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## (54) Zinc-containing metal-plated composite steel article and method of producing the same.

(57) A zinc-containing metal-plated composite steel article having an enhanced paint-coating property has 0.3 to 3.0 g/m$^2$ of a zinc phosphate composite coating layer formed on a zinc-containing metal-plated steel substrate by a cathodic electrolysis treatment or a first chemical conversion treatment and including zinc and phosphorus in a weight ratio Zn/P of 2.504 :1 to 3.166 :1 and 0.06 to 9.0% by weight of Fe, Co, Ni, Ca, Mg and/or Mn, and a phosphate chemical conversion layer formed on the composite coating layer by a second chemical conversion treatment and including fine phosphate crystals.

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## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

The present invention relates to a zinc-containing metal-plated composite steel article and a method of producing the same.

More particularly, the present invention relates to a zinc-containing metal-plated composite steel article having an excellent paint-coating property, especially an excellent close paint-adherence property for an electrodeposition paint-coating, and enabling the paint-coated article to exhibit an excellent corrosion resistance, and a method of producing the same.

### 2. Description of Related Art

It is well known that a steel strip plated with a metal containing zinc and having enhanced resistance to perforating corrosion and red rust, which will be referred to as a zinc-containing metal-plated steel strip hereinafter, is popularly employed as a motorcar body-forming steel strip.

Recently, to further enhance the corrosion resistance, the thickness of the zinc-containing metal-plating layer on the steel strip tends to be further increased.

However, the conventional zinc-containing metal plated steel strip which has been treated with a phosphate, and then coated with a paint, is disadvantageous in that when it is practically employed in a wetted environment, the paint-coating film on the steel strip is easily blistered.

As a conventional attempt for solving the above-mentioned problem, Japanese Examined Patent Publication (Kokoku) No. 5-5905 discloses a plated steel strip produced by coating a surface of a zinc-containing alloy or aluminum-containing alloy layer plated on a steel strip with a specific amount of a nickel-iron alloy deposited by an anodic electrolysis, and having an applicability to a chemical conversion treatment, for example, phosphate treatment. This method is carried out by utilizing the anodic electrolysis, and thus is disadvantageous in that the necessary equipment is expensive, and the running cost is high due to the consumption of electric power.

As another attempt, Japanese Unexamined Patent Publication (Kokai) No. 2-228,482 discloses a method of forming a zinc phosphate coating having an enhanced paint-coating property by treating a metal surface with an acidic aqueous zinc phosphate solution having an isoelectric point of 3 or less and containing colloidal particles having a dispersed particle size of 0.1 μm or less. This method is, however, disadvantageous in that the necessary treating time is too long and thus the production cost becomes too high, and the productivity is low.

Under the above-mentioned circumstance of the prior art, there is a strong demand for providing a zinc-containing metal-plated composite steel article having an excellent paint-coating applicability, an excellent paint-adherence property, and causing a paint-coated article produced therefrom to exhibit an excellent corrosion resistance, and a method of producing the zinc-containing metal-plated steel strip having a high paint-coating applicability at a high efficiency and low cost.

## SUMMARY OF THE INVENTION

The zinc-containing metal-plated composite steel article of the present invention comprises:

a substrate comprising a steel article plated on at least one surface thereof with a plating layer consisting essentially of a zinc-containing metal;

a zinc phosphate composite coating layer formed on the at least one plated surface of the zinc-containing metal-plated steel article and comprising zinc and phosphorus in a weight ratio of zinc to phosphorus of 2.504:1 to 3.166:1, and 0.06 to 9.0% by weight of at least one additional metal selected from the group consisting of iron, cobalt, nickel, calcium, magnesium and manganese, and

a phosphate chemical conversion layer comprising fine phosphate crystals and formed on the surface of the zinc phosphate composite coating layer.

