of a metal Co amount, Mg, and Zn; and an organic resin film that is provided in an upper layer of the Co-Mg-Zn layer.

[0013]

(2) In the hot-dip galvanized steel sheet according to (1), the hot-dip galvanized layer may further contain one or more of Li: 0.001 mass% to 0.200 mass%, Na: 0.001 mass% to 0.200 mass%, K: 0.001 mass% to 0.200 mass%, Ca: 0.001 mass% to 0.200 mass%, Sr: 0.001 mass% to 0.200 mass%, Sc: 0.001 mass% to 0.200 mass%, Y: 0.001 mass% to 0.200 mass%, Ti: 0.001 mass% to 0.200 mass%, Zr: 0.001 mass% to 0.200 mass%, Cu: 0.001 mass% to 0.200 mass%, Sn: 0.001 mass% to 0.200 mass%, Si: 0.001 mass% to 0.200 mass%, and misch metal: 0.001 mass% to 0.200 mass%.

[0014]

(3) In the hot-dip galvanized steel sheet according to (1) or (2), the organic resin film may contain one or more of phosphoric acid and salts thereof, pyrophosphoric acid and salts thereof, metaphosphoric acid and salts thereof, polyphosphoric acid and salts thereof, phytic acid, and 1-hydroxyethylidene-1,1-diphosphonic acid, and one or more of a V compound, a Si compound, a Ti compound, and a Zr compound.

[0015]

(4) A method for producing a hot-dip galvanized steel sheet according to another aspect of the present invention is a method for producing the hot-dip galvanized steel sheet according to any one of (1) to (3), including forming a hot-dip galvanized layer containing Mg: 0.05 mass% to 2.00 mass%, Al: 0.1 mass% or more and less than 1.0 mass%, Ni: 0.05 mass% to 2.00 mass%, and a remainder including Zn and impurities on a surface of a steel sheet; forming a Co-Mg-Zn layer by contacting the steel sheet having the hot-dip galvanized layer with an acidic aqueous

solution containing 0.1 g/L to 0.5 g/L of Co ions, 0.2 g/L to 2.0 g/L of Zn ions, and 0.1 g/l to 2.0 g/l of Mg ions; and forming an organic resin film by applying a liquid for forming organic resin film to a surface of the Co-Mg-Zn layer and drying the liquid for forming organic resin film.

[0016]

(5) In the method for producing the hot-dip galvanized steel sheet according to (4), a concentration of the Co ions contained in the acidic aqueous solution may be lower than a concentration of the Zn ions, and lower than a concentration of the Mg ions.

[0017]

(6) In the method for producing the hot-dip galvanized steel sheet according to (4) or (5), a pH of the acidic aqueous solution may be 1 to 3, a temperature of the acidic aqueous solution may be 40°C or lower, and a time for contacting the steel sheet having the hot-dip galvanized layer with the acidic aqueous solution may be 5 seconds or shorter.

[Effects of the Invention]

[0018]

The hot-dip galvanized steel sheet of the present invention is excellent in all of white rust resistance, red rust resistance, and blackening resistance.

[Brief Description of the Drawings]

[0019]

Fig. 1 is a graph showing the relationship between the adhesion amount of Co and the blackening resistance in a hot-dip galvanized steel sheet including a Co-Mg-Zn layer and a chromate-free organic resin film.

Fig. 2 is a graph showing the relationship between the adhesion amount of Co

and the white rust resistance in the hot-dip galvanized steel sheet including a Co-Mg-Zn layer and a chromate-free organic resin film.

Fig. 3 is a graph showing the relationship between the adhesion amount of Co and the red rust resistance in the hot-dip galvanized steel sheet including a Co-Mg-Zn layer and a chromate-free organic resin film.

Fig. 4 is a graph showing the relationship between the adhesion amount of Co and the blackening resistance in a hot-dip galvanized steel sheet including a Co-Mg-Zn layer and a chromate film.

Fig. 5 is a graph showing the relationship between the adhesion amount of Co and the white rust resistance in the hot-dip galvanized steel sheet including a Co-Mg-Zn layer and a chromate film.

Fig. 6 is a graph showing the relationship between the adhesion amount of Co and the red rust resistance in the hot-dip galvanized steel sheet including a Co-Mg-Zn layer and a chromate film.

Fig. 7 is a schematic view showing a layer configuration of a hot-dip galvanized steel sheet according to an embodiment.

Fig. 8 is a graph showing the result of the analysis of the hot-dip galvanized steel sheet according to the embodiment by a GDS.

Fig. 9 is a graph showing the result of the analysis of a hot-dip galvanized steel sheet by a GDS in a case where an organic resin film containing Co is formed on a hot-dip galvanized layer.

[Embodiments of the Invention]

[0020]

Hereinafter, a hot-dip galvanized steel sheet according to an embodiment and a method for producing the same will be described with reference to drawings.

Unless otherwise specified, "%" means "mass%".

(Hot-dip galvanized steel sheet 10)

First, a hot-dip galvanized steel sheet 10 according to an embodiment will be described.

Fig. 7 is a schematic view showing a layer configuration of the hot-dip galvanized steel sheet 10 according to the embodiment. As shown in Fig. 7, the hot-dip galvanized steel sheet 10 includes a steel sheet 1, a hot-dip galvanized layer 3 that is provided on the surface of the steel sheet 1 and contains Mg: 0.05 mass% to 2.00 mass%, Al: 0.1 mass% or more and less than 1.0 mass%, Ni: 0.05 mass% to 2.00 mass%, and a remainder consisting of Zn and impurities, a Co-Mg-Zn layer 5 that is provided on the surface of the hot-dip galvanized layer 3 and contains 0.1 mg/m^2 to 2.0 mg/m^2 of Co precipitates 4 in terms of a metal Co amount, Mg 6 and Zn 8, and an organic resin film 7 that is provided in the upper layer of the Co-Mg-Zn layer 5.

[0021]

<Steel Sheet 1>

The steel sheet 1 used for the hot-dip galvanized steel sheet 10 is not particularly limited and a steel sheet that is typically used for a hot-dip galvanized steel sheet can be used. The production method, materials, and the like for the steel sheet 1 are not particularly limited and the steel sheet may be produced through steps of hot rolling, pickling, cold rolling, annealing, temper rolling, and the like from a normal steel piece producing step.

[0022]

<Hot-Dip Galvanized Layer 3>

The hot-dip galvanized layer 3 is provided on the surface of the steel sheet 1 and contains Mg: 0.05 mass% to 2.00 mass%, Al: 0.1 mass% or more and less than 1.0

mass%, Ni: 0.05 mass% to 2.00 mass%, and a remainder consisting of Zn and impurities.

