following examples are illustrative in nature. The present invention is not limited to the following examples.

[0063]

A finished product precoated steel sheet generally is supplied to the demand side in a form with a coating satisfying the design requirements sought by the demand side working the sheet to produce a final product and is provided at a first surface arranged at the outside in the final product and visible to the eye. As opposed to this, the coating of the other surface is not required to meet design requirements to the extent sought from the coating on the first surface. The coating of the other surface contains constituents not directly affecting the design property sought by the demand side like the end face red rust corrosion resistant pigment. Generally, the surface on which warning stickers or foam members etc. for improving air-tightness are attached by a tackifier is this other surface not visible to the eye in the final product. Therefore, below, for convenience, the surface provided with the coating of the performance sought by the demand side will be referred to as the “front surface” and the surface provided with the coating containing the end face red rust corrosion resistant pigment and the topmost layer coating adjacent to this will be referred to as the “back surface”.

[0064]

As the base sheets, a 11%Al-3%Mg-0.2%Si-zinc plated steel sheet (0.6 mm thick, amount of deposition per surface of 80 g/m²) (below, referred to as “SD”) and a hot dip galvanized steel sheet (0.6 mm thick, amount of deposition per surface of 80 g/m²) (after this, referred to as “GI”) were used. The surfaces of these base sheets were degreased by alkali, then
5 were treated for chemical conversion by a chromate-free chemical conversion treatment solution (silane coupling agent, tannic acid, silica, and polyester resin mixed treatment solution) (amount of deposition: one surface 100 mg/m²) (after this, referred to as the “Treatment A”). Due to this chemical conversion treatment, a chromate-free type chemical conversion treatment layer was formed on the surface layer of the galvanized steel sheet.

10 **[0065]**

On the front surface, a general bottom coating layer (polyester/melamine+isocyanate joint use curing type FLC687 resin coating material (containing general pigment) made by Japan Fine Coatings Co., Ltd.) was formed on the chromate-free type chemically converted layer of the chemically converted base sheet. This was dried by hot air to a dried film thickness of 2 μm by a
15 PMT: peak metal temperature of 215°C. On top of that, as a general top coating material, a polymeric polyester/melamine curing type coating material (FLC8500 resin coating material (light beige color) made by Japan Fine Coatings Co., Ltd.) was dried by hot air to a dried film thickness of 10 μm by a PMT: peak metal temperature of 230°C to form a top coating.

[0066]

20 On the back surface, three types of coating materials were coated as the lower layer coating on the chromate-free type chemically converted layer of the chemically converted base sheet. Two types among these contain 18 wt% of sodium tungstate or potassium dihydrogen phosphate as the deliquescent end face red rust corrosion resistant pigment (second pigment). The remaining one type did not contain a deliquescent end face red rust corrosion resistant
25 pigment and was a general coating containing only general pigment (same coating material as above-mentioned front surface bottom coating layer). The resins used for these coating materials were all a polyester/melamine+ isocyanate joint use curing type resin (FLC687 resin made by Japan Fine Coatings Co., Ltd.). These coating materials were coated and formed so that the lower layer coatings become predetermined dried film thicknesses (dried by hot air by PMT:
30 peak metal temperature of 215°C).

[0067]

The base coating materials (coating materials before addition of wax) used for the topmost layer coating formed on the lower layer coating correspond to the coating materials used for the water permeable/water vapor impermeable film of the above-mentioned PTL 4. Among
35 these, the base coating material labeled as Type I in Table 1 is a coating material prepared by mixing into NKC1200SC Clear (clear type coating material of low polluting (silanol group

surface concentrating) bake on type polyester resin made by Japan Fine Coatings Co., Ltd.) 40 wt% of titania (Tipaque CR-90 made by Ishihara Sangyo Kaisha Ltd.), 5 wt% of aluminum tripolyphosphate (K-WHITE #82 made by Tayca Corporation), and 5 wt% of porous silica (H-33 made by AGC Si-Tech Co., Ltd.) (pigment content 50 wt% with respect to mass of the dried coating). The total amount of the pigment with an average primary particle size of 1 μm or more in the coating material was calculated as being 10% with respect to the mass of the dried coating. The base coating materials of the other Type II to Type IX satisfied the conditions of the topmost layer coating of the present application, but were prepared so that the various conditions changed in various ways.

