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COATED STEEL SHEET AND METHOD FOR MANUFACTURING SAME

FIELD OF THE INVENTION

The present invention relates to a coated steel sheet having excellent heat resistance and damage resistance at forming, applicable to various parts of automobiles, household electric appliances, and building materials, and also to a method for manufacturing thereof.

DESCRIPTION OF RELATED ARTS

Owing to the durability and economy, zinc-base coated steel sheets are used in wide fields including automobiles, household electric appliances, and building materials. Aiming to provide functions such as corrosion resistance and paintability, chromate coating is conventionally applied to the surface of the zinc-base coated steel sheets, and further a thin-film resin coating treatment or the like is given to the chromated surface to form a several micrometers thick of thin resin film thereon.

Those zinc-base coated steel sheets, however, have no heat resistance, thus they raise problems of discoloration, smoke emission, reduction in corrosion resistance caused by heating thereof when they are exposed to high temperature environments such as peripheral sections of automobile engine-room, oven, electronic oven, shrink band on cathode-ray tube of TV, and adjacent portions to welded section. For the case of sole chromate coating, the steel sheets raise problems of causing



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scarathes to degrade the appearance during forming thereof caused by very thin film, and of degrading the corrosion resistance at the damaged section, though the discoloration is suppressed to some extent during heating thereof owing to the absence of organic component.

Several countermeasures to those problems have been proposed, for example, in (1) JP-A-4-33844, (the term "JP-A" referred to herein signifies "Japanese Patent Laid-Open Publication", (2) JP-A-6-179981, and (3) JP-A-7-278837.

As the technology using silicone resin, there are (4) JP-A-63-102929 and JP-A-2000-15741.

Although the chromate coating uses hexavalent chromium which is classified as a regulated substance against pollution, contamination of environment and human body by the hexavalent chromium does substantially not occur because the treatment process is carried out in a closed system in which the hexavalent chromium is completely recovered and is not emitted to environment and because the elution of the hexavalent chromium from the chromate film is almost zero owing to the sealing action of organic composite film. Nevertheless, recent global environmental concern has enhanced the autonomous actions to decrease the use of heavy metals including hexavalent chromium. In addition, to prevent pollution of environment when shredder dust as a wasted product is disposed, action to zero or decrease the quantity of heavy metals in the products has appeared.

Responding to those movements, there are proposed many non-pollution treatment technologies not using chromate coating

aiming to prevent the generation of white rust on zinc-base coated steel sheets. Those technologies include several methods that utilize organic-base compounds and organic resins. Examples of them are the following:

(1) Method of using tannic acid, (for example, JP-A-51-71233);

(2) Method of using a thermosetting coating of a mixture of an epoxy resin, an amino-resin, and tannic acid, (for example, JP-A-63-90581);

(3) Method of using chelating force of tannic acid, such as a method of using a mixed product of a water-base resin and a polyphenol carboxylic acid, (for example, JP-A-8-325760);

(4) Surface-treatment method of applying an aqueous solution of a hydrazine derivative onto the surface of tin plate or galvanized steel sheet, (for example, JP-B-53-27694, (the term "JP-B" referred to herein signifies "Examined Japanese Patent Publication"), and JP-B-56-10386);

(5) Method of using an antirust agent containing an amine-added salt prepared by adding an amine to a mixture of acylsarcosine and benzotriazole, (JP-A-58-130284);

(6) Method of using a treatment agent prepared by mixing tannic acid and a heterocyclic compound such as a benzothiazole compound, (JP-A-57-198267); and

(7) Method of using a surface-treatment composition containing an organic resin containing a hydroxyl group-laid monomer as the copolymerizing component, phosphoric acid, and a phosphoric acid compound of metal, (JP-A-9-208859 and JP-

A-9-241856).

According to the prior arts (1) and (2), the chromate coating is given on a coated steel sheet, and further a treatment solution containing silicic acid as the base which is solubilized to water using an alkali metal oxide, (water glass), is applied thereon to form the upper layer, followed by drying the upper layer. Since the prior arts (1) and (2) left the alkali metal component in the upper layer, a problem of poor water resistance to result in poor corrosion resistance arises. Furthermore, since the prior art (2) uses only inorganic component, the lubrication property is poor, which raises a problem of poor damage resistance at forming. The prior art (3) forms a chromate film prepared by adding silica to a Zn-Ni alloy plating. Sole addition of silica is difficult to suppress the discoloration during heating, and raises a drawback of poor damage resistance at forming.

The prior art (4) forms a rudder type silicone resin on a chemical conversion film formed on a zinc-base coated steel sheet. The formed silicone resin has a network structure (as understandable from the name of "rudder type"), so the cured film becomes excessively hard, which raises problems of poor damage resistance at forming and of poor adhesiveness of the film during forming. The prior art (5) satisfies both the heat resistance and the damage resistance. However, the prior art (5) uses chromate (containing hexavalent chromium) to improve the corrosion resistance, thus the material is not a non-pollutant material.

The prior arts (1) through (7) that do not use chromate use organic component as the main component. Accordingly, when these materials are heated to high temperatures, the organic component is thermally decomposed to fail in attaining sufficient corrosion resistance, and further the material surface blackens, thus fails to use as a heat-resistant material.

As described above, no prior art provides zinc-base coated steel sheet which has excellent heat resistance at high temperatures and damage resistance, further provides excellent corrosion resistance without using chromium.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a coated steel sheet that has excellent heat resistance at high temperatures and excellent damage resistance, that does not use chromium in the treatment process, that assures environmental safety, and that has excellent corrosion resistance, and to provide a method for manufacturing thereof.

The inventors of the present invention found a zinc-base coated steel sheet that has excellent resistance to thermal discoloration, resistance to smoke emission under heating, corrosion resistance after heated, and damage resistance, by forming (1) a composite oxide film containing oxide fine particles and phosphoric acid-base compounds as the first layer, and (2) a resin film as the second layer, containing a specific straight silicone resin as the main component, on the surface of the zinc-base coated steel sheet.

The present invention was completed based on the finding, and the features of the present invention are the following.

[1] A coated steel sheet which is produced by: forming a composite oxide film on the surface of a zinc-base coated steel sheet, as the first layer, which composite oxide film contains structural components of (α) oxide fine particles and (β) phosphoric acid and/or phosphoric acid compound, at a total coating weight of the component (α) and the component (β) converted to P_2O_5 in a range of from 5 to 4000 mg/m²; and forming a straight silicone resin film, as the second layer, on the surface of the composite oxide film, at a coating weight converted to SiO_2 of from 0.1 to 3 g/m².