The method of the present invention for producing the above-mentioned zinc-containing metal-plated composite steel article comprises:

applying a cathodic electrolysis treatment to a substrate comprising a steel strip plated on at least one surface thereof with zinc-containing metal, at the at least one plated surface thereof, with an aqueous electrolytic plating liquid comprising:

(1) 5 to 30 g/liter of phosphate ions;
(2) 1.0 to 15 g/liter of nitrate ions,

(3) 0.1 to 8.0 g/liter of zinc ions,
(4) 0.1 to 8.0 g/liter of ions of at least one additional metal selected from the group consisting of iron, nickel, manganese, cobalt, calcium and magnesium,
the weight ratio of the zinc ions to the total additional metal ions being 1:10 to 10:1, to form a zinc phosphate composite layer; and
subjecting the zinc phosphate composite layer surface to a phosphate chemical conversion treatment to form a phosphate chemical conversion layer comprising fine phosphate crystals.

Another method of the present invention for producing the above-mentioned zinc-containing metal-plated composite steel article comprises:

applying a first chemical conversion treatment to a substrate comprising a steel article plated on at least one surface thereof with zinc-containing metal, at the at least one plated surface thereof, with an aqueous treating liquid comprising:

(1) 5 to 30 g/liter of phosphate ions;
(2) 1.0 to 15 g/liter of nitrate ions,
(3) 0.1 to 8.0 g/liter of zinc ions,
(4) 0.1 to 8.0 g/liter of ions of at least one additional metal selected from the group consisting of iron, nickel, manganese, cobalt, calcium and magnesium,
the weight ratio of the zinc ions to the total additional metal ions being 1:10 to 10:1; and
(5) 0.01 to 8.0 g/liter of a reaction accelerator comprising at least one member selected from the group consisting of peroxides, fluoride ions, fluoride complex ions and nitrous acid, the amounts of the fluoride ions and the fluoride complex ions being indicated in terms of fluorine ions, to form a zinc-phosphate composite coating layer; and
subjecting the zinc phosphate composite layer surface to a second phosphate chemical conversion treatment to form a phosphate chemical conversion layer comprising fine phosphate crystals.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the zinc-containing metal plated composite steel article of the present invention the substrate is a steel article plated on at least one surface thereof with a plating layer consisting essentially of a zinc-containing metal, for example, zinc and alloys of zinc and at least one other metal than zinc, selected from, for example, nickel, iron, aluminum, manganese, chromium, lead and antimony. There is no limitation to the plating method, and thus, the zinc-containing metal plating layer may be formed by any of hot zinc-galvanizing method, a hot zinc-alloying galvanizing method, electric zinc plating method, electric zinc alloy (Zn-Ni, Zn-Fe, Zn-Mn or Zn-Cr alloy) plating method, hot Zn-Al alloy galvanizing method and deposition plating method.

The zinc-containing metal-plated composite steel article of the present invention has a zinc phosphate composite coating layer formed on the at least one plated surface of the substrate. This zinc phosphate composite coating layer comprises, as principal components, zinc and phosphorus in a weight ratio of zinc to phosphorus (Zn/P) of 2.504:1 to 3.166:1, and as an additional component, 0.06 to 9.0% by weight of at least one additional metal selected from the group consisting of iron, cobalt, nickel, calcium, magnesium and manganese.

In the zinc phosphate composite coating layer, a portion of zinc atoms in zinc phosphate molecules is supposed to be substituted by the additional metal atoms, namely, iron, cobalt, nickel, calcium, magnesium and/or manganese which has a di- or more valency. If the weight ratio Zn/P is more than 3.166:1, and/or the content of the additional metal component (consisting of at least one member selected from iron, cobalt, nickel, calcium, magnesium and manganese) is less than 0.06% by weight, the resultant composite steel article having a phosphate chemical conversion layer formed on the zinc phosphate composite coating layer, exhibits an unsatisfactory paint-coating property and the paint-coating formed thereon exhibits unsatisfactory performance. Also, if the weight ratio Zn/P is less than 2.504:1 and/or the content of the additional metal component is more than 9.0% by weight, the point-coating property of the resultant composite steel article is saturated and the cost for forming the zinc phosphate composite coating layer becomes too high. This is economically disadvantageous.