The hot-dip galvanized layer 3 may further contain one or two or more elements of Li, Na, K, Ca, Sr, Sc, Y, Ti, Zr, Cu, Sn, Si, misch metal, and the like in an amount of 0.200 mass% or less, preferably 0.001 mass% to 0.200 mass%, and more preferably 0.001 mass% to 0.100 mass%, respectively. The above-described elements contribute to achieving uniform solidification of the hot-dip galvanized layer 3 and improving external appearance, blackening resistance, and corrosion resistance, particularly, white rust resistance and red rust resistance in a case of a thick coating.

The hot-dip galvanized layer 3 does not contain Co except a case where Co is unavoidably mixed in the production process.

[0023]

In a case where Mg is less than 0.05%, while blackening resistance and white rust resistance are improved, red rust resistance is deteriorated and thus this case is not preferable. In a case where Mg is more than 2.00%, the external appearance is likely to be deteriorated and the blackening resistance and white rust resistance are also deteriorated. Thus, this case is not preferable. Therefore, the Mg is set to 0.05% to 2.00%. The Mg concentration is more preferably in a range of 0.30% to 1.00%.

[0024]

In a case where Al is less than 0.1%, a Zn-Fe alloy layer is developed at the interface between the steel sheet 1 and the hot-dip galvanized layer 3 and thus red rust resistance is deteriorated. Thus, this case is not preferable. In a case where Al is 1.0% or more, it is difficult to increase the adhesion amount of the hot-dip galvanized layer 3 and red rust resistance is deteriorated in some cases. Thus, this case is not preferable. Therefore, Al is set to 0.1% or more and less than 1.0%.

The upper limit of the Al concentration is preferably 0.85% and may be 0.8%, 0.75%, or 0.5%. The lower limit of the Al concentration is preferably 0.2% and more preferably 0.25%.

[0025]

In a case where the hot-dip galvanized layer 3 contains Mg, a Mg concentrated portion (not shown) is easily generated near the surface of the hot-dip galvanized layer 3. That is, as the hot-dip galvanized layer 3 is viewed from a depth direction, the Mg concentration near the surface is higher than the Mg concentration on the inner side. In addition, since Mg has a higher tendency to ionize than Fe and Zn in the steel sheet 1, Mg tends to be dissolved out before Fe and Zn are dissolved out (sacrificial protection action). In a case where the hot-dip galvanized layer 3 contains Mg, it is assumed that Mg is locally eluted by the uneven localization of Mg in the depth direction and the sacrificial protection action of Mg, and blackening resistance and white rust resistance are deteriorated.

[0026]

The above-described deterioration of blackening resistance and white rust resistance is remarkable in a case where the Al concentration of the hot-dip galvanized layer 3 is lower than the Mg concentration.

In a case where the Al concentration is higher than the Mg concentration in the hot-dip galvanized layer 3, at least one of an Al phase and a Zn-Al-Mg ternary eutectic phase is formed in the hot-dip galvanized layer 3. In these structures, it is assumed that due to the effect of the passivation action of Al, the sacrificial protection action of Mg is alleviated.

On the other hand, in a case where the Al concentration is lower than the Mg concentration in the hot-dip galvanized layer 3, the sacrificial protection action of Mg

is stronger than the passivation action of Al. Therefore, it is assumed that blackening resistance and white rust resistance are likely to be deteriorated by the sacrificial protection action of Mg and the uneven localization of Mg in the depth direction.

In addition, in a case where Co is caused to adhere to the surface layer of the hot-dip galvanized layer 3 due to the sacrificial protection action of Mg, the adhered Co tends to be easily unevenly distributed. This is also assumed to cause deterioration in blackening resistance and corrosion resistance.

[0027]

In a case where the Ni content of the hot-dip galvanized layer 3 is less than 0.05%, it is difficult to achieve both blackening resistance and white rust resistance and thus this case is not preferable. In a case where the Ni content of the hot-dip galvanized layer 3 is more than 2.00%, the external appearance of the hot-dip galvanized layer 3 is likely to be deteriorated and red rust resistance is deteriorated. Thus, this case is not preferable. Therefore, Ni is set to 0.05% to 2.00%. The Ni content of the hot-dip galvanized layer 3 is more preferably in a range of 0.10% to 1.00%.

Since the hot-dip galvanized layer 3 contains Ni in addition to Mg, it is considered that the uneven distribution of Mg in the depth direction can be alleviated.

[0028]

The content of each element included in the hot-dip galvanized layer 3 can be measured by a wet ICP-MS method.

[0029]

The adhesion amount of the hot-dip galvanized layer 3 is 150 g/m^2 or more, preferably 200 g/m^2 or more, and more preferably 300 g/m^2 or more per one surface from the viewpoint of suitably securing red rust resistance. By setting a large

adhesion amount as described above, for example, red rust resistance at a level at which red rust is not generated for SST 2000 hours or longer can be secured.

The adhesion amount of the hot-dip galvanized layer 3 is not limited to the above adhesion amount and even in a case where the adhesion amount is smaller than the above adhesion amount, the steel sheet can be used depending on the required level of red rust resistance. In the related art, particularly, in a case where the adhesion amount of the hot-dip galvanized layer 3 is large, it is difficult to achieve both blackening resistance and white rust resistance. Thus, in a case where the adhesion amount of the hot-dip galvanized layer 3 is large, the effects of the present invention become more remarkable.

The upper limit of the adhesion amount of the hot-dip galvanized layer 3 is not particularly limited and considering practical manufacturability, the upper limit is about 600 g/m^2.

[0030]

<Co-Mg-Zn Layer 5>

The hot-dip galvanized steel sheet 10 includes the Co-Mg-Zn layer 5 containing 0.1 mg/m^2 to 2.0 mg/m^2 of Co precipitates 4 in terms of a metal Co amount, Mg 6 and Zn 8 on the hot-dip galvanized layer 3.

The Co-Mg-Zn layer 5 contains the Co precipitates 4 precipitated on the surface of the hot-dip galvanized layer 3, Mg 6, and Zn 8. As shown in Fig. 7, it is assumed that the Co-Mg-Zn layer 5 covers a part of the surface of the hot-dip galvanized layer 3 and a part of the surface of the hot-dip galvanized layer 3 is not covered by the Co-Mg-Zn layer 5.

[0031]

The Co precipitates 4 precipitated on the hot-dip galvanized layer 3 are stably

present in the Co-Mg-Zn layer 5. It is considered that suitable adhesion between the hot-dip galvanized layer 3 and the organic resin film 7 is exhibited by the stably present Co precipitates 4, resulting in excellent white rust resistance, red rust resistance, and blackening resistance of the steel sheet of the present invention.

The Co precipitates 4 contained in the Co-Mg-Zn layer 5 may be any of metal Co, Co oxide, and Co hydroxide.

[0032]

In a case where the Co content of the Co-Mg-Zn layer 5 is more than 2.0 mg/m^2 in terms of metal Co, white rust resistance is deteriorated. Thus, the upper limit of the Co content of the Co-Mg-Zn layer 5 is 2.0 mg/m^2. The upper limit of the Co content of the Co-Mg-Zn layer 5 is preferably 1.0 mg/m^2.