[2] The coated steel sheet according to [1], wherein the composite oxide film further contains (γ) at least one element selected from the group consisting of Mg, Ca, Sr, Li, Mn, Fe, Co, Ni, Zn, Al, La, and Ce; the total coating weight of the (α) oxide fine particles, the component (β) converted to P_2O_5 , and the component (γ) converted to metal, in the composite oxide film, is in a range of from 5 to 4000 mg/m².

[3] The coated steel sheet according to [2], wherein the metal of the component (γ) in the composite oxide film is Mn and/or Al.

[4] The coated steel sheet according to any one of [1]-[3], wherein the component (α) in the composite oxide film is silicon dioxide.

[5] The coated steel sheet according to any one of [1]-[3], wherein the component (α) in the composite oxide film is silicon

oxide, and the coating weight of the silicon dioxide converted to SiO_2 is in a range of from 5 to 95 wt% as the mass ratio to the total coating weight of the composite oxide film.

[6] The coated steel sheet according to any one of [2]-[5], wherein the molar ratio of the component (β) converted to P_2O_5 to the component (γ) at least one element selected from the group consisting of Mg, Ca, Sr, Li, Mn, Fe, Co, Ni, Zn, Al, La, and Ce, converted to metal, (for the case of two or more of metals, the sum of respective metal-converted values), ($\text{P}_2\text{O}_5/\text{Me}$), being contained in the composite oxide film, is in a range of from 1/2 to 2/1.

[7] The coated steel sheet according to any one of [1]-[6], wherein the organic group in the straight silicone resin film is methyl group as an organic group.

[8] The coated steel sheet according to any one of [1]-[7], wherein the SiO_2 component in the straight silicone resin occupies 60% or more of the total film mass.

[9] The coated steel sheet according to any one of [1]-[8], wherein the straight silicone resin film contains 20 parts by mass or less of a crystalline lubricant to 100 parts by mass of the straight silicone resin.

[10] The coated steel sheet according to any one of [1]-[8], wherein the straight silicone resin film contains 20 parts by mass or less of an organic-base lubricant having 70 °C or higher softening point to 100 parts by mass of the straight silicone resin.

[11] A method for manufacturing coated steel sheet

comprising the steps of:

treating at least one side of a zinc-base coated steel sheet by an aqueous solution containing (i) 0.001 to 3.0 mol/l of oxide fine particles and (ii) 0.001 to 6.0 mol/l of phosphoric acid and/or phosphoric acid compound, converted to P_2O_5 ;

forming a composite oxide film as the first layer film on the surface of the plated steel sheet by heating to dry the plated steel sheet after treated by the aqueous solution to a coating weight in a range of from 5 to 4000 mg/m², which composite oxide film contains (α) oxide fine particles and (β) phosphoric acid and/or phosphoric acid compound, as structuring components thereof; and

applying a coating composition consisting mainly of a straight silicone resin onto the composite oxide film, and heating to dry thereof, thus forming the second layer film at a coating weight converted to SiO₂ in a range of from 0.1 to 3 g/m².

[12] A method for manufacturing coated steel sheet comprising the steps of:

treating at least one side of a zinc-base coated steel sheet by an aqueous solution according to [11] which further contains (iii) 0.0001 to 3.0 mol/l of at least one element selected from the group consisting of Mg, Ca, Sr, Li, Mn, Fe, Co, Ni, Zn, Al, La, and Ce, as the sum of respective metal-converted values;

forming a composite oxide film as the first layer film on the surface of the plated steel sheet by heating to dry the coated steel sheet after treated by the aqueous solution to a coating

weight in a range of from 5 to 4000 mg/m², which composite oxide film contains (α) oxide fine particles, (β) phosphoric acid and/or phosphoric acid compound, and (γ) at least one element selected from the group consisting of Mg, Ca, Sr, Li, Mn, Fe, Co, Ni, Zn, Al, La, and Ce, as structuring components thereof; and applying a coating composition consisting mainly of a straight silicone resin onto the composite oxide film, and heating to dry thereof, thus forming the second layer film at a coating weight converted to SiO₂ in a range of from 0.1 to 3 g/m².

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 shows a schematic front view of a testing apparatus for evaluating the damage resistance of test material.

EMBODIMENT FOR CARRYING OUT THE INVENTION

According to the coated steel sheet of the present invention, a composite oxide film is formed as the first layer on the surface of a zinc-base coated steel sheet. Quite different from conventional alkali-silicate treated film represented by the treatment composition containing LiO₂ and SiO₂, the composite oxide film according to the present invention contains (α) oxide fine particles and (β) phosphoric acid and/or phosphoric acid compound as the structuring components, and, if necessary, further contains (γ) at least one element selected from the group consisting of Mg, Ca, Sr, Li, Mn, Fe, Co, Ni, Zn, Al, La, and Ce.

As for the (α) oxide fine particles which are one of the structuring components of the above-described composite oxide film, silicon dioxide is preferred. Applicable silicon dioxide includes colloidal silica such as: Snowtex O, OS, OXS, OUP, AK, O40, OL, and OZL, (acidic solutions), Snowtex XS, S, NXS, NS, N, OAS-25, LSS-35, LSS-45, and LSS-75, (alkaline solutions), produced by Nissan Chemical Industries, Ltd.; Cataloid S, SI-350, SI-40, and SA, (alkaline solutions), and Cataloid SN (acidic solution), produced by Catalysts & Chemicals Co., Ltd.; and Adelite AT-20 through 50, AT-20N, AT-300, and AT-300S, (alkaline solutions), and Adelite AT20Q (acidic solution), produced by Asahi Denka Kogyo K.K.

As of these silicon dioxides, the ones having 14 nm or finer particle size are preferred, and further fine ones having 8 nm or smaller particle size are more preferred from the point of corrosion resistance. Alternatively, a film composition solution containing dispersed dry-silica fine particles is applicable. Preferred dry-silica includes AEROSIL 200, 300, 300CF, and 380 produced by Nippon Aerosil Co., Ltd., and the ones having 12 nm or smaller particle size are preferable, and the ones having 7 nm or smaller particle size are more preferable.

Other than the above-given oxide fine particles, colloidal solution of fine particles of aluminum oxide, zirconium oxide, titanium oxide, cerium oxide, and antimony oxide may be used.

As for the (β) phosphoric acid and/or phosphoric acid compound, which is a structural component of the composite oxide film, orthophosphoric acid, diphosphoric acid, polyphosphoric acid, metaphosphoric acid, or the like, and metallic salt or

compound thereof may be added to the film composition as the film component. As of these components, primary phosphate is preferable from the point of stability of the film composition solution. When ammonium primary phosphate, ammonium secondary phosphate, or ammonium tertiary phosphate was added to the film composition solution, the corrosion resistance increased. Although the reason of increase in the corrosion resistance is not fully analyzed, use of these kinds of ammonium salt does not induce gelling of the solution even when the pH value of the film composition solution is increased. Since metallic salts generally become insoluble in alkaline domain, when a film is formed from a composition solution having high pH value, a compound more difficult in dissolving is presumably formed during the drying step.