In the zinc phosphate composite coating layer, when the additional metal other than zinc is selected from iron, cobalt, nickel, calcium, magnesium and manganese, and the content of the additional metal component is controlled to a range of from 0.06 to 9.0% by weight, and a phosphate chemical conversion layer is formed on the zinc phosphate composite coating layer, the resultant composite steel article exhibit an enhanced paint-coating property, and the paint-coated article exhibits enhanced coating performance.

Among the above-mentioned group of the additional metals, preferably at least one member selected from nickel and manganese is contained in a content of 1.0 to 9.0% by weight, and more preferably nickel is contained in a content of 1.5 to 8.0% by weight in the zinc phosphate composite coating layer.

The zinc phosphate composite coating layer is not limited to a specific amount. However, the zinc phosphate composite layer is preferably present in an amount of 0.3 to 3.0 g/m$^2$ on the surface of the substrate comprising the zinc-containing metal-plated steel article. If the amount of the zinc phosphate composite coating layer is less than 0.3 g/m$^2$, the resultant composite coating layer is easily broken by a press-working applied thereto, and the even after a phosphate chemical conversion treatment is applied to the press-worked article, the resultant composite steel article exhibits an unsatisfactory paint-coating property and/or the resultant paint-coated composite steel article exhibits an unsatisfactory performance. Also, if the amount of the zinc phosphate composite coating layer is more than 3.0 g/m$^2$, when a phosphate chemical conversion treatment is applied, the zinc phosphate composite coating layer becomes difficult to etch, and thus it becomes impossible to form a satisfactory amount of the phosphate chemical conversion layer.

In the composite steel article of the present invention, a phosphate chemical conversion layer is formed on the zinc phosphate composite coating layer. The treatment liquid for forming the phosphate chemical conversion coating layer is not limited to ones having a specific composition, as long as the resultant phosphate chemical conversion coating layer comprises fine phosphate crystals. The composition of the phosphate chemical conversion treatment liquid is established in consideration of the type of the steel article, the type of the plating layer, the composition and thickness of the composite coating layer and the use of the resultant product. The treating temperature, time and type of method of producing the phosphate chemical conversion coating layer, and the thickness of the layer may be established as desired.

In the present invention, the phosphate chemical conversion coating layer is formed on the zinc phosphate composite coating layer, surprisingly, the resultant phosphate crystals in the chemical conversion coating layer have a size significantly smaller than that of the phosphate crystals formed directly on the zinc-containing metal-plated steel substrate free from the zinc phosphate composite coating layer, and thus the resultant composite steel article exhibits a significantly enhanced paint-coating property and the paint coated composite steel article exhibits a significantly improved performance. This specific type of the phosphate chemical conversion coating layer has been found by the inventors of the present invention for the first time.

Also, the inventors of the present invention have found an industrial applicability of the specific phosphate chemical conversion coating layer and succeeded to industrially utilize the specific phosphate chemical conversion coating layer.

In the present invention, the phosphate chemical conversion coating layer formed on the zinc phosphate composite coating layer preferably has a phosphate crystal size of 1 to 12 $\mu$m, more preferably 2 to 7 $\mu$m, still more preferably 3 to 6 $\mu$m.

In the present invention, the composite steel article may be in the form of a strip, sheet or plate. Also, the composite steel strip may be in a press-worked form.

The zinc phosphate composite coating layer effectively imparts an enhanced high speed press-formability to the zinc-containing metal-plated steel strip. Therefore, after the zinc phosphate composite coating layer is formed on the zinc-containing metal-plated steel strip substrate, the resultant composite steel strip is preferably press-worked into a desired form, and then the resultant press-formed composite steel article is coated with the phosphate chemical conversion coating layer having a fine phosphate crystal size.

In the present invention, the formation of the zinc phosphate composite coating layer is preferably completed within as short a time as possible to reduce the production cost thereof. Particularly, the zinc phosphate composite coating layer should be formed within a short time of from 1 to 20 seconds at a high efficiency.