Even at a Co content of about 0.1 mg/m^2, which is the detection limit, in the Co-Mg-Zn layer 5, a sufficient blackening resistance effect is exhibited but in the embodiment, the lower limit of the Co content is determined as 0.1 mg/m^2.

Accordingly, the Co content of the Co-Mg-Zn layer 5 is 0.1 mg/m^2 to 2.0 mg/m^2 and preferably 0.1 mg/m^2 to 1.0 mg/m^2.

The Co content can be measured by a wet ICP-MS method.

[0033]

The formation of the Co-Mg-Zn layer 5 between the hot-dip galvanized layer 3 and the organic resin film 7 can be confirmed by using a Glow Discharge Spectrometer (GDS).

Fig. 8 is a graph showing the analysis result of the hot-dip galvanized steel sheet 10 according to the embodiment by a GDS. Fig. 9 is a graph showing the analysis result of a hot-dip galvanized steel sheet by a GDS in a case where an organic resin film containing Co is formed on a hot-dip galvanized layer (that is, in a case

where a Co-Mg-Zn layer is not formed).

[0034]

In Figs. 8 and 9, the position where C is present represents a depth position in which the organic resin film 7 is formed, the position where Co is present represents depth position in which the Co-Mg-Zn layer 5 is formed, and the positions where Mg and Zn are present represent a depth position in which the hot-dip galvanized layer 3 is formed.

From the result shown in Fig. 8, it is found that the Co-Mg-Zn layer 5 is formed between the organic resin film 7 and the hot-dip galvanized layer 3 in the hot-dip galvanized steel sheet 10. On the other hand, from the result shown in Fig. 9, it is found that in a case where the Co-Mg-Zn layer 5 is not formed, the peak of Co is not detected between the organic resin film 7 and the hot-dip galvanized layer 3 and the peak of Co is generally consistent with the peak of C (that is, Co is dispersed in the organic resin film 7).

[0035]

The Mg content and the Zn content in the Co-Mg-Zn layer 5 are not particularly limited as long as the Co precipitates 4 are allowed to be stably present.

[0036]

<Organic Resin Film 7>

The hot-dip galvanized steel sheet 10 has the organic resin film 7 in the upper layer of the Co-Mg-Zn layer 5.

[0037]

Examples of the organic resin included in the organic resin film 7 are a polyolefin-based resin, a urethane-based resin, an acrylic resin, an epoxy-based resin, and a polyester-based resin.

The organic resin content in the organic resin film 7 is an arbitrary content and not particularly limited.

[0038]

These organic resins has an action of improving red rust resistance by increasing the barrier properties of the organic resin film 7, particularly by increasing a corrosion product (white rust) retaining effect after the lapse of a long period of time. In addition, it is assumed that the organic resins exhibit an action of improving blackening resistance and corrosion resistance by the action of the Co precipitates 4 which are stably present on the outermost layer of the hot-dip galvanized layer 3 after the Co-Mg-Zn layer 5 is formed.

The formation of the organic resin film 7 can be confirmed by observing the peak peculiar to the organic resin by an FT-IR method. In addition, the organic resin film 7 being chromate-free can be confirmed by the component analysis of the organic resin film 7 (for example, chemical analysis such as a wet ICP-MS method or the like or physical analysis such as GDS or the like). Form the above analysis, the organic resin film 7 is evaluated to be chromate-free as long as the amount of Cr is below the detection limit or the background level or lower.

[0039]

It is preferable that the organic resin film 7 has the organic resin as the main component and further contains one or more of phosphoric acid and salts thereof, pyrophosphoric acid and salts thereof, metaphosphoric acid and salts thereof, polyphosphoric acid and salts thereof, phytic acid, and 1-hydroxyethylidene-1,1-diphosphonic acid.

[0040]

One or more of phosphoric acid and salts thereof, pyrophosphoric acid and

salts thereof, metaphosphoric acid and salts thereof, polyphosphoric acid and salts thereof, phytic acid, and 1-hydroxyethylidene-1,1-diphosphonic acid (hereinafter, phosphoric acid and salts thereof, pyrophosphoric acid and salts thereof, metaphosphoric acid and salts thereof, polyphosphoric acid and salts thereof, phytic acid, and 1-hydroxyethylidene-1,1-diphosphonic acid are generally referred as phosphate compounds and the like) has the effect of improving white rust resistance by causing Zn ions and Mg ions which are generated in the initial stage of corrosion to be precipitated in the form of hardly soluble salts. In addition, it is assumed that the phosphate compound in the organic resin film 7 is likely to have any interaction with the outermost layer of the hot-dip galvanized layer 3, particularly, the outermost layer of the hot-dip galvanized layer 3 after the Co-Mg-Zn layer 5 is formed, and thus the effect of improving blackening resistance and corrosion resistance is exhibited.

The phosphate compound content in the organic resin film 7 is arbitrary and not particularly limited.

[0041]

It is preferable that the organic resin film 7 further contains one or more selected from the group consisting of a V compound, a Si compound, a Ti compound, and a Zr compound, in addition to the organic resin and the phosphate compound and the like.

[0042]

Examples of the V compound include vanadium pentoxide, metavanadic acid and salts thereof, polyvanadic acid and salts thereof, vanadium trioxide, vanadium dioxide, vanadyl oxalate, vanadium oxy acetylacetonate, vanadium acetylacetonate, and vanadium acetate.

The V compound also has the effect of improving white rust resistance by

causing Zn ions and Mg ions generated in the initial stage of corrosion to be precipitated in the form of hardly soluble salts, similar to the phosphate compound and the like. Although the mechanism is not clear, the effect of improving white rust resistance by the V compound becomes remarkable in a case where the V compound and the phosphate compound and the like co-exist.

[0043]

The V compound content in the organic resin film 7 is arbitrary and not particularly limited.

[0044]

Examples of the Si compound include silica, silicate, and silane coupling agents.

Preferable examples of silica include a water-based dispersion of colloidal silica or the like and SNOWTEX C, SNOWTEX O, SNOWTEX N (all manufactured by Nissan Chemical Industries, Ltd.), and the like can be used. Examples of silicate include Na silicate, Li silicate, and K silicate.

[0045]

Examples of silane coupling agents that can be used include vinylmethoxysilane, vinyltrimethoxysilane, vinylethoxysilane, vinyltriethoxysilane, 3-aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane, N-(1,3-dimethylbutylidene)-3-(triethoxysilyl)-1-propanamine, N,N'-bis(3-(trimethoxysilyl)propyl)ethylenediamine, N-(β-aminoethyl)-γ-aminopropylmethyldimethoxysilane, N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane, γ-aminopropyltrimethoxysilane, γ-aminopropyltriethoxysilane, γ-glycidoxypropyltrimethoxysilane, γ-glycidoxypropyltriethoxysilane, γ-

glycidoxypropylmethyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ-methacryloxypropyltrimethoxysilane, γ-methacryloxypropyltriethoxysilane, γ-mercaptopropyltrimethoxysilane, γ-mercaptopropyltriethoxysilane, and N-(2-(vinylbenzylamino)ethyl)-3-aminopropyltrimethoxysilane, and polycondensates thereof can be also used.