No specific limitation is given to the state of existence of phosphoric acid and/or phosphoric acid compound in the film, and the phosphoric and/or phosphoric acid compound may be in crystal state or non-crystal state. Furthermore, the ionic property and the solubility of phosphoric acid and/or phosphoric acid compound in the film are not specifically limited.

The existing state of (γ) Mg, Ca, Sr, Li, Mn, Fe, Co, Ni, Zn, Al, La, and Ce, which are the components added to the film at need, in the film is not specifically limited. Those elements presumably exist as metals, or as compounds or composite compounds such as oxide, hydroxide, hydrated oxide, and phosphoric compound. The ionic property and the solubility of these compounds, hydroxides, hydrated oxides, and phosphoric

acid compounds are also not specifically limited.

Among the components of (γ), Mn and Al are superior in corrosion resistance to other (γ) components. Although the reason is not fully analyzed, hydroxide is easily generated in neutral pH domain which is a corrosive environment, thus presumably forming a network for composite-forming together with phosphoric acid compound, silica, and the like to form a dense film.

Method for introducing the component (γ) to the film is not specifically limited. Phosphate, nitrate, sulfate, chloride, or the like of Mg, Ca, Sr, Li, Mn, Fe, Co, Ni, Zn, Al, La, and Ce may be added to the film composition solution.

A typical range of the coating weight of composite oxide film is, when the (α) oxide fine particles, above-described component (β) converted to P_2O_5 , and above-described component (γ) exist, from 5 to 4000 mg/m², preferably from 50 to 1000 mg/m², more preferably from 100 to 500 mg/m², and most preferably from 200 to 400 mg/m². If the coating weight thereof is smaller than 5 mg/m², the corrosion resistance becomes not sufficient. If the coating weight exceeds 4000 mg/m², the coating appearance and the appearance after heated degrade, and the electric conductivity decreases, which degrades the weldability and other characteristics.

To obtain particularly high corrosion resistance, it is preferred that the component (α) in the composite oxide film is silicon dioxide and that the coating weight of the silicon dioxide converted to SiO₂ is in a range of from 5 to 95 wt% as

the mass ratio to the total coating weight of the composite oxide film defined before, preferably from 10 to 60 wt%.

The reason to attain particularly high corrosion resistance when the coating weight of the silicon dioxide is within the above-given range is not fully analyzed. Presumable reason of attaining the high corrosion resistance is that phosphoric acid component enhances the barrier function which is not attained solely by silicon dioxide, thus allowing forming a dense film, and that the synergy effect of phosphoric acid and silicon dioxide for suppressing the corrosion appears, thus providing the excellent corrosion resistance.

From similar point of view, higher corrosion resistance is attained when the ratio of the phosphoric acid and/or phosphoric acid compound which is the component (β) of the composite oxide to the metallic composition which is the component (γ) thereof is in a molar ratio range, (P_2O_5/Me) as the ratio of the component (β) converted to P_2O_5 to the component (γ) converted to metal, (for the case of two or more of metals, the sum of respective metal-converted values), of from 1/2 to 2/1.

The reason to attain particularly high corrosion resistance when the ratio of the phosphoric acid component to the metallic component is within the above-given range is not fully analyzed. Presumable reason of attaining the high corrosion resistance is that, since the solubility of phosphoric acid component varies with the ratio of the phosphoric acid to the metal, the solubility of the film becomes particularly

insoluble within the above-given range of the ratio of phosphoric acid to metallic component, which results in stronger barrier property of the film.

As for the first layer film, the film composition may further contain an additive of controlling the corrosion resistance. Examples of that type of additive are polyphosphate and phosphate (such as zinc phosphate, ammonium dihydrogen phosphate, and zinc phosphite), molybdate, phosphomolybdate (such as aluminum phosphomolybdate), organic phosphoric acid and salt thereof (such as phytic acid, phytate, phosphonic acid, phosphonate, and their metallic salt and alkali metal salt), and organic inhibitor (such as hydrazine derivative, thiol compound, dithiocarbamate). As further additives, coupling agent (such as silane coupling agent and titanium coupling agent) may be applied. However, addition of organic resin and the like is not preferable because that kind of additive induces smoke emission and degradation in appearance when the material is heated to high temperatures.

The coated steel sheet according to the present invention has a film formed by applying a treatment solution as the second layer containing specified straight silicone resin as the main component onto the above-described first layer, followed by baking thereof. The term "silicone" is a generic name of base materials having siloxane (-Si-O-Si-) portion therein, and generally resin, oil, rubber, and the like are used as the silicone.

Regarding the straight silicone resin according to the

present invention, the base material of that type of resin has a skeleton of siloxane (-Si-O-Si-), has silicon atoms binding with hydroxyl group (-OH), alkoxyl group (-OR : R designates an organic group), and organic group, and has both of organic property and inorganic property, while receiving no modification with other organic resin. Furthermore, the straight silicone resin has no bridge structure so that the resin is elastic in the film shape and has excellent damage resistance. The organic group binding with the silicon atoms may be methyl group (-CH_3), ethyl group ($\text{-C}_2\text{H}_5$), phenyl group ($\text{-C}_6\text{H}_5$), vinyl group (-CH=CH_2), butyl group ($\text{-C}_4\text{H}_9$), or the like. The applicable straight silicone resin may contain one of these organic groups or may contain two or more thereof. When a modified silicone resin, not the straight silicone resin, is used, the modified organic resin component thermally decomposes during the heating step to induce discoloration and smoke emission, so the use of modified silicone resin is not preferable.

Among organic groups, methyl group which has smaller number of carbons is more preferable from the point of prevention of smoke emission caused by the decomposition of organic component under heating.

The content of SiO_2 component in the straight silicone resin is preferably 60% or more to the total film mass. The preferable range is specified because components other than SiO_2 in the straight silicone resin are hydroxyl group or organic group so that the increase in the content of organic group degrades the smoke emission preventive property.

The reason to add an organic-base lubricant to the above-described silicone resin film is that the organic-base lubricant has a function to further effectively prevent the flaw and the galling on the resin film and the coating surface caused by roll-forming, press-forming, and the like. The reason to adopt the organic-base lubricant having 70 °C or higher softening point is that below 70 °C of softening point is not preferable because of easy decomposition of organic component to degrade the prevention of smoke emission. Examples of applicable organic-base lubricant having 70 °C or higher softening point are MICROSTALIN WAX (70-90 °C of softening point), polyethylene (90-140 °C of softening point), polypropylene (140-170 °C of softening point), and tetrafluoroethylene (320 °C of softening point). The above-described lubricants may be added separately or may be used two or more thereof. The acid value of MICROSTALIN WAX, polyethylene, and polypropylene may be zero or more than zero, and their combined use may be applied. Since the silicone resin is a solvent system, the adding state of the lubricant is preferably in powder form or in a state of dispersed in a solvent in advance. The particle size of the lubricant is preferably 20 μm or smaller in view of damage resistance.