The method of forming the zinc phosphate composite coating layer within a short time is not limited to specific methods. Namely, the zinc phosphate composite coating layer may be formed from zinc phosphate and at least one orthophosphate of the additional metal component, for example, nickel phosphate, manganese phosphate, calcium phosphate, iron phosphate, magnesium phosphate and cobalt phosphate, by a plasma spray coating method, vacuum spraying method or sputtering method. However, these methods need a very expensive apparatus and thus cause an economical disadvantage.

Preferably, the zinc phosphate composite coating layer is formed by an electric plating procedure or a first chemical conversion procedure, which can be carried out by a simple and cheap apparatus, in accordance with the methods of the present invention.

In the electric plating procedure, a zinc-containing metal-plated steel strip is subjected to a cathodic electrolysis treatment with an aqueous electrolytic plating liquid comprising:

(1) 5 to 30 g/liter of phosphate ions,
(2) 10 to 15 g/liter of nitrate ions,
(3) 0.1 to 8.0 g/liter of zinc ions,
(4) 0.1 to 8.0 g/liter of ions of at least one additional metal selected from the group consisting of iron, cobalt, nickel, calcium, magnesium and manganese; the weight ratio of the zinc ions to the total additional metal irons being 1:10 to 10:1.

In the first chemical conversion procedure, a zinc-containing metal-plated steel strip is subjected to a first chemical conversion treatment with an aqueous treating liquid comprising:

(1) 5 to 30 g/liter, preferably 10 to 30 g/liter, of phosphate ions,

(2) 1.0 to 15 g/liter of nitrate ions,

(3) 0.1 to 8.0 g/liter of zinc ions,

(4) 0.1 to 8.0 g/liter of ions of at least one additional metal selected from the group consisting of iron, cobalt, nickel, calcium, magnesium and manganese, the weight ratio of the zinc ions to the total additional metal ions being 1:10 to 10:1,

(5) 0.01 to 8.0 g/liter of a reaction accelerator comprising at least one member selected from the group consisting of peroxides, fluoride ions, fluoride complex ions and nitrous acid, the amounts of the fluoride ions and the fluoride complex ions being indicated in terms of fluorine ions.

In the aqueous electrolytic plating liquid and the aqueous chemical plating liquid, the sources of the metal ions are not limited to specific substances and can be selected from oxides, hydroxides and carbonate of the metals, for example, zinc oxide, iron oxides, cobalt oxide, nickel oxide, calcium oxide, magnesium oxide, manganese oxide, zinc hydroxide, iron hydroxides, cobalt hydroxide, nickel hydroxide, calcium hydroxide, magnesium hydroxide, manganese hydroxide, zinc carbonate, cobalt carbonate, nickel carbonate, calcium carbonate, magnesium carbonate, and manganese carbonate. Also, these metal compounds can be supplied to the plating liquid by dissolving in an inorganic acid, for example, phosphoric acid, nitric acid, sulfuric acid, hydrochloric acid, hydrofluoric acid, or silicohydrofluoric acid, or in an organic acid, for example, formic acid, acetic acid, or citric acid. Further, the metals can be supplied in the form of a water-soluble salt, for example, a nitrate, sulfate, chloride, fluoride, silicofluoride, acetate, formate or citrate thereof to the plating liquid.

Where the zinc phosphate composite coating layer is formed by the electrolytic plating procedure, the necessary current density for the electrolytic plating is not limited to a specific level and can be established in consideration of the concentrations of the components, the composition of the plating liquid and electrolytic plating temperature.

To complete the formation of the zinc phosphate composite coating layer within a desired short time, for example, 1 to 20 seconds, the current density is controlled preferably in a range of from 0.2 to 30 A/dm$^2$. If the current density is less than 0.2 A/dm$^2$, sometimes, it becomes difficult to complete the formation of the zinc phosphate composite coating layer within the desired short time. Also, if the current density is more than 30 A/dm$^2$, sometimes the current efficiency becomes too low and an economical disadvantage is caused.