[0068]

The coating material obtained by including in these substrate coating materials the various types of waxes shown in Table 1 changed in contents in various ways were used as the coating materials for topmost layer coating use. In the table, “PTFE”, “PE/PTFE”, and “High MW PE” respectively indicate the SST series polytetrafluoroethylene (PTFE) wax (average particle sizes 2, 4, 10 μm , melting point 321°C) of Shamrock Technologies, the FLUOROSLIP series polyethylene/PTFE codispersed wax (average particle sizes 4, 6, 13 μm , melting point 110 to 130°C) of Shamrock Technologies, and the TEXTURE series polymeric polyethylene wax (average particle sizes 5 and 30 μm , melting point 166°C) of Shamrock Technologies. The melting points of the microcrystalline wax and carnauba wax were respectively 90°C and 80°C.

[0069]

The contact angle of the topmost layer coating formed was measured in accordance with the above-mentioned measurement method by a CA-A type contact angle measuring device made by Kyowa Interface Science Co., Ltd. As a result, in all cases where wax was added, no change was seen in the contact angle with the substrate coating material.

[0070]

On the other hand, for the general coating other than Types I to IX, the Polyester/Melamine Curing Type FLC100HQ resin made by Japan Fine Coatings was used as the coating resin. The topmost layer coating of the back surface was formed to a film thickness shown in Table 1 as the dried film thickness (dried by hot air by PMT: peak metal temperature 230°C).

[0071]

The outlines of the prepared precoated steel sheets are shown in Table 1.

[0072]

[Table 1]

Table 1 (1/2)

	Base sheet	Chemical conversion treatment	Front surface		Back surface						
			Bottom coating layer	Top coating	Lower layer coating		Topmost layer coating				
					Type	Film thickness/ μm	Type	wax (Particle size/ μm)	Content/wt%	Protruding height/ μm	Film thickness/ μm
Ex. 1	SD	Treatment A	General	General	Sodium tungstate added	1	Type I	PTFE(4)	3	3	1
Ex. 2	SD	Treatment A	General	General	Sodium tungstate added	2	Type I	PTFE(4)	3	3	1
Comp. Ex. 1	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PTFE(4)	3	3.5	0.3
Comp. Ex. 2	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PTFE(2)	0.5	1	1
Ex. 3	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PTFE(2)	1	1	1
Ex. 4	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PTFE(2)	3	1	1
Ex. 5	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PTFE(2)	5	1	1
Ex. 6	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PTFE(2)	10	1	1
Comp. Ex. 3	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PTFE(2)	12	1	1
Ex. 7	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PTFE(4)	3	3	1
Comp. Ex. 4	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PTFE(10)	3	9	1
Comp. Ex. 5	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PE/PTFE(4)	0.5	1.5	1
Ex. 8	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PE/PTFE(4)	1	1.5	1
Ex. 9	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PE/PTFE(4)	3	1.5	1
Ex. 10	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PE/PTFE(4)	5	1.5	1
Ex. 11	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PE/PTFE(4)	10	1.5	1
Comp. Ex. 6	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PE/PTFE(4)	12	1.5	1
Ex. 12	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PE/PTFE(6)	3	2.5	1
Comp. Ex. 7	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PE/PTFE(13)	3	5	1
Ex. 13	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	High MW PE(5)	3	3	1
Comp. Ex. 8	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	High MW PE(30)	3	12	1
Ex. 14	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PE/PTFE(4)	3	1	2
Ex. 15	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PE/PTFE(4)	3	0.5	3
Ex. 16	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PE/PTFE(4)	3	0.1	5
Comp. Ex. 9	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PE/PTFE(4)	3	0.1	10
Comp. Ex. 10	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	PE/PTFE(4)	3	0.1	12

[0073]

[Table 2]

Table 1 (2/2)