Other than the above-described organic-base lubricants, the crystalline lubricant of inorganic-base one including graphite, boron nitride, and molybdenum disulfide may be applied. When the smoke emission prevention is emphasized, those kinds of inorganic-base lubricants are preferably used. They are, however, inferior in the damage resistance to the organic-base

lubricants so that the use of inorganic-base lubricant may be adequately selected depending on the use objectives.

A preferable adding quantity of the organic-base lubricant is 20 parts by mass or less to 100 parts by mass of the straight silicone resin. If the added quantity of the organic-base lubricant exceeds 20 parts by mass, the quantity of organic component increases to degrade the smoke emission resistance under heating, which is not preferable. From the point of smoke emission prevention, a preferred added quantity is 10 parts by mass or less. For the case of inorganic-base lubricant, adding quantity of more than 20 parts by mass is not preferable because the damage resistance degrades.

A preferred range of coating weight of the straight silicone resin is from 0.1 to 3 g/m² converted to SiO₂. When the coating weight is below 0.1 g/m², the damage resistance during roll-forming and press-forming degrades. When the coating weight exceeds 3 g/m², the smoke emission prevention in heating and the adhesiveness during bending work degrade, which is not preferable.

The film is formed by applying a coating consisting mainly of above-described straight silicone resin onto the surface of the zinc-base coated steel sheet, followed by heating to dry the coating.

Examples of the coated steel sheets on which above-described film is formed include: galvanized steel sheets prepared by electroplating, hot-dip coating, and vapor deposition coating; zinc alloy coated steel sheets containing

zinc and one or more elements of nickel, iron, aluminum, cobalt, molybdenum, and the like; and composite coated steel sheets having a coating film containing silica, alumina, and the like. A zinc-nickel alloy coated steel sheet and a zinc-55% aluminum alloy coated steel sheet which have high melting point of the coated metal are more preferable from the point of heat resistance. Alternatively, hot-dip aluminum coated steel sheet, not the zinc-base coating, and cold-rolled steel sheet and hot-rolled steel sheet, having no plating film, are also applicable.

The steel as the substrate of the zinc-base coated steel sheet is not specifically limited, and the steel coils or sheets having various kinds of compositions and surface roughness, or prepared by various rolling methods can be applied.

Formation of the composite oxide film and the resin film on the surface of the zinc-base coated steel sheet are conducted as follows. The above-described composite oxide film composition treatment solution is applied onto the surface of the zinc-base coated steel sheet using known method such as roll coating, curtain flow coating, and spray coating. Thus applied solution is dried by a known method using hot-air furnace, induction-heating furnace, or the like to form the composite oxide film. The coating consisting mainly of above-described straight silicone resin is applied onto the surface of thus prepared composite oxide film using a known method to form a predetermined coating weight of film. The zinc-base coated steel sheet on which the coating is applied is then heated to bake thereof to a temperature range of from 80 °C to 300 °C in a hot-air

furnace or an induction-heating furnace to vaporize the solvent in the coating, thus to form the resin film.

The reason to specify the concentration of the treatment solution to above-given range is the following. If the content of phosphoric acid and/or phosphoric acid compound is below 0.001 mol/l converted to P_2O_5 , the wanted coating weight cannot be attained, which is not preferable. If the content thereof exceeds 6.0 mol/l, the stability of the treatment solution degrades, which is also not preferable. If the content of oxide fine particles is below 0.001 mol/l, the wanted coating weight cannot be attained, which is not preferable. If the content thereof exceeds 3.0 mol/l, the stability of the treatment solution degrades, which is also not preferable. For a compound which contains at least one of the metallic ions of Mg, Ca, Sr, Li, Mn, Fe, Co, Ni, Zn, Al, La, and Ce, if the total of the above-given metals converted to metal is below 0.001 mol/l, the effect of metallic ion addition cannot be attained, which is not preferable. If the total thereof exceeds 3.0 mol/l, the stability of the treatment solution degrades, which is also not preferable.

The above-described baking temperature of the resin film should be in a range of from 80 °C to 300 °C. If the baking temperature is below 80 °C, the hardening of resin film becomes insufficient, which degrades the damage resistance during working, thus the temperature range is not preferable. If the baking temperature exceeds 300 °C, the hardening of resin film excessively proceeds to induce decomposition and vaporization

of organic group in the straight silicone resin, which results in poor damage resistance, which is not preferable.

EXAMPLE

The first layer film-forming treatment solutions (film compositions) shown in Table 1 and Table 2 were prepared. The second layer film-forming treatment solutions (coating compositions) shown in Tables 3 through 5 were prepared.

Table 1

No.	Oxide fine particles (α)			Phosphoric acid / phosphoric acid compound (β)			Metallic component (γ)				pH of composition	Satisfaction of the range of the present invention*3
	Kind	Trade name	Primary particle diameter (nm)	Concentration (mol/l)*1	Kind	Concentration (mol/l)*2	Molar ratio (β)/(γ)	Kind	Concentration (mol/l)	Concentration (mol/l)	Total molar quantity	
1	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.33	Ortho-phosphoric acid	0.30	1.00	Li	0.30	-	0.30	○
2	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.33	Ortho-phosphoric acid	0.06	1.50	Mn	0.04	-	0.04	○
3	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.40	Ortho-phosphoric acid	0.13	1.30	Fe	0.10	-	0.10	○
4	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.30	Ortho-phosphoric acid	0.22	1.22	Co	0.18	-	0.18	○
5	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.33	Ortho-phosphoric acid	0.15	1.25	Ni	0.12	-	0.12	○
6	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.33	Ortho-phosphoric acid	0.22	1.10	Zn	0.20	-	0.20	○
7	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.33	Ortho-phosphoric acid	0.15	1.50	Al	0.10	-	0.10	○
8	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.33	Ortho-phosphoric acid	0.09	1.80	La	0.05	-	0.05	○
9	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.33	Ortho-phosphoric acid	0.09	1.80	Ce	0.05	-	0.05	○
10	Silicon dioxide	AEROSIL 200 by Nippon Aerosil Co., Ltd.	12	0.50	Ortho-phosphoric acid	0.15	1.50	Mn	0.10	-	0.10	○
11	Silicon dioxide	AEROSIL 200 by Nippon Aerosil Co., Ltd.	12	0.50	Ortho-phosphoric acid	0.10	1.20	Ni	0.08	-	0.08	○
12	Silicon dioxide	AEROSIL 200 by Nippon Aerosil Co., Ltd.	12	0.33	Ortho-phosphoric acid	0.10	1.20	Co	0.08	-	0.08	○
13	Silicon dioxide	AEROSIL 200 by Nippon Aerosil Co., Ltd.	12	0.33	Ortho-phosphoric acid	0.12	1.50	Al	0.08	-	0.08	○
14	Silicon dioxide	Snowtex OUP by Nissan Chemical Industries, Ltd.	12 to 14	0.20	Ortho-phosphoric acid	0.12	1.20	Mn	0.10	-	0.10	○
15	Silicon dioxide	Snowtex OUP by Nissan Chemical Industries, Ltd.	12 to 14	0.20	Ortho-phosphoric acid	0.12	1.20	Al	0.10	-	0.10	○
16	Aluminum oxide	Alumina Sol 200 by Nissan Chemical Industries, Ltd.	*4	0.33	Ortho-phosphoric acid	0.10	1.00	Mn	0.10	-	0.10	○