In the method of the present invention, there is no limitation of an additive to be added to the electrolytic plating liquid. The electrolytic plating procedure optionally contains means for enhancing an economical efficiency of the zinc phosphate composite coating layer-forming reaction by increasing the zinc phosphate composite coating layer-forming reaction efficiency. The efficiency-enhancing means are not limited to specific means. For example, the reaction efficiency can be enhanced by controlling the ratio of a total acidity to a free acidity of the electrolytic plating liquid, to thereby control the etching power of the electrolytic plating liquid to the zinc-containing metal-plated steel strip substrate. The total acidity/free acidity ratio can be controlled by using a popular acid, for example, phosphoric acid or nitric acid or a popular alkali, for example, sodium carbonate or sodium hydroxide. Generally, the total acidity/free acidity ratio is preferably controlled to 8:1 to 30:1.

In the first chemical conversion procedure, to complete the formation of the zinc phosphate composite coating layer within a desired short time, for example, 1 to 20 seconds, a reaction accelerator is advantageously added to the aqueous treating liquid. As a reaction accelerator, usually known oxidizing agents and/or etching agents can be used. A preferred reaction accelerator can be selected from oxidizing agents, for example, inorganic peroxides, hydrogen peroxide, and nitrite ions, and etching agents, for example, fluoride ions and fluoride complex ions. The content of the reaction accelerator is 0.01 to 8.0 g/liter. The contents of the fluoride ions and the fluoride complex ions are indicated in terms of fluorine ions.

In the electrolytic plating liquid and the first chemical conversion treatment liquid, the phosphate ions are contained in a content of 5 to 30 g/liter. If the phosphate ion content is less than 5 g/liter, it becomes difficult to complete the formation of the desired zinc phosphate composite coating layer within a desired short time. Also, if the content is more than 30 g/liter, an excessive amount of the phosphate ion source is uselessly consumed, while the formation of the desired zinc phosphate composite coating layer within a short time can be completed, and thus an economical disadvantage is caused.

The nitrate ions are contained in a content of 1.0 to 15 g/liter in the electrolytic plating liquid or the first chemical conversion coating liquid.

If the content of the nitrate ions is less than 1.0 g/liter, it becomes difficult to complete the formation of the zinc phosphate composite coating layer within a desired short time. Also, if this content is more than 15 g/liter, the composite coating layer-forming effect within a short time is saturated, an excessive amount of the nitrate ions are uselessly consumed and thus an economical disadvantage is caused.

In the electrolytic plating liquid or the first chemical conversion coating liquid, the additional di- or more valent metal (iron, cobalt, nickel, calcium, magnesium and/or manganese) ions are contained in a total content of 0.1 to 8.0 g/liter. If the additional ion content is less than 0.1 g/liter, it becomes difficult to complete the formation of the zinc phosphate composite coating layer within a target short time. Also, if the content is more than 8 g/liter, an excessive amount of the additional metal ions is uselessly consumed and thus an economical disadvantage occurs, while the short time formation of the zinc phosphate composite coating layer can be effected.

The weight ratio of the zinc ions to the total additional metal ions is controlled to 1:10 to 10:1, if the ratio is less than 1:10, the resultant composite steel article having the phosphate chemical conversion coating layer formed on the zinc phosphate composite coating layer exhibits a saturated paint-coating property and the resultant paint-coated composite steel article exhibit saturated performance, and production cost uselessly increases. Also, the zinc ion/additional metal ion ratio is more than 10:1, the content of the additional metal in the resultant zinc phosphate composite coating layer becomes too low, the resultant composite steel article exhibits an unsatisfactory paint-coating property, and the resultant paint-coated composite steel article exhibits an unsatisfactory performance.

When the zinc phosphate composite coating layer is formed by the first chemical conversion treatment, the treatment temperature is preferably 30°C to 70°C.

