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 mass% or so. If less than 6 mass%, the end face red rust corrosion resistance is insufficiently expressed while if becoming greater than 50 mass%, 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 mass%, most preferably 10 to 30 mass%.

[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 mass% or so. If less than 5 mass%, the end face red rust corrosion resistance is insufficiently expressed while if becoming greater than 50 mass%, 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 mass%, most preferably 10 to 30 mass%.

[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 mass%. 1 to 20 mass% is more preferable.

[0036]

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

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/m^2) (below, referred to as "SD") and a hot dip galvanized steel sheet (0.6 mm thick, amount of deposition per surface of 80 g/m^2) (after this, referred to as "GI") were used. The surfaces of these base sheets were degreased by alkali, then 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/m^2) (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.

[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 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]

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 mass% 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 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: 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 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 mass% of titania (Tipaque CR-90 made by Ishihara Sangyo Kaisha Ltd.), 5 mass% of aluminum tripolyphosphate (K-WHITE #82 made by Tayca Corporation), and 5 mass% of porous silica (H-33 made by AGC Si-Tech Co., Ltd.) (pigment content 50 mass% 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/mass %	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/mass %	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
Ex. 20	GI	Treatment A	General	General	Sodium tungstate added	5	Type I	PE/PTFE(4)	3	1.5	1
Comp. Ex. 18	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°