*1) converted to SiO₂, *2) converted to P₂O₅, *3) ○: satisfying the requirements of the present invention X: not satisfying the requirements of the present invention, *4) featherlike particles

Table 2

No.	Oxide fine particles (α)				Phosphoric acid / phosphoric acid compound (β)			Metallic component (γ)				pH of composition	Satisfaction of the range of the present invention*3	
	Kind	Trade name	Primary particle diameter (nm)	Concentration (mol/l) *1	Kind	Concentration (mol/l) *2	Molar ratio (β)/(γ)	(Component 1)			Total molar quantity			
								Kind	Concentration (mol/l)	Kind				
17	Zirconium oxide	NZS-30A by Nissan Chemical Industries, Ltd.	60 to 70	0.33	Ortho-phosphoric acid	0.15	1.50	Mn	0.10	-	-	0.10	2.6	○
18	Silicon dioxide	Snowtex N by Nissan Chemical Industries, Ltd.	12 to 14	0.33	Ammonium dihydrogen phosphate	0.15	-	-	-	-	-	-	8.0	○
19	Silicon dioxide	AEROSIL 200 by Nippon Aerosil Co., Ltd.	12	0.33	Ortho-phosphoric acid	0.12	1.20	Ni	0.08	Mn	0.02	0.10	2.8	○
20	Silicon dioxide	AEROSIL 200 by Nippon Aerosil Co., Ltd.	12	0.33	Ortho-phosphoric acid	0.12	1.09	Al	0.08	Mg	0.03	0.11	2.9	○
21	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.33	Ortho-phosphoric acid	0.25	2.50	Mn	0.10	-	-	0.10	2.1	○
22	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.90	Ortho-phosphoric acid	0.01	2.00	Mn	0.005	-	-	0.005	3.5	○
23	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.005	Ortho-phosphoric acid	0.24	1.20	Mn	0.20	-	-	0.20	2.0	○
24	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.16	Ortho-phosphoric acid	0.08	1.33	Mn	0.06	-	-	0.06	3.5	○
25	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.33	Ortho-phosphoric acid	0.15	0.25	Mn	0.60	-	-	0.06	3.2	○
26	Silicon dioxide	Snowtex N by Nissan Chemical Industries, Ltd.	12 to 14	0.33	Diphosphoric acid	0.20	1.00	Li	0.20	-	-	0.20	4.0	○
27	Silicon dioxide	Snowtex N by Nissan Chemical Industries, Ltd.	12 to 14	0.33	Ortho-phosphoric acid	0.13	-	-	-	-	-	-	2.9	○
28	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	1.00	Ortho-phosphoric acid	0.72	1.20	Mn	0.60	-	-	0.60	2.1	○
29	-	-	-	-	Ortho-phosphoric acid	0.22	1.10	Mn	0.20	-	-	0.20	3.5	×
30	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.30	Diphosphoric acid	0.33	-	-	-	-	-	-	2.0	○
31	Silicon dioxide	Snowtex OS by Nissan Chemical Industries, Ltd.	6 to 8	0.50	-	-	-	Mn	0.20	-	-	0.20	2.2	×

*1) converted to SiO₂, *2) converted to P₂O₅, *3) ○: satisfying the requirements of the present invention X: not satisfying the requirements of the present invention, *4) featherlike particles

Table 3

No.	Test material #1	First layer film					Second layer film					Classification			
		Film composition #2	Drying temp. (°C)	Percentage as converted to SiO ₂ (mass%) #3	Component (γ)	Phosphoric acid molar ratio β/γ #4	Total coating weight (mg/m ²) #5	Film main component	Organic group	Percentage of SiO ₂ component in resin (mass%)	Organic lubricant		Softening point (°C)	Added quantity (parts by mass)	Coating weight of silicone resin (g/m ²)
1	EZN	1	120	40	Li	1.00	320	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
2	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
3	EZN	3	120	40	Fe	1.30	320	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
4	EZN	4	120	40	Co	1.22	315	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
5	EZN	5	120	40	Ni	1.25	300	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
6	EZN	6	120	40	Zn	1.10	280	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
7	EZN	7	120	40	Al	1.50	350	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
8	EZN	8	120	40	La	1.80	350	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
9	EZN	9	120	40	Ce	1.80	350	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
10	EZN	10	120	60	Mn	1.50	360	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
11	EZN	11	120	60	Ni	1.20	290	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
12	EZN	12	120	40	Co	1.20	290	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
13	EZN	13	120	40	Al	1.50	280	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
14	EZN	14	120	20	Mn	1.20	320	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
15	EZN	15	120	20	Al	1.20	330	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
16	EZN	16	120	-	Mn	1.00	290	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
17	EZN	17	120	-	Mn	1.50	320	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
18	EZN	18	120	40			320	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
19	EZN	19	120	40	Ni, Mn	1.20	290	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
20	EZN	20	120	40	Al, Mg	1.09	300	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
21	EZN	21	120	40	Mn	2.50	320	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet

- *1) UZ: Electroalvanized steel sheet, EZN: Zn-Ni alloy plated steel sheet, GI: Hot-dip galvanized steel sheet, GA: Hot-dip galvanized steel sheet, GF: Hot-dip Zn-5% Al alloy coated steel sheet, GL: Hot-dip Zn-55% Al alloy coated steel sheet
- *2) Numerals correspond to the respective Nos. given in Table 1.
- *3) Mass ratio to the total mass of the first layer (composite oxide film).
- *4) Ratio of the molar quantity of the ((γ) phosphoric acid and/or phosphoric acid compound converted to P₂O₅) to the [sum of the molar quantity of the components (γ) converted to respective metals]
- *5) Total coating weight = [(the mass of (α) oxide fine particles + (the (β) phosphoric acid and/or phosphoric acid compound converted to P₂O₅ + the component (γ) converted to metal)].