If the treatment temperature is less than 30°C, the coating layer-forming rate becomes too low, and thus it is difficult to complete the formation of the zinc phosphate composite coating layer within a target short time. If the coating temperature is more than 70°C, the coating layer-forming rate is saturated so that no further effect is obtained and an economical disadvantage occurs.

To shorten the necessary time for the formation of the zinc phosphate composite coating layer, preferably the zinc-containing metal-plated steel strip substrate is cleaned, and surface-activated, and then the zinc phosphate composite coating layer is formed on the surface activated substrate.

The surface-activation of the zinc-containing metal-plated steel strip can be effected by any conventional metal-surface-activating method. For example, the surface activation can be attained by treating the surface with (i) an aqueous treating liquid containing ions of at least one metal selected from the group consisting of nickel and cobalt to cause the at least one metal to deposit in an amount of 0.2 to 50 mg/m$^2$ on the zinc-containing metal-plated surface of the substrate; or (ii) an aqueous titanium colloidal solution; or (iii) an aqueous etching solution to remove metal oxides from the zinc-containing metal-plated surface of the substrate.

The surface-activation method (i) will be further explained below.

In this method (i), the surface of the zinc-containing metal-plated steel strip substrate is treated with a treating liquid containing at least one member selected from nickel ions and cobalt ions to deposit the nickel and/or cobalt in an amount of 0.2 to 50 mg/m$^2$ on the surface. If the deposition amount of the surface-activating metal is less than 0.2 mg/m$^2$, the plated steel strip surface cannot be satisfactorily activated, and thus it becomes difficult to shorten the composite coating layer-forming time. If the deposition amount is increased to more than 50 mg/m$^2$, the surface-activating effect is saturated and no further effect is obtained.

The supply sources of the nickel and cobalt ions for the surface activating liquid (i) are not limited to specific ones. For the supply sources, water-soluble nickel salts, for example, nickel sulfate, nickel nitrate, nickel chloride, and nickel silicofluoride, and water-soluble cobalt salts, for example, cobalt sulfate, cobalt nitrate, cobalt chloride and cobalt silicofluoride can be used alone or in a combination of two or more thereof.

With respect to the titanium colloid treating liquid for the surface-activating method (ii), there is no limitation of the supply source of the titanium colloid. For example, the titanium colloidal solution can be prepared from titanium sulfate, titanyl sulfate, titanium dioxide and titanium phosphate which may be used alone or in a combination of two or more thereof.

With respect to the surface-activating method (iii), the aqueous etching solution is not limited to specific ones. The aqueous etching solution preferably contains at least one member selected from inorganic acids, for example, sulfuric acid, nitric acid, phosphoric acid, hydrofluoric acid, silicohydrofluoric acid and pyrophosphoric acid, organic acids, for example, citric acid, tartaric acid, acetic acid, oxalic acid and gluconic acid, and chelating organic compounds, for example, EDTA and NTA. The aqueous etching liquid can etch-remove an upper surface portion of a metal oxide layer formed on a surface of the zinc-containing metal-plated steel strip.

By applying the surface-activating procedure (i), (ii) or (iii) to the surface of the zinc-containing metal-plated steel strip, the zinc phosphate composite coating layer can be formed in an amount of 0.3 to 3.0 g/m$^2$ from the electrolytic plating liquid or the first chemical conversion coating liquid within a shorter time with an enhanced efficiency.

Among various surface treatments for the steel material, the zinc phosphate chemical conversion treatment is a long historic technique and now widely utilized as an undercoat treatment for paint-coating. The undercoating effect of the zinc phosphate chemical conversion coating layer for the paint-coating layer is variable depending on the physical form thereof, and is an anchoring effect for a paint-coating layer formed thereof. Namely, the zinc phosphate chemical conversion coating layer is contributory to enhance the paint-adherence property.

In the present invention, the additional di- or more valent metal atoms namely iron, cobalt, nickel, calcium, magnesium and/or manganese atoms substitute a portion of zinc atoms in the zinc phosphate molecules in the composite coating layer so as to enhance the alkali resistance of the composite coating layer. Especially, if the composite steel article is placed in a corrosive environment, the additional metal in the composite coating layer prevents a rise in pH due to consumption of hydrogen cations in the coating layer interface, and exhibits an excellent corrosion resistance-enhancing effect for the composite coating layer.