[0046]

The Si compound content in the organic resin film 7 is arbitrary and not particularly limited.

[0047]

Examples of the Ti compound include titanium acetate, titanium carbonate, tetraisopropyl titanate, titanium acetyl acetonate, titanium tetraacetyl acetonate, titanium lactate, titanium triethanol aminate, titanium diethanol aminate, titanium aminoethyl aminoethanolate, titanium hydrofluoric acid, and ammonium titanium fluoride.

The Ti compound content in the organic resin film 7 is arbitrary and not particularly limited.

[0048]

Examples of the Zr compound include zirconyl acetate, ammonium zirconyl carbonate, normal propyl zirconate, zirconium tetraacetylacetonate, zirconium ethylacetoacetate, zirconium stearate, ammonium zirconium lactate, zirconium hydrofluoric acid, and ammonium zirconium fluoride.

The Zr compound content in the organic resin film 7 is arbitrary and not particularly limited.

[0049]

All of the Si compound, the Ti compound, and the Zr compound reinforce the

barrier properties of the organic resin film 7 and exhibit the action of improving both white rust resistance and red rust resistance.

The respective component contents in the organic resin film 7 can be measured by a GDS.

[0050]

The organic resin film 7 may contain a wax or the like, in addition to the above-described compounds, for the purpose of improving sliding ability and the like. In addition, the organic resin film 7 may contain an antirust agent for the purpose of further improving corrosion resistance. The organic resin film 7 may further contain a pigment, a dye, a coloring agent, a surfactant, and the like for the purpose of improving or controlling the external appearance.

[0051]

The thickness of the organic resin film 7 is 0.1 μm to 10.0 μm, preferably 0.3 μm to 3.0 μm, and more preferably 0.5 μm to 2.0 μm. In a case where the thickness of the organic resin film 7 is less than 0.1 μm, corrosion resistance may be not sufficient and thus this case is not preferable. In addition, in a case where the thickness of the organic resin film 7 is more than 10.0 μm, not only is the cost increased but also the welding becomes difficult in some cases. Thus, this case is not preferable.

The thickness of the organic resin film 7 can be measured by vertically embedding and polishing a sample whose thickness is to be measured and observing the sample with an SEM.

[0052]

(Method for Producing Hot-dip galvanized steel sheet 10)

Next, a method for producing the hot-dip galvanized steel sheet 10 will be

described.

<Formation of Hot-Dip Galvanized Layer 3>

A method for forming the hot-dip galvanized layer 3 on the steel sheet 1 is not particularly limited and any known hot-dip coating method such as an oxidation reduction method, an all reduction method, or a pre-coating method can be used.

[0053]

The concentration of a coating bath is adjusted so that the hot-dip galvanized layer 3 has the above-described chemical composition. In a case where the chemical composition of the coating bath and the chemical composition of the hot-dip galvanized layer 3 are compared, there is a tendency that the amount of Mg and the amount of Ni are almost equal in the both chemical compositions, but the amount of Al is slightly larger in the chemical composition of the hot-dip galvanized layer 3 than in the chemical composition of the coating bath. In addition, since the concentration of Ni that is soluble in the coating bath is about 0.1% at most, in a case where Ni of which the amount is equal to or more than 0.1% is incorporated in the hot-dip galvanized layer 3, it is preferable that Ni is pre-coated and then hot-dip coating is performed.

After the hot-dip galvanized layer 3 is formed, as required, temper rolling can be performed. Thus, the surface roughness degree and the external appearance can be controlled.

[0054]

<Formation of Co-Mg-Zn Layer 5>

After the hot-dip galvanized layer 3 is formed or after temper rolling is performed, the surface of the hot-dip galvanized layer 3 is subjected to a flash treatment using an acidic aqueous solution containing Co ions. Thus, the Co-Mg-Zn

layer 5 containing 0.1 mg/m^2 to 2.0 mg/m^2 of Co precipitates 4 in terms of a metal Co amount, Mg 6, and Zn 8 is formed on the hot-dip galvanized layer 3.

[0055]

The acidic aqueous solution containing Co ions contains 0.1 g/L to 0.5 g/L of Co ions, 0.2 g/L to 2.0 g/L of Zn ions, and 0.1 g/l to 2.0 g/l of Mg ions.

It is assumed that since the hot-dip galvanized layer 3 has a low Al content, the reactivity with the acidic aqueous solution is high. Therefore, it is considered that in a case of using an alkaline water-based surface conditioner, the adhesion amount of the Co precipitates 4 is not stable and suitable corrosion resistance and blackening resistance are hardly obtained.

[0056]

In a case where the amount of Co ions in the acidic aqueous solution containing Co ions is less than 0.1 g/L, Co does not adhere to the hot-dip galvanized layer in some cases and is not stable. In addition, in a case where the amount of Co ions in the acidic aqueous solution containing Co ions is more than 0.5 g/L, the adhesion amount of the Co precipitates 4 is excessive in some cases and thus this case is not preferable.

In a case where the amount of Zn ions is less than 0.2 g/L, the Co precipitates 4 are not stable, and thus the adhesion state of the Co precipitates 4 is likely to be uneven. In a case where the amount of Zn ions is more than 2.0 g/L, the surface of the hot-dip galvanized layer 3 is stained in some cases and thus this case is not preferable.

In a case where the amount of Mg ions is less than 0.1 g/L, the Co precipitates 4 are not stable, and thus the adhesion state of the Co precipitates 4 is likely to be uneven. In a case where the amount of Mg ions is more than 2.0 g/L, the surface of

the hot-dip galvanized layer 3 is stained in some cases and thus this case is not preferable.

[0057]

It is considered that in a case where the acidic aqueous solution containing Co ions including Co ions, Zn ions, and Mg ions is brought into contact with the hot-dip galvanized layer 3, the most active Mg concentrated portion in the hot-dip galvanized layer 3 undergoes reaction and a metal, oxide, or hydroxide including Co, Zr, and Mg is precipitated here. That is, it is assumed that Zn and Mg in the acidic aqueous solution containing Co ions are partially co-deposited to contribute to the stabilization of the adhesion amount of Co and the performance of the Co-Mg-Zn layer 5. It was first found by the invention of this application that by adding not only Co ions but also Zn ions and Mg ions to the acidic aqueous solution containing Co ions, the above-described effect can be obtained.

It is considered that Co and Zn are precipitated in a state of metal, oxide, or hydroxide and Mg is precipitated in a state of oxide or hydroxide. However, since the precipitated amount of these compounds is very small and the hot-dip galvanized layer 3 below the Co-Mg-Zn layer 5 also includes Zn and Mg, these compounds cannot be identified.