Table 4

No.	Test material *1	First layer film					Second layer film					Classification			
		Film compo- sition *2	Drying temp. (°C)	Percentage as converted to SiO ₂ (mass%) *3	Compo- nent (γ)	Phosphoric acid molar ratio β/γ *4	Total coating weight (mg/m ²) *5	Film main component	Organic group	Percentage of SiO ₂ component in resin (mass%)	Organic lubricant		Softening point (°C)	Added quantity (parts by mass)	Coating weight of silicone resin (g/m ²)
22	EZN	22	120	98	Mn	2.00	280	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
23	EZN	23	120	4	Mn	1.20	320	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
24	EZN	24	120	40	Mn	1.33	350	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
25	EZN	25	120	40	Mn	1.33	350	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
26	EZN	26	120	40	Li	1.00	280	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
27	EZN	27	120	40			500	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
28	EZN	28	120	40	Mn	1.20	4200	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
29	EZN	29	120	0	Mn	1.10	360	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Comparative example
30	EZN	30	120	60			290	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Comparative example
31	EZN	31	120	60	Mn		290	Straight silicone resin	Methyl group	80%	-	-	-	1.0	Inventive steel sheet
32	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Phenyl group	70%	-	-	-	1.0	Inventive steel sheet
33	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Ethyl group	75%	-	-	-	1.0	Inventive steel sheet
34	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Vinyl group	75%	-	-	-	1.0	Inventive steel sheet
35	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Butyl group	70%	-	-	-	1.0	Inventive steel sheet
36	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Phenyl group	70%	-	-	-	1.0	Inventive steel sheet
37	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	50%	-	-	-	1.0	Inventive steel sheet
38	EZN	2	120	40	Mn	1.50	290	Acrylic- modified silicone resin	-	-	-	-	-	1.0	Comparative example
39	EZN	2	120	40	Mn	1.50	290	Epoxy-modified silicone resin	-	-	-	-	-	1.0	Comparative example
40	EZN	2	120	40	Mn	1.50	290	Polyurethane resin	-	-	-	-	-	0	Comparative example
41	EZN	2	120	40	Mn	1.50	290	Lithium silicate	-	-	-	-	-	1.0	Comparative example
42	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	MICROSTALIN WAX	70	10	1.0	Inventive steel sheet

- *1) UZ: Electroalvanized steel sheet, EZN: Zn-Ni alloy plated steel sheet, GI: Hot-dip galvanized steel sheet, GA: Hot-dip galvanized steel sheet, GF: Hot-dip Zn-5% Al alloy coated steel sheet, GL: Hot-dip Zn-55% Al alloy coated steel sheet
- *2) Numerals correspond to the respective Nos. given in Table 1.
- *3) Mass ratio to the total mass of the first layer (composite oxide film).
- *4) Ratio of the molar quantity of the [(β) phosphoric acid and/or phosphoric acid converted to P₂O₅] to the [sum of the molar quantity of the components (γ) converted to respective metals]
- *5) Total coating weight = [(the mass of (α) oxide fine particles + (the (β) phosphoric acid and/or phosphoric acid compound converted to P₂O₅ + the component (γ) converted to metal)].

Table 5

No.	Test material	First layer film				Second layer film					Classification				
		Film composition #2	Drying temp. (°C)	Percentage converted to SiO ₂ (mass%) #3	Component (γ)	Phosphoric acid molar ratio β/γ #4	Total coating weight (mg/m ²) #5	Film main component	Organic group	Percentage of SiO ₂ component in resin (mass%)		Organic lubricant	Softening point (°C)	Added quantity (parts by mass)	Coating weight of silicone resin (g/m ²)
43	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	Poly-ethylene	105	10	1.0	Inventive steel sheet
44	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	Poly-ethylene	113	10	1.0	Inventive steel sheet
45	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	Oxidized polyethylene	113	10	1.0	Inventive steel sheet
46	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	Poly-propylene	150	10	1.0	Inventive steel sheet
47	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	Tetrafluoro-ethylene	320	10	1.0	Inventive steel sheet
48	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	Molybdenum disulfide	—	10	1.0	Inventive steel sheet
49	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	Paraffin wax	50	10	1.0	Inventive steel sheet
50	EZN	2	120	40	Mn	1.50	290	Lithium silicate	—	—	Poly-ethylene	113	10	1.0	Comparative example
51	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	Poly-ethylene	113	1	1.0	Inventive steel sheet
52	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	Poly-ethylene	113	20	1.0	Inventive steel sheet
53	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	—	—	—	0.1	Inventive steel sheet
54	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	—	—	—	3.0	Inventive steel sheet
55	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	—	—	—	4.0	Comparative example
56	EZN	2	120	40	Mn	1.50	290	—	—	—	—	—	—	0	Comparative example
57	UZ	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	Poly-ethylene	113	10	1.0	Inventive steel sheet
58	EZN	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	Poly-ethylene	113	10	1.0	Inventive steel sheet
59	GI	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	Poly-ethylene	113	10	1.0	Inventive steel sheet
60	GA	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	Poly-ethylene	113	10	1.0	Inventive steel sheet
61	GF	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	Poly-ethylene	113	10	1.0	Inventive steel sheet
62	GL	2	120	40	Mn	1.50	290	Straight silicone resin	Methyl group	80%	Poly-ethylene	113	10	1.0	Inventive steel sheet

*1) UZ: Electroplated steel sheet, EZN: Zn-Ni alloy plated steel sheet, GI: Hot-dip galvanized steel sheet, GA: Hot-dip galvanized steel sheet, GF: Hot-dip Zn-5% Al alloy coated steel sheet, GL: Hot-dip Zn-55% Al alloy coated steel sheet

*2) Numerals correspond to the respective Nos. given in Table 1.

*3) Mass ratio to the total mass of the first layer (composite oxide film).

*4) Ratio of the molar quantity of the [(β) phosphoric acid and/or phosphoric acid compound converted to P₂O₅] to the [sum of the molar quantity of the components (γ) converted to respective metals]

*5) Total coating weight = {the mass of (α) oxide fine particles + {the (β) phosphoric acid and/or phosphoric acid compound converted to P₂O₅ + the component (γ) converted to metal}}.