In the present invention, the zinc phosphate composite coating layer is coated with a phosphate chemical conversion layer. The phosphate chemical conversion layer formed on the zinc phosphate composite coating layer in accordance with the present invention, surprisingly contains phosphate crystals having a significantly smaller size than that of phosphate crystals formed directly on the zinc-containing metal-plated steel strip or article. These fine phosphate crystals effectively enhance the paint-coating property of the resultant composite steel article, and thus the paint-coated composite steel article exhibits enhanced performance, for example, enhanced corrosion resistance and paint-adherence property.

Particularly, the fine phosphate crystals in the phosphate chemical conversion layer have an increased specific surface area, and exhibit an enhanced anchoring effect for the paint-coating layer, and the paint-coating layer is firmly bonded to the composite steel article surface. Also, the decrease in the phosphate crystal size causes pinholes formed in the phosphate chemical conversion layer to become smaller. Therefore, the resultant phosphate chemical a conversion layer exhibits an enhanced barrier effect against a corrosive environment. Therefore, the composite steel article of the present invention exhibits an excellent paint-coating property and the paint-coated composite steel article has an excellent corrosion resistance and a paint-adherence property.

As mentioned above, the zinc-containing metal-plated steel strip coated with the zinc phosphate composite coating layer has an excellent high speed press-working property. Therefore, this intermediate composite steel strip is usually press-worked into a desired form and then the phosphate chemical conversion coating step is applied thereto.

In the press-working procedure, the surface of the zinc phosphate composite coating layer formed by the cathodic electrolysis plating procedure or the first phosphate conversion treatment procedure, is preferably coated with a lubricant to form a lubricant layer.

The lubricant preferably comprises at least one member selected from the group consisting of mineral oils, natural fats, synthetic ester oils and waxes.

The lubricant layer is preferably present in an amount of 0.2 to 2 g/m$^2$.

## EXAMPLES

The present invention will be further explained by way of the following specific examples which are merely representative and do not restrict the scope of the present invention in any way.

In the examples, the following zinc-plated steel strips, surface-activating liquids and coating (plating) liquids were employed and the following cleaning, surface-activating, plating (first chemical conversion) treatments were carried out.

### 1. Zinc-containing metal-plated steel strip substrate

(a) A steel strip with both surfaces alloyed and hot zinc galvanized having a basis weight of 60 g/m$^2$ and a thickness of 0.8 mm was employed as a substrate.

This will be referred to as GA material hereinafter.

(b) A steel strip with both surfaces electrically zinc-plated having a basis weight of 20 g/m$^2$ and a thickness of 0.8 mm was employed as a substrate.

This will be referred to as EG material hereinafter.

### 2. Treatment for the formation of zinc phosphate composite coating layer

### 2.1 Cleaning of substrate surface

Onto the surface of the substrate, a cleaning liquid consisting of an aqueous liquid containing 18 g/liter of a sodium phosphate type alkaline degreasing agent (available under the trademark of Fine Cleaner L4480, from Nihon Parkerizing Co.) was sprayed at a treating temperature of 45°C for a treating time of 120 seconds, to degrease the substrate surface, and the residual alkaline substance on the substrate surface was removed by rinsing with tap water. A surface-cleaned substrate was prepared.

2.2 Surface-activation

[Surface-activating treatment I]

A surface-activating aqueous liquid containing 1.5 g/liter of a titanium colloid-containing surface-activating agent (available under the trademark of prepalene Z, from Nihon Parkerizing Co.) was sprayed onto the surface of the cleaned substrate at room temperature for a treating time of 2 seconds.

[Surface-activating treatment II]

An aqueous solution of 20 g/liter of nickel sulfate was sprayed onto the cleaned substrate surface at a treating temperature of 60°C for a treating time of 2 seconds to deposit-fix nickel onto the substrate surface, and then the surface-activated substrate surface was rinsed with water.