[0058]

For the Co ions, Zn ions, and Mg ions included in the acidic aqueous solution containing Co ions, sulfate, chloride, nitrate, and the like can be used. For the Co ions, Zn ions, and Mg ions, phosphate and fluoride are preferably used.

[0059]

Examples of other ions that the acidic aqueous solution containing Co ions may contain are Al ions (aluminate ions). Since Al ions do not affect the precipitation

behavior of Co, the acidic aqueous solution containing Co ions may contain Al ions.

Although the acidic aqueous solution containing Co ions may contain Fe ions, Fe ions tend to deteriorate the corrosion resistance of the hot-dip galvanized steel sheet 10. Thus, it is preferable that the Fe ion concentration of the acidic aqueous solution containing Co ions is limited to 0.1 g/L or less.

[0060]

In order to stably control the Co-Mg-Zn layer 5, it is preferable to set the Zn ion concentration to be higher than the Co ion concentration in the acidic aqueous solution containing Co ions. In the same manner, it is preferable to set the Mg ion concentration to be higher than the Co ion concentration in the acidic aqueous solution containing Co ions.

It is more preferable that in the acidic aqueous solution containing Co ions, the Zn ion concentration is set to be two times higher than the Co ion concentration and the Mg ion concentration is set to be higher than the Co ion concentration.

[0061]

It is preferable that the pH of the acidic aqueous solution containing Co ions is 1 to 3, the temperature of the acidic aqueous solution containing Co ions is 40°C or lower, and the time for contacting the hot-dip galvanized layer 3 with the acidic aqueous solution containing Co ions is 5 seconds or shorter from the viewpoint of stabilizing the Co-Mg-Zn layer 5. The method for contacting the acidic aqueous solution containing Co ions with the hot-dip galvanized layer 3 is not particularly limited and an immersion method, a spray method, and the like may be used.

[0062]

<Formation of Organic Resin Film 7>

After the Co-Mg-Zn layer 5 is formed, washing with water and drying are

performed. Then, the liquid for forming organic resin film having the above-described chemical composition is applied and dried to form the organic resin film 7. The methods for application and drying are not particularly limited.

[Examples]

[0063]

Next, the present invention will be described in more detail with reference to Examples and Comparative Examples.

<Example 1>

The features of the present invention are described using Figs. 1 to 6. Hot-dip galvanized steel sheets having three kinds of coating compositions produced in a continuous hot dip galvanizing line were used. For the coating compositions, the following three kinds of compositions were adopted and in all the compositions, the adhesion amount of coating was 250 g/m^2 (per one surface). Herein, "%" represents "mass%".

(1) Al: 0.2%, Mg: 0.5%, Ni: 0.1%, and a remainder of Zn and unavoidable impurities (referred to as Zn-0.2Al-0.5Mg-0.1Ni)

(2) Al: 0.2%, Mg: 0.5%, and a remainder of Zn and unavoidable impurities (referred to as Zn-0.2Al-0.5Mg)

(3) Al: 0.2%, and a remainder of Zn and unavoidable impurities (referred to as Zn-0.2Al)

[0064]

The hot-dip galvanized steel sheets produced above were treated with an acidic aqueous solution containing Co ions. For the acidic aqueous solution containing Co ions, C or J in Table 1 was used.

A chromate film or an organic resin film was formed in the upper layer of the

Co-Mg-Zn layer. For the organic resin film, a1 in Table 2 was used and the thickness of the organic resin film was set to 1 μm. For the chromate film, a general chromate film formed of reduced chromic acid, silica, and phosphoric acid (a chromate film having an adhesion amount of Cr of 58 mg/m^2, which is corresponding to Invention Example 6 in Table 1 of Japanese Examined Patent Application, Second Publication No. H04-20992) was used.

[0065]

The above hot-dip galvanized steel sheets were used to investigate blackening resistance, white rust resistance, and red rust resistance.

The blackening resistance was measured as follows. First, the evaluation surfaces of the hot-dip galvanized steel sheets (the surfaces of the organic resin film) were overlapped to face each other and packaged (the packaged hot-dip galvanized steel sheets are referred to as a blackening resistance test piece). Thereafter, the blackening resistance test piece was retained in an environment at 70°C and 85% RH for 1 week and a change in brightness (ΔL*) before and after retention was measured. A case where a change in brightness was 3.0 or less was evaluated as pass.

[0066]

The white rust resistance was measured as follows. That is, a salt spray test (SST) defined in JIS Z2371 was carried out on the hot-dip galvanized steel sheet for 72 hours to determine an area ratio where white rust generated. A case where the area ratio where white rust generated was 5.0% or less was evaluated as pass.

The red rust resistance was measured as follows. First, a cross-cut flaw extending from the outermost layer of the hot-dip galvanized steel sheet (the outermost surface of the organic resin film) to the hot-dip galvanized layer was formed (the hot-dip galvanized steel sheet having a cross-cut flaw formed therein is referred to as a red

rust resistance test piece). Next, a salt spray test (SST) defined in JIS Z2371 was carried out on the red rust resistance test piece for 2000 hours. A case where red rust was not generated was evaluated as pass.

[0067]

The results obtained as described above were shown in Figs. 1 to 6.

Fig. 1 is a graph showing the relationship between the adhesion amount of Co and the blackening resistance in a hot-dip galvanized steel sheet including a Co-Mg-Zn layer and a chromate-free organic resin film. Fig. 2 is a graph showing the relationship between the adhesion amount of Co and the white rust resistance in the hot-dip galvanized steel sheet including a Co-Mg-Zn layer and a chromate-free organic resin film. Fig. 3 is a graph showing the relationship between the adhesion amount of Co and the red rust resistance in the hot-dip galvanized steel sheet including a Co-Mg-Zn layer and a chromate-free organic resin film.

Fig. 4 is a graph showing the relationship between the adhesion amount of Co and the blackening resistance in a hot-dip galvanized steel sheet including a Co-Mg-Zn layer and a chromate film. Fig. 5 is a graph showing the relationship between the adhesion amount of Co and the white rust resistance in the hot-dip galvanized steel sheet including a Co-Mg-Zn layer and a chromate film. Fig. 6 is a graph showing the relationship between the adhesion amount of Co and the red rust resistance in the hot-dip galvanized steel sheet including a Co-Mg-Zn layer and a chromate film.

[0068]

In a case where the hot-dip galvanized steel sheet has a Co-Mg-Zn layer and a chromate-free organic resin film, as seen from Figs. 1 and 2, with an increase in the adhesion amount of Co, while the blackening resistance is improved, the white rust resistance is deteriorated. Thus, it is found that the blackening resistance and the

white rust resistance are in a trade-off relationship.

As shown in Figs. 1 and 2, in a case of Zn-0.2Al-0.5Mg, both the blackening resistance and the white rust resistance could not be evaluated as pass even in a case where the adhesion amount of Co was changed.

[0069]

On the other hand, as shown in Figs. 1 and 2, in a case of Zn-0.2Al-0.5Mg-0.1Ni, by setting the adhesion amount of Co to 2.0 mg/m^2 or less and using an organic resin film, both the blackening resistance and the white rust resistance could be evaluated as of pass.