Both sides of the respective zinc-base plated steel sheets described below were subjected to alkali degreasing and water rinsing. Respective first film-forming treatment solutions shown in Tables 1 and 2 were applied onto the surface of respective plated steel sheets using roll coater (while adjusting the coating weight by the wet-coating weight), which were then heated to dry to form the respective first layer films. After that, respective coating compositions consisting mainly of straight silicone resin, given in Tables 3 to 5, were applied onto the respective first layer films by roll coating method (while adjusting the coating weight by the wet-coating weight), which were then baked in an induction-heating furnace to the ultimate plate temperatures of from 60 °C to 400 °C, thus the test materials were prepared.

(1) Electrogalvanized steel sheet (sheet thickness of 0.8 mm, coating weight of 20 mg/m²)

(2) Zinc-nickel alloy coated steel sheet (sheet thickness of 0.8 mm, coating weight of 20 mg/m²)

(3) Hot-dip galvanized steel sheet (sheet thickness of 0.8 mm, coating weight of 90 mg/m²)

(4) Hot-dip galvanneled steel sheet (thickness of 0.8 mm, coating weight of 45 mg/m²)

(5) Hot-dip Zn-5% Al alloy coated steel sheet (sheet thickness of 0.8 mm, coating weight of 90 mg/m²)

(6) Hot-dip Zn-55% Al alloy plated steel sheet (sheet thickness of 0.8 mm, coating weight of 70 mg/m²)

The coating weight of composite oxide of the first layer and the coating weight of resin film of the second layer are given on Tables 3 to 5.

For each of thus prepared test materials, resistance to thermal discoloration, resistance to smoke emission, corrosion resistance before and after heating, and damage resistance were evaluated. The results are shown in Tables 6 to 8.

The method for evaluating the performance is described below.

[Performance evaluation]

(1) Resistance to thermal discoloration

After reaching the ultimate temperature of 600 °C, every test material was subjected to soaking for one hour, then the state of discoloration on the surface thereof was determined by a colorimeter. The criterion of the evaluation is the following.

◎: $\Delta E \leq 2$

○: $2 < \Delta E \leq 5$

△: $5 < \Delta E \leq 10$

×: $\Delta E > 10$

(2) Resistance to smoke emission

Visual observation was given to each test material to watch the smoke emission up to 600 °C of ultimate plate temperature. The criterion of the evaluation is the following.

- ◎: No smoke was emitted.
- : Slight smoke was observed.
- △: Smoke emission was found.
- ×: Significant smoke emission was observed.

(3) Corrosion resistance before heating

Plurality of test specimens (70 mm x 150 mm) was cut from each test material. Each of the test specimens was subjected to salt spray test specified by JIS Z2371. The area of generated white rust after 500 hours was visually determined. The criterion of the evaluation is the following.

- ◎: No white rust was generated.
- +: Area of generated white rust was 5% or less.
- : Area of generated white rust was more than 5% and not more than 10%.
- △: Area of generated white rust was more than 10% and not more than 30%.
- ×: Area of generated white rust was more than 30%.

(4) Corrosion resistance after heating

Plurality of test specimens (70 mm x 150 mm) were cut from each test material which was preliminarily treated by heating to 600 °C of ultimate sheet temperature, followed by soaking for one hour. Each of the test specimens was subjected to salt spray test specified by JIS Z2371. The area of generated red rust after 500 hours was visually determined. The criterion of the evaluation is the following.

⊙: No red rust was generated.

○: Area of generated red rust was 5% or less.

△: Area of generated red rust was more than 5% and not more than 30%.

×: Area of generated red rust was more than 30%.

The applied testing apparatus is given in Fig. 1 showing schematic front view thereof. As illustrated in Fig. 1, the testing apparatus has: a female die 1 which has a flat face and which is fixed to a side 2a of a box frame 2; a male die 4 which faces the female die 1 and which has a substantially horizontal projection 3 positioned at a specified height; and a hydraulic cylinder 5 which supports the male die 4 and drives the male die 4 horizontally toward the female die 1, and which is fixed to other side 2b of the frame 2. The male die 4 is fixed to a rod 5a of the hydraulic cylinder 5 via a load cell 6. The width of the projection 3 of the male die 4 is 10 mm, and the length of the tip thereof is 1 mm.

A test material was vertically inserted into the gap between the female die 1 and the male die 4. Using the female die 1 and the male die 4, the test material 7 was compressed by the hydraulic cylinder 5 under 50 kgf (500 kgf/cm²) of pressure. Then, the test material was pulled-out upward at a speed of 500 mm/min to the "arrow" direction. Visual observation was given to the portion slid during the pulling out action to evaluate the damages on the film and the plating at the portion. The criterion of evaluation is the following.

◎: No damage occurred.

○: Slight damage appeared on the film, but no damage on plating occurred.

△: Film was damaged, while plating damage was slight.

×: Film was damaged, and plating damage was serious.

Table 6

No.	Resistance to thermal discoloration	Resistance to smoke emission	Corrosion resistance before heating	Corrosion resistance after heating	Damage resistance
1	◎	◎	○	◎	○
2	◎	◎	◎	◎	○
3	◎	◎	○+	◎	○
4	○	◎	○+	◎	○
5	○	◎	○+	◎	○
6	◎	◎	○+	◎	○
7	◎	◎	◎	◎	○
8	◎	◎	◎	◎	○
9	◎	◎	◎	◎	○
10	◎	◎	◎	◎	○
11	○	◎	○+	◎	○
12	○	◎	○+	◎	○
13	◎	◎	◎	◎	○
14	○	◎	◎	◎	○
15	◎	◎	◎	◎	○
16	◎	◎	◎	◎	○
17	◎	◎	◎	◎	○
18	◎	◎	○	◎	○
19	◎	◎	◎	◎	○
20	◎	◎	◎	◎	○
21	◎	◎	◎	◎	○

Table 7

No.	Resistance to thermal discoloration	Resistance to smoke emission	Corrosion resistance before heating	Corrosion resistance after heating	Damage resistance
22	◎	◎	◎	◎	○
23	◎	◎	◎	◎	○
24	◎	◎	◎	◎	○
25	◎	◎	◎	◎	○
26	◎	◎	○+	○	○
27	◎	◎	○	○	○
28	△	◎	◎	◎	○
29	◎	◎	△	△	○
30	◎	◎	○	○	○
31	◎	◎	×	○	○
32	◎	○	◎	○	○
33	◎	○	◎	○	○
34	◎	○	◎	○	○
35	◎	○	◎	○	○
36	◎	○	◎	○	○
37	◎	○	◎	○	○
38	△	×	◎	×	○
39	×	×	◎	×	○
40	×	×	◎	×	○
41	◎	◎	△	×	×
42	◎	○	◎	◎	◎