	Base sheet	Chemical conversion treatment	Front surface		Back surface						
			Bottom coating layer	Top coating	Lower layer coating		Topmost layer coating				
					Type	Film thickness/ μm	Type	Wax (particle size/ μm)	Content/wt%	Protruding height/ μm	Film thickness/ μm
Ex. 17	SD	Treatment A	General	General	Sodium tungstate added	10	Type I	PE/PTFE(4)	3	1.5	1
Ex. 18	SD	Treatment A	General	General	Sodium tungstate added	20	Type I	PE/PTFE(4)	3	1.5	1
Ex. 19	SD	Treatment A	General	General	Potassium dihydrogen phosphate added	8	Type I	PE/PTFE(4)	3	0.5	3
Comp. Ex. 11	SD	Treatment A	General	General	General	5	General	Microcrystalline	3	-	5
Comp. Ex. 12	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	Microcrystalline	0.5	-	1
Comp. Ex. 13	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	Microcrystalline	1	-	1
Comp. Ex. 14	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	Microcrystalline	3	-	1
Comp. Ex. 15	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	Carnauba	0.5	-	1
Comp. Ex. 16	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	Carnauba	1	-	1
Comp. Ex. 17	SD	Treatment A	General	General	Sodium tungstate added	5	Type I	Carnauba	3	-	1
Comp. Ex. 18	GI	Treatment A	General	General	Sodium tungstate added	5	Type I	PE/PTFE(4)	3	1.5	1
	GI	Treatment A	General	General	General	5	General	Microcrystalline	3	-	5
Ex. 21	SD	Treatment A	General	General	Sodium tungstate added	5	Type II	PE/PTFE(4)	3	1.5	1
Ex. 22	SD	Treatment A	General	General	Sodium tungstate added	5	Type III	PE/PTFE(4)	3	1.5	1
Ex. 23	SD	Treatment A	General	General	Sodium tungstate added	5	Type IV	PE/PTFE(4)	3	1.5	1
Ex. 24	SD	Treatment A	General	General	Sodium tungstate added	5	Type V	PE/PTFE(4)	3	1.5	1
Ex. 25	SD	Treatment A	General	General	Sodium tungstate added	5	Type VI	PE/PTFE(4)	3	1.5	1
Ex. 26	SD	Treatment A	General	General	Sodium tungstate added	5	Type VII	PE/PTFE(4)	3	1.5	1
Ex. 27	SD	Treatment A	General	General	Sodium tungstate added	5	Type VIII	PE/PTFE(4)	3	1.5	1
Ex. 28	SD	Treatment A	General	General	Sodium tungstate added	5	Type IX	PE/PTFE(4)	3	1.5	1

Type I: (Basic coating) Pigment content 50%, average primary particle size 1 μm or more 10%, contact angle 70°Type II: Pigment content 50%, average primary particle size 1 μm or more 10%, contact angle 65°Type III: Pigment content 50%, average primary particle size 1 μm or more 10%, contact angle 75°Type IV: Pigment content 15%, average primary particle size 1 μm or more 8%, contact angle 70°Type V: Pigment content 70%, average primary particle size 1 μm or more 12%, contact angle 70°Type VI: Pigment content 50%, average primary particle size 1 μm or more 5%, contact angle 70°Type VII: Pigment content 50%, average primary particle size 1 μm or more 15%, contact angle 70°Type VIII: Pigment content 50%, average primary particle size 1 μm or more 30%, contact angle 70°Type IX: Pigment content 50%, average primary particle size 1 μm or more 40%, contact angle 70°

[0074]

[Evaluation 1] Wetting of back surface coating due to absorption of moisture

50×100 mm test pieces cut out from the prepared examples and comparative examples were exposed for 30 minutes to test environments adjusted to various temperatures and relative humidities and examined for wetting of the coatings by absorption of moisture of the back surfaces. The results are summarized in the three patterns shown in FIGS. 1(a) to 1(c) which were evaluated as “Very good”, “Good”, and “Poor”. A summary of the test results is given in Table 2.

[0075]

[Evaluation 2] Adhesion of attachment member at high humidity

The adhesion of attachment members on the back surface coatings of the test pieces under high humidity conditions was tested. The test pieces were allowed to stand for 30 minutes in an environment of 20°C and a relative humidity of 95%, then the attachment members (adhesive tapes) (15 mm width) used in the field of air-conditioners were attached to the coatings of the test pieces. Right after that, single ends of the attachment members were pulled in directions vertical to the coating surfaces and measured for peeling load by a spring balance. A case with a peeling load of 1.96N or more was evaluated as “Good”, while a case of less than 1.96N was evaluated as “Poor”. The results are shown in Table 2.