In a case of Zn-0.2Al not containing Mg, as shown in Figs. 1 and 2, the adhesion amounts of Co in which the blackening resistance and the white rust resistance are evaluated as pass existed but as shown in Fig. 3, the red rust resistance was evaluated as fail in the adhesion amounts of Co.

[0070]

In a case where the hot-dip galvanized steel sheet has a chromate film, as shown in Figs. 4 and 5, both the blackening resistance and the white rust resistance could be evaluated as pass by increasing the adhesion amounts of Co. However, as shown in Fig. 6, in the adhesion amounts of Co, even in a case where the hot-dip galvanized layer contained Mg, the red rust resistance was evaluated as fail.

[0071]

As described above, by using a layer of Zn-0.2Al-0.5Mg-0.1Ni as the hot-dip galvanized layer, setting the adhesion amount of Co of the Co-Mg-Zn layer, which is formed between the hot-dip galvanized layer and the organic resin film, to 0.1 mg/m^2 to 2.0 mg/m^2, and using a chromate-free organic resin film was used in the upper layer of Co, the properties that all of the blackening resistance, the white rust resistance and

the red rust resistance are satisfactory can be obtained.

[0072]

<Example 2>

In Tables 1 to 5, underlines are attached to numerical values and items out of the ranges of the present invention.

[0073]

(Examples 1 to 31 and Comparative Examples 1 to 7)

A steel sheet having a hot-dip galvanized layer having an adhesion amount per one surface of about 250 g/m^2, and a chemical composition of Mg: 0.5%, Al: 0.2%, Ni: 0.1%, and a remainder consisting of Zn and unavoidable impurities was subjected to temper rolling.

[0074]

Thereafter, a spray treatment using an acidic aqueous solution containing Co ions at 40°C was performed on the surface of the hot-dip galvanized layer for 1 to 3 seconds. Then, the hot-dip galvanized layer was washed with water and dried.

In Table 1, the compositions of acidic aqueous solution containing Co ions are shown. In all aqueous solutions, sulfate was dissolved, and pH was adjusted with sulfuric acid.

[0075]

Next, a chromate-free organic resin was applied and dried to form an organic resin film.

For the organic resin film, resin films shown in Table 2 were used. Each aqueous coating obtained by formulating materials to have the solid content concentration shown in Table 2 was applied with a bar coater and baked in a hot air drying furnace at 100°C to form a film. The thickness of each film was adjusted to 1

μm.

In some of Comparative Examples, films other than the organic resin film were used.

[0076]

The amount of Co was determined by a wet ICP-MS method and the amount in terms of metal Co was shown in the table.

In Comparative Examples 4 to 6, the Co-Mg-Zn layer was not formed.

[0077]

The performance evaluation was performed as follows.

(Blackening Resistance)

First, the evaluation surfaces of the hot-dip galvanized steel sheets were overlapped to face each other and packaged (the packaged hot-dip galvanized steel sheets are referred to as a blackening resistance test piece). Then, the blackening resistance test piece was retained in an environment at 70°C and 85% RH for 1 week and a change in brightness (ΔL*) before and after retention was measured. A case where a change in brightness was 3.0 or less was evaluated as pass.

[0078]

(White Rust Resistance)

The white rust resistance was measured as follows. That is, a salt spray test (SST) defined in JIS Z2371 was carried out on the hot-dip galvanized steel sheet for 72 hours to determine an area ratio where white rust generated. A case where the area ratio where white rust generated was 5.0% or less was evaluated as pass.

[0079]

(Red Rust Resistance)

The red rust resistance was measured as follows. First, a cross-cut flaw

extending from the outermost layer of the hot-dip galvanized steel sheet (the outermost surface of the organic resin film) to the hot-dip galvanized layer was formed (the hot-dip galvanized steel sheet having a cross-cut flaw formed therein is referred to as a red rust resistance test piece). Next, a salt spray test (SST) defined in JIS Z2371 was carried out on the red rust resistance test piece for 2000 hours. A case where red rust was not generated was evaluated as pass.

[0080]

In Table 3, the conditions and the evaluation results of Examples 1 to 31 and Comparative Examples 1 to 7 are shown.

As shown in Table 3, Examples 1 to 31 exhibited good properties.

[0081]

On the other hand, in Comparative Examples 1 to 3, since the adhesion amount of Co was more than the range of the present invention, the white rust resistance was evaluated as fail.

In Comparative Example 1, for the acidic aqueous solution containing Co ions, J in Table 1 was used, the amount of Co ions was excessive, and the acidic aqueous solution containing Co ions did not contain Zn ions and Mg ions. Thus, it is considered that the adhesion amount of Co of the hot-dip galvanized steel sheet became excessive.

[0082]

In Comparative Example 2, for the acidic aqueous solution containing Co ions, K in Table 1 was used, the amount of Co ions was excessive, and the acidic aqueous solution containing Co ions did not contain Mg ions. Thus, it is considered that the adhesion amount of Co became excessive. In addition, in Comparative Example 2, the blackening resistance was evaluated as fail.

In Comparative Example 3, for the acidic aqueous solution containing Co ions, L in Table 1 was used and the amount of Co ions was excessive. Thus, it is considered that the adhesion amount of Co became excessive. In Comparative Example 3, the white rust resistance and the blackening resistance were also evaluated as fail.

In Comparative Example 4, Co was not caused to adhere to the steel sheet and thus the blackening resistance evaluated as fail.

[0083]

In Comparative Example 5, as in Patent Document 3, the Co-Mg-Zn layer was not formed and an organic resin film containing Co was formed. However, the blackening resistance and the red rust resistance were evaluated as fail. The Co precipitates were not precipitated at the interface between the organic resin film and the hot-dip galvanized layer and were dispersed over the entire organic resin film. For this reason, it is considered that suitable blackening resistance could not be obtained.

In Comparative Example 6, an organic resin film was formed directly on the hot-dip galvanized layer, but suitable blackening resistance could not be obtained.

[0084]

In Comparative Example 7, instead of the organic resin film, a chromate film was formed, but the blackening resistance and the red rust resistance were evaluated as fail.