Table 8

No.	Resistance to thermal discoloration	Resistance to smoke emission	Corrosion resistance before heating	Corrosion resistance after heating	Damage resistance
43	⊙	○	⊙	⊙	⊙
44	⊙	○	⊙	⊙	⊙
45	⊙	○	⊙	⊙	⊙
46	⊙	○	⊙	⊙	⊙
47	⊙	○	⊙	⊙	⊙
48	⊙	⊙	⊙	⊙	○
49	⊙	△	⊙	⊙	○
50	⊙	⊙	△	×	○
51	⊙	⊙	⊙	⊙	○
52	○	○	⊙	⊙	⊙
53	⊙	⊙	⊙	○	○
54	⊙	○	⊙	⊙	⊙
55	⊙	△	⊙	⊙	⊙
56	△	⊙	△	×	×
57	○	○	○	○	○
58	⊙	○	⊙	⊙	⊙
59	○	○	○+	○	⊙
60	○	○	○+	○	⊙
61	○	○	○+	⊙	⊙
62	⊙	○	⊙	⊙	⊙

As seen in Tables 3 to 5 and Tables 6 to 8, all of the zinc-base coated steel sheets that have film according to the present invention gave excellent resistance to thermal discoloration, resistance to smoke emission, resistance to corrosion before and after heating, and damage resistance. To the contrary, Comparative Examples are inferior to the Examples according to the present invention in terms of any of the resistance to thermal discoloration, the resistance to smoke emission, the resistance to corrosion before and after heating, and the damage resistance.

As described above, the coated steel sheets according to the present invention have excellent resistance to thermal discoloration and resistance to smoke emission in environments exposed to high temperatures, and have excellent resistance to corrosion before and after heating without using chromium. Furthermore, the coated steel sheets according to the present invention show excellent resistance to flaw on the film and the coating surface, and excellent adhesiveness of the film on being worked to form various parts.

What is claimed is:

1. A coated steel sheet comprising:

a zinc-base plated steel sheet;

a composite oxide film formed on the surface of the zinc-base coated steel sheet;

the composite oxide film containing structural components of (α) oxide fine particles and (β) phosphoric acid and/or phosphoric acid compound;

the composite oxide film having a total coating weight of the component (α) and the component (β) converted to P_2O_5 in a range of from 5 to 4000 mg/m²;

a straight silicone resin film formed on the surface of the composite oxide film;

the straight silicone resin film containing a SiO_2 component at a coating weight converted to SiO_2 of from 0.1 to 3 g/m².

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

the composite oxide film further contains at least one component (γ) selected from the group consisting of Mg, Ca, Sr, Li, Mn, Fe, Co, Ni, Zn, Al, La, and Ce; and

the composite oxide film has a total coating weight of the (α) oxide fine particles, the component (β) converted to P_2O_5 , and the at least one component (γ) converted to metal in a range from 5 to 4000 mg/m².

3. The coated steel sheet according to claim 2, wherein the at

least one component (γ) in the composite oxide film is Mn and/or Al.

4. The coated steel sheet according to any one of claims 1 to 3, wherein the oxide fine particles (α) in the composite oxide film are those of silicon dioxide.

5. The coated steel sheet according to claim 4, wherein the silicon dioxide has a coating weight in terms of SiO_2 , said coating weight has a mass ratio of from 5 to 95 wt% to the total coating weight of the composite oxide film.

6. The coated steel sheet according to any one of claims 2 to 5, wherein

the composite oxide film has a molar ratio ($\text{P}_2\text{O}_5/\text{Me}$) of the component (β) converted to P_2O_5 to the at least one component (γ) selected from the group consisting of Mg, Ca, Sr, Li, Mn, Fe, Co, Ni, Zn, Al, La, and Ce, converted to metal, (for the case of two or more of metals, the sum of respective metal-converted values);

the molar ratio ($\text{P}_2\text{O}_5/\text{Me}$) is in a range of from 1/2 to 2/1.

7. The coated steel sheet as in any of claims 1 to 6, wherein the straight silicone resin film contains methyl group as an organic group.

8. The coated steel sheet according to any one of claims 1 to

7, wherein the straight silicone resin film has a SiO_2 component in an amount of 60 mass% or more thereof.

9. The coated steel sheet according to any one of claims 1 to 8, wherein the straight silicone resin film contains a crystalline lubricant in an amount of 20 parts by mass or less to 100 parts by mass of the straight silicone resin.

10. The coated steel sheet according to any one of claims 1 to 8, wherein the straight silicone resin film contains an organic-base lubricant having 70°C or higher softening point in an amount of 20 parts by mass or less to 100 parts by mass of the straight silicone resin.

11. A method for manufacturing coated steel sheet comprising the steps of:

(a) treating at least one side of a zinc-base coated steel sheet by an aqueous solution containing (i) 0.001 to 3.0 mol/l of oxide fine particles and (ii) 0.001 to 6.0 mol/l of phosphoric acid and/or phosphoric acid compound, converted to P_2O_5 ;

(b) forming a composite oxide film as a first layer film on the surface of the coated steel sheet by heating to dry the coated steel sheet after treated by the aqueous solution to a coating weight in a range of from 5 to 4000 mg/m^2 , which composite oxide film contains (α) oxide fine particles and (β) phosphoric acid and/or phosphoric acid compound, as structuring components thereof; and

(c) applying a painting composition consisting mainly of a straight silicone resin onto the composite oxide film, and heating to dry thereof, thus forming a second layer film at a coating weight converted to SiO_2 in a range of from 0.1 to 3 g/m².

12. A method for manufacturing coated steel sheet comprising the steps of:

(a) treating at least one side of a zinc-base plated steel sheet by an aqueous solution containing (i) 0.001 to 3.0 mol/l of oxide fine particles, (ii) 0.001 to 6.0 mol/l of phosphoric acid and/or phosphoric acid compound, converted to P_2O_5 , and (iii) 0.0001 to 3.0 mol/l of at least one element selected from the group consisting of Mg, Ca, Sr, Li, Mn, Fe, Co, Ni, Zn, Al, La, and Ce, as the sum of respective metal-converted values;

(b) forming a composite oxide film as a first layer film on the surface of the coated steel sheet by heating to dry the coated steel sheet after treated by the aqueous solution to a coating weight in a range of from 5 to 4000 mg/m², which composite oxide film contains (α) oxide fine particles, (β) phosphoric acid and/or phosphoric acid compound, and (γ) at least one element selected from the group consisting of Mg, Ca, Sr, Li, Mn, Fe, Co, Ni, Zn, Al, La, and Ce, as structuring components thereof; and

(c) applying a painting composition consisting mainly of a straight silicone resin onto the composite oxide film, and heating to dry thereof, thus forming a second layer film at a coating weight converted to SiO_2 in a range of from 0.1 to 3 g/m².