[0076]

[Evaluation 3] End face red rust corrosion resistance

A distilled water immersion test was performed. It was learned that by the distilled water immersion test, it is possible to easily evaluate the resistance to red rust formed in a short period in a nonelectrolyte wet environment. Twenty 10×40 mm test pieces of the respective precoated steel sheets of the examples and comparative examples were immersed in 40 ml of distilled water placed in diameter 80 mm Petri dishes and examined for trends in formation of red rust at the end face.

[0077]

Usually, if no red rust is formed in 168 hours, it is learned there is no problem in practice. Here, a case where no red rust is formed at all even with a distilled water immersion time of over 500 hours was evaluated as “Very good”, a case where very light red rust (five or less diameter 1 mm or less spots of rust) is formed in 500 hours, but is not formed in 168 hours was evaluated as “Very good to good”, a case where red rust (six or more diameter 1 mm spots of rust) is formed in 500 hours, but is not formed in 168 hours was evaluated as “Good”, while a case where red rust is formed from less than 168 hours was evaluated as “Poor”. The results are shown in Table 2.

[0078]

[Evaluation 4] Scratch resistance of front and back coatings

The resistance to scratching of the front and back coatings occurring due to sliding action of the front and back coatings when transporting precoated steel sheets stacked together or wound in coils and the resistance to galling of the coatings occurring at the time of press working at the user side were evaluated by the following method. The precoated steel sheets of the examples and comparative examples were cut into 50×50 mm pieces. Two each were prepared. The front surface of one was superposed on the back surface of the other. These were pressed from above and below by a 98N load. In that state, one steel sheet was made to turn 90°, then the load was removed and two coated surfaces rubbed against were examined.

A case where the coating is not scratched at both the coating surfaces was evaluated as “Very good”,

a case where scratches are seen at the coating of either of the surfaces, but do not expose the base sheet was evaluated as “Good”,

a case where scratches are seen at the coating of both of the surfaces, but neither expose the base sheet was evaluated as “Good to fair”,

a case where scratches are seen at the coating on both surfaces and the base sheet is exposed at the back surface, but the base sheet is not exposed at the front surface and the scratches stop at the inside of the top layer and do not reach the primer layer was evaluated as “Fair”,

a case where scratches are seen at the coating on both surfaces and the base sheet is exposed at the back surface, but the base sheet is not exposed at the front surface, but the scratches reach the primer layer was evaluated as “Fair-”, and

a case where scratches exposing the base sheet are seen at the coating on both surfaces was evaluated as “Poor”. Cases evaluated as “Fair” and better were evaluated as passing. The results are shown in Table 2.

[0079]

Note that, the detachment of wax was also evaluated. The results are shown in the remarks column of Table 2. When scraping off the coatings at the back surface sides of the examples and comparative examples by a metal blade, specimens in which detachment of wax particles was observed were indicated as “Poor”. In this case, if actually press-forming the specimens by dies, the wax would detach and be transferred to the dies making frequent cleaning of the dies necessary, so this is not preferable in practice.

[0080]

[Table 3]