[0085]

[Table 1]

Co treatment bath		A	B	C	D	E	F	G	H	I	J	K	L
Treatment bath concentration (g/L)	Co^{2+}	0.2	0.5	0.5	0.1	0.2	0.2	0.2	0.2	0.2	1.0	1.0	1.0
	Zn^{2+}	0.9	0.8	0.2	0.5	1.5	2.0	0.9	0.9	0.9	0	1.5	1.5
	Mg^{2+}	0.1	0.2	0.6	0.1	0.2	0.2	1.0	1.5	2.0	0	0	1.5

Treatment bath pH	2.1	1.9	1.6	2.0	2.0	2.0	2.0	2.0	2.0	2.0	1.9	1.9

[0086]

[Table 2]

Kind of film			Content (mass%)									
			a1	a2	a3	a4	a5	b1	b2	b3	c1	c2
Organic resin		Acrylic resin	35			30			30	35		
		Urethane resin		40			70	75				
		Olefin resin			60	30			30			
Phosphate compound and the like		Phosphoric acid		10		10		5				5
		Diammonium hydrogenphosphate			5				10		10	
		Mg biphosphate	5				10			5		
		1-Hydroxyethylidene-1,1-diphosphonic acid	15		10			10		15	10	
V compound		Ammonium metavanadate	10		10					10		
		Vanadium oxy acetylacetonate		5		10	5	5			15	
Si compound	Silica	Colloidal silica			10				20			15
	Silicate	Li silicate			5							
	Silane coupling agent	3-Glycidoxypropyltrimethoxysilane		20								
		3-Aminopropyltriethoxysilane		20			5		5			
Ti compound		Titanium hydrofluoric acid		5					5			
		Titanium acetyl acetonate				10						
Zr compound		Ammonium zirconyl carbonate	35							34	60	
		Zirconium hydrofluoric acid					10					
Others		Polyethylene wax				5		5				
		Benzotriazole				5					4.5	
		Cobalt sulfate								1	0.5	
		Chromic anhydride (CrO_3)										80
Total			100	100	100	100	100	100	100	100	100	100

[0087]

[Table 3]

No.		Co treatment bath	Adhesion amount of Co (mg/m^2)	Kind of film	Performance evaluation result		
					Blackening resistance Evaluation score	White rust resistance White rust generation rate (%)	Red rust resistance Red rust generated or not generated
Example	1	A	0.1	a1	2.1	0	Not generated
	2	A	0.5	a1	1.3	0	Not generated
	3	A	0.1	a2	2.0	0	Not generated
	4	A	0.5	a2	1.2	0	Not generated
	5	A	0.1	a3	2.0	0	Not generated
	6	A	0.5	a3	1.3	0	Not generated
	7	A	0.1	a4	2.0	0	Not generated
	8	A	0.5	a4	1.2	0	Not generated
	9	A	0.1	a5	2.1	0	Not generated
	10	A	0.5	a5	1.3	0	Not generated
	11	A	0.1	b1	2.2	0.3	Not generated
	12	A	0.5	b1	1.5	1.0	Not generated
	13	A	0.1	b2	2.0	0.2	Not generated
	14	A	0.5	b2	1.4	1.0	Not generated
	15	B	0.9	a1	1.2	0.1	Not generated
	16	B	0.9	a2	1.1	0.1	Not generated
	17	B	0.9	a3	1.1	0	Not generated
	18	B	0.9	a4	1.2	0.1	Not generated
	19	B	0.9	a5	1.2	0	Not generated
	20	B	0.9	b1	1.2	5.0	Not generated
	21	B	0.9	b2	1.2	4.0	Not generated
	22	C	0.9	a1	1.1	1.0	Not generated
	23	C	1.9	a1	1.2	5.0	Not generated
	24	D	0.3	a1	1.6	0.1	Not generated
	25	D	0.7	a1	1.3	1.0	Not generated
	26	A	0.1	b3	2.2	5.0	Not generated
	27	E	0.9	a1	1.1	0.0	Not generated
	28	F	0.9	a1	1.6	0.0	Not generated
	29	G	0.9	a1	1.2	0.0	Not generated
	30	H	0.9	a1	1.5	0.1	Not generated
	31	I	0.9	a1	1.9	0.3	Not generated
Comparative Example	1	J	2.6	a1	1.1	40.0	Not generated
	2	K	2.7	a1	3.5	30.0	Not generated
	3	L	2.7	a1	3.4	20.0	Not generated
	4	-	-	a1	10.1	0	Not generated
	5	-	-	c1	8.8	0	Generated
	6	-	-	b3	10.1	5.0	Not generated
	7	A	0.5	c2	3.4	0	Generated

[0088]

(Examples 32 to 45 and Comparative Examples 8 to 11)

A pickled hot-rolled steel sheet was used as a base steel sheet and a hot-dip galvanized layer having a composition shown in Table 4 was formed. In a case of forming the hot-dip galvanized layer having the composition shown in Table 4, Mg, Al, and Ni concentrations and minor additive components were changed by a hot-dip galvanizing simulator. In some simulations, a steel sheet with Ni pre-coating was used.

The adhesion amount of the hot-dip galvanized layer was 150 g/m^2 to 220 g/m^2. Then, the steel sheet having a hot-dip galvanized layer formed thereon was immersed in an acidic aqueous solution containing Co ions of A in Table 1 at a temperature of 30°C for 5 seconds and thus Co was caused to adhere to the layer in the adhesion amount shown in Table 4. Then, a chromate-free organic resin film of a1 in Table 2 was formed at a thickness of 1 μm.

The evaluation was performed by the same manner as in Examples 1 to 31 and Comparative Examples 1 to 7. However, regarding the red rust resistance, the red rust resistance was evaluated based on the presence or absence of the generation of red rust at the time when the SST was carried out for 1500 hours.

[0089]

As shown in Table 4, Examples 32 to 45 exhibited good properties.

Here, in Examples 32 and 35 to 38, among various conditions, only the Mg content of the hot-dip galvanized layer was varied. As clearly seen from the evaluation results of the blackening resistance of these examples, the blackening resistance was varied by the Mg content of the hot-dip galvanized layer.

[0090]

On the other hand, in Comparative Example 8, since the hot-dip galvanized layer did not contain Mg and Ni, the red rust resistance was evaluated as fail.

In Comparative Example 9, since the hot-dip galvanized layer did not contain Ni, the blackening resistance and the white rust resistance were evaluated as fail.

In Comparative Examples 10 and 11, since the Al content of the hot-dip galvanized layer was excessive, the blackening resistance and the red rust resistance were evaluated as fail.

[0091]

[Table 4]

No.		Coated layer composition (mass%)				Adhesion amount of Co (mg/m^2)	Performance evaluation result		
		Mg	Al	Ni	Others		Blackening resistance Evaluation score	White rust resistance White rust generation rate (%)	Red rust resistance Red rust generated or not generated
Example	32	0.50	0.3	0.08	-	0.6	1.2	0	Not generated
	33	0.50	0.2	0.05	-	0.6	1.2	0	Not generated
	34	0.40	0.1	0.06	-	0.6	1.3	0	Not generated
	35	0.10	0.3	0.08	-	0.6	1.9	0	Not generated
	36	1.00	0.3	0.08	-	0.6	1.2	0	Not generated
	37	1.50	0.3	0.08	-	0.6	1.2	0	Not generated
	38	2.00	0.3	0.08	-	0.6	1.6	0	Not generated
	39	1.00	0.3	0.08	-	1.3	1.5	0	Not generated
	40	2.00	0.9	0.08	-	1.5	2.1	2.0	Not generated
	41	0.60	0.4	0.50	-	0.9	1.2	0	Not generated
	42	0.80	0.4	2.00	-	0.9	1.2	0	Not generated
	43	0.80	0.4	0.20	Ca:0.080	0.7	1.1	0	Not generated
	44	0.80	0.4	0.20	Si:0.005	0.7	1.0	0	Not generated
	45	0.80	0.4	0.20	Sn:0.020	0.8	1.0	0	Not generated
Comparative Example	8	0	0.2	0	-	0.1	1.0	0	Generated
	9	0.70	0.2	0	-	1.3	3.6	20.0	Not generated
	10	0.05	4.0	0.08	-	0.1	4.2	0	Generated
	11	0.20	1.0	0.05	-	0.1	4.5	0	Generated

[0092]

(Examples 46 to 48 and Comparative Example 12)

Hot-dip galvanizing, temper rolling, and a treatment using an acidic aqueous solution containing Co ions were continuously performed in a continuous hot dip galvanizing line.

In the hot-dip galvanizing, the adhesion amount per one surface was about 300 g/m^2, and the composition of the coating bath included Mg: 0.5%, Al: 0.3%, Ni: 0.07%, and a remainder consisting of Zn and unavoidable impurities.

[0093]

Next, a spray treatment using an acidic aqueous solution containing Co ions having a concentration shown in Table 5 was performed for 3 seconds to 5 seconds. The counter anion was a sulfuric acid ion and the pH was adjusted with sulfuric acid. The bath temperature was 30°C to 35°C.

Sampling was performed at a total of 30 points from the front and rear surfaces of the produced coated steel sheet in the width direction and the longitudinal direction and the adhesion amount of Co was measured by a wet ICP-MS method.

[0094]

In Table 5, regarding the measurement result of the adhesion amount of Co, the minimum value, the maximum value, the average value, and the standard deviation (σ) are shown. As shown in Table 5, in Examples 46 to 48, variation of the adhesion amounts of Co at each portion was small. Particularly, it was found that variation of the adhesion amount of Co was small in a case where the Zn ion concentration was higher than the Co ion concentration and the Mg ion concentration was higher than the Co ion concentration in the acidic aqueous solution containing Co ions.

The chromate-free organic resin film of a1 in Table 2 was formed in the upper

layer in Examples 46 to 48 and various performance evaluations were performed. As a result, all steel sheets exhibited good properties.

[0095]

On the other hand, in Comparative Example 12, since the acidic aqueous solution containing Co ions did not contain Zn ions and Mg ions, the adhesion amount of Co was large and the variation was large.

[0096]

[Table 5]

No.		Treatment bath concentration (g/L)			Treatment bath pH	Adhesion amount of Co (mg/m^2)			
		Co^{2+}	Zn^{2+}	Mg^{2+}		Minimum value	Maximum value	Average	σ
Example	46	0.3	0.4	0.1	1.9	0.3	0.9	0.62	0.16
	47	0.4	0.9	0.5	2.2	0.3	0.5	0.48	0.06
	48	0.2	1.0	0.5	1.9	0.2	0.4	0.38	0.06
Comparative Example	12	0.5	0	0	1.9	1.1	4	2.3	1.1

[Industrial Applicability]

[0097]

According to the embodiment, it is possible to provide a hot-dip galvanized steel sheet which is excellent in all of white rust resistance, red rust resistance, and blackening resistance and a method for producing the same.

[Brief Description of the Reference Symbols]

[0098]

1: steel sheet

3: hot-dip galvanized layer

4: Co precipitate

5: Co-Mg-Zn layer

6: Mg

7: organic resin film

8: Zn

10: hot-dip galvanized steel sheet

[Document Type] CLAIMS

1. A hot-dip galvanized steel sheet comprising:

a steel sheet;

a hot-dip galvanized layer that is provided on a surface of the steel sheet and contains Mg: 0.05 mass% to 2.00 mass%, Al: 0.1 mass% or more and less than 1.0 mass%, Ni: 0.05 mass% to 2.00 mass%, and a remainder including Zn and impurities;

a Co-Mg-Zn layer that is provided on a surface of the hot-dip galvanized layer and contains 0.1 mg/m^2 to 2.0 mg/m^2 of Co precipitates in terms of a metal Co amount, Mg, and Zn; and

an organic resin film that is provided in an upper layer of the Co-Mg-Zn layer.

2. The hot-dip galvanized steel sheet according to claim 1,

wherein the hot-dip galvanized layer further contains one or more of

Li: 0.001 mass% to 0.200 mass%,

Na: 0.001 mass% to 0.200 mass%,

K: 0.001 mass% to 0.200 mass%,

Ca: 0.001 mass% to 0.200 mass%,

Sr: 0.001 mass% to 0.200 mass%,

Sc: 0.001 mass% to 0.200 mass%,

Y: 0.001 mass% to 0.200 mass%,

Ti: 0.001 mass% to 0.200 mass%,

Zr: 0.001 mass% to 0.200 mass%,

Cu: 0.001 mass% to 0.200 mass%,

Sn: 0.001 mass% to 0.200 mass%,

Si: 0.001 mass% to 0.200 mass%, and

misch metal: 0.001 mass% to 0.200 mass%.

3. The hot-dip galvanized steel sheet according to claim 1 or 2,

wherein the organic resin film contains one or more of phosphoric acid and salts thereof, pyrophosphoric acid and salts thereof, metaphosphoric acid and salts thereof, polyphosphoric acid and salts thereof, phytic acid, and 1-hydroxyethylidene-1,1-diphosphonic acid, and one or more of a V compound, a Si compound, a Ti compound, and a Zr compound.

4. A method for producing the hot-dip galvanized steel sheet according to any one of claims 1 to 3, comprising:

forming a hot-dip galvanized layer containing Mg: 0.05 mass% to 2.00 mass%, Al: 0.1 mass% or more and less than 1.0 mass%, Ni: 0.05 mass% to 2.00 mass%, and a remainder including Zn and impurities on a surface of a steel sheet;

forming a Co-Mg-Zn layer by contacting the steel sheet having the hot-dip galvanized layer with an acidic aqueous solution containing 0.1 g/L to 0.5 g/L of Co ions, 0.2 g/L to 2.0 g/L of Zn ions, and 0.1 g/l to 2.0 g/l of Mg ions; and

forming an organic resin film by applying a liquid for forming organic resin film to a surface of the Co-Mg-Zn layer and drying the liquid for forming organic resin film.

5. The method for producing the hot-dip galvanized steel sheet according to claim 4,

wherein a concentration of the Co ions contained in the acidic aqueous solution is lower than a concentration of the Zn ions, and lower than a concentration of

the Mg ions.

6. The method for producing the hot-dip galvanized steel sheet according to claim 4 or 5,

wherein a pH of the acidic aqueous solution is 1 to 3,

a temperature of the acidic aqueous solution is 40°C or lower, and

a time for contacting the steel sheet having the hot-dip galvanized layer with the acidic aqueous solution is 5 seconds or shorter.