Table 2

	Various performance				Remarks
	[Evaluation 1] Wetting of coating of back surface by absorption of moisture	[Evaluation 2] Adhesion of attachment member in high humidity	[Evaluation 3] End face red rust corrosion resistance	[Evaluation 4] Scratch resistance of front and back coatings	Detachment of wax (transfer to die)
Ex. 1	Good	Good	Good	Good	
Ex. 2	Good	Good	Good	Good	
Comp. Ex. 1	Poor	Poor	Very good	Good	Poor
Comp. Ex. 2	Good	Good	Very good	Poor	
Ex. 3	Good	Good	Very good	Good	
Ex. 4	Good	Good	Very good	Good	
Ex. 5	Good	Good	Very good	Good	
Ex. 6	Good	Good	Very good	Good	
Comp. Ex. 3	Good	Good	Very good	Poor	
Ex. 7	Good	Good	Very good	Good	
Comp. Ex. 4	Good	Good	Very good	Good	Poor
Comp. Ex. 5	Good	Good	Very good	Poor	
Ex. 8	Good	Good	Very good	Good	
Ex. 9	Good	Good	Very good	Good	
Ex. 10	Good	Good	Very good	Good	
Ex. 11	Good	Good	Very good	Good	
Comp. Ex. 6	Good	Good	Very good	Poor	
Ex. 12	Good	Good	Very good	Good	
Comp. Ex. 7	Good	Good	Very good	Good	Poor
Ex. 13	Good	Good	Very good	Good	
Comp. Ex. 8	Good	Good	Very good	Good	Poor
Ex. 14	Good	Good	Very good	Good	
Ex. 15	Good	Good	Very good to good	Good	
Ex. 16	Good	Good	Very good to good	Good	
Comp. Ex. 9	Good	Good	Very good to good	Fair-	
Comp. Ex. 10	Good	Good	Poor	Fair-	
Ex. 17	Good	Good	Very good	Good	
Ex. 18	Good	Good	Very good	Fair	
Ex. 19	Good	Good	Very good	Good	
Comp. Ex. 11	Very good	Good	Poor	Good	
Comp. Ex. 12	Good	Good	Good	Poor	
Comp. Ex. 13	Good	Good	Poor	Good	
Comp. Ex. 14	Good	Good	Poor	Good	
Comp. Ex. 15	Good	Good	Good	Poor	
Comp. Ex. 16	Good	Good	Poor	Good	
Comp. Ex. 17	Good	Good	Poor	Good	
Ex. 20	Good	Good	Good	Good	
Comp. Ex. 18	Very good	Good	Poor	Very good	
Ex. 21	Good	Good	Very good	Good	
Ex. 22	Good	Good	Good	Good	
Ex. 23	Good	Good	Good	Good	
Ex. 24	Good	Good	Very good	Good	
Ex. 25	Good	Good	Good	Good	
Ex. 26	Good	Good	Very good	Good	
Ex. 27	Good	Good	Very good	Good to Fair	
Ex. 28	Good	Good	Very good	Fair	

CLAIMS

[Claim 1]

A chromate-free type precoated steel sheet comprising a galvanized steel sheet having a
5 chromate-free type chemical conversion treatment layer on both surfaces, and pluralities of
coatings formed thereon comprising a topmost layer coating and a lower layer coating adjacent
thereto,

the topmost layer coating of one surface satisfies the conditions of the following
conditions (1) to (5):

10 (1) a contact angle of a surface of the topmost layer coating with water is 65
to 75°,

(2) a film thickness of the topmost layer coating is 0.5 to 5 μm ,

(3) the topmost layer coating comprises a first pigment, and a content of the
pigment is 15 to 70 mass% with respect to the mass of the dried coating,

15 (4) in the first pigment, a total of the pigment with an average primary particle
size of 1 μm or more is 5 mass% or more with respect to the mass of the dried coating, and

(5) the topmost layer coating contains granular wax of an average particle size
of 1 to 8 μm in a content with respect to the mass of the dried coating of 1 to 10 mass%, at least
part of the granular wax particles present in a state partially protruding from the coating surface,
20 and

the lower layer coating adjacent to the topmost layer coating comprises a second
pigment that is one or more types of a deliquescent antirust pigment effective for preventing
formation of red rust on the end face.

25 [Claim 2]

The chromate-free type precoated steel sheet according to claim 1, wherein the wax is
selected from a group consisting of PTFE wax, polyethylene/PTFE codispersed wax, and
polymeric polyethylene wax.

30 [Claim 3]

The chromate-free type precoated steel sheet according to claim 1 or 2, wherein the
second pigment is selected from a group consisting of tungstates and silicates, phosphates and
chlorides of alkali metals, and hypophosphites of alkali earth metals.

35 [Claim 4]

The chromate-free type precoated steel sheet according to claim 3, wherein the tungstate

is sodium tungstate, calcium tungstate, ammonium tungstate, lithium tungstate, magnesium tungstate, or a mixture thereof.

[Claim 5]

5 The chromate-free type precoated steel sheet according to claim 3, wherein the silicate is sodium silicate, potassium silicate, lithium silicate, or a mixture thereof.

[Claim 6]

10 The chromate-free type precoated steel sheet according to claim 3, wherein the alkali metal phosphate is sodium dihydrogen phosphate, potassium dihydrogen phosphate, dipotassium hydrogen phosphate, sodium tripolyphosphate, sodium dihydrogen phosphate monohydrate, sodium dihydrogen phosphate dihydrate, or a mixture thereof.

[Claim 7]

15 The chromate-free type precoated steel sheet according to claim 3, wherein the alkali metal chloride is sodium chloride.

[Claim 8]

20 The steel sheet according to claim 3, wherein the hypophosphite is calcium hypophosphite.