[Surface-activating treatment III]

The surface-cleaned substrate was immerse-treated in an aqueous solution of 29.6 g/liter of a 67.5% nitric acid at room temperature for a treating time of 3 seconds, to etch the substrate surface, and then rinsed with water.

[Surface-activating treatment IV]

The cleaned substrate surface was sprayed with an aqueous solution of 30 g/liter of cobalt sulfate at a treating temperature of 60°C for a treating time of 2 seconds to deposit-fix cobalt onto the substrate surface, and then rinsed with water.

Table 1 shows the compositions, component contents and treating conditions of the surface activating treatments I to IV.

2.3 Treating liquid for the formation of zinc phosphate composite coating layer

[Treating liquid A]

A first chemical conversion treating liquid was prepared by mixing an aqueous solution containing 20 g/liter, in terms of $PO_4$, of phosphoric acid, 3 g/liter, in terms of $NO_3$, of nitric acid and 1.5 g/liter, in terms of fluorine ions, of hydrofluoric acid with zinc oxide in an amount of 1.3 g/liter in terms of zinc ions, basic nickel carbonate in an amount of 0.5 g/liter in terms of nickel ions, and manganese carbonate in an amount of 0.5 g/liter in terms of manganese ions; by adjusting the total acidity/free acidity ratio of the resultant aqueous solution to a level of 21:1 by using sodium carbonate; and then adding sodium nitrite in an amount of 0.3 g/liter in terms of nitrite ions to the solution.

[Treating liquid B]

A first chemical conversion treating liquid was prepared by mixing an aqueous solution containing 20 g/liter, in terms of $PO_4$, of phosphoric acid, 3 g/liter, in terms of $NO_3$, of nitric acid and 1.5 g/liter, in terms of fluorine ions, of hydrofluoric acid with zinc oxide in an amount of 2.0 g/liter in terms of zinc ions, and basic nickel carbonate in an amount of 2.5 g/liter in terms of nickel ions; by adjusting the total acidity/free acidity ratio of the resultant aqueous solution to a level of 17:1 by using sodium carbonate; and then adding sodium nitrite in an amount of 0.3 g/liter in terms of nitrite ions to the solution.

[Treating liquid C]

A cathodic electrolysis treating liquid was prepared by mixing an aqueous solution containing 6 g/liter, in terms of $PO_4$, of phosphoric acid, and 1 g/liter, in terms of $NO_3$, of nitric acid with zinc oxide in an amount of

2.0 g/liter in terms of zinc ions, nickel nitrate in an amount of 0.5 g/liter in terms of nickel ions.

[Treating liquid D]

A first chemical conversion treating liquid was prepared by mixing an aqueous solution containing 30 g/liter, in terms of $PO_4$, of phosphoric acid, 8 g/liter, in terms of $NO_3$, of nitric acid and 2.5 g/liter, in terms of fluorine ions, of silicohydrofluoric acid with zinc oxide in an amount of 1.3 g/liter in terms of zinc ions, manganese nitrate in an amount of 0.5 g/liter in terms of manganese ions, and calcium carbonate in an amount of 0.4 g/liter in terms of calcium ions; by adjusting the total acidity/free acidity ratio of the resultant aqueous solution to a level of 9:1 by using sodium carbonate; and then adding sodium nitrite in an amount of 0.7 g/liter in terms of nitrite ions to the solution.

[Treating liquid E]

A cathodic electrolysis treating liquid was prepared by mixing an aqueous solution containing 5 g/liter, in terms of $PO_4$, of phosphoric acid, and 2 g/liter, in terms of $NO_3$, of nitric acid with zinc oxide in an amount of 1.0 g/liter in terms of zinc ions, cobalt nitrate in an amount of 0.5 g/liter in terms of cobalt ions, and ferrous sulfate in an amount of 0.1 g/liter in terms of iron ions.

[Comparative treating liquid F]

A comparative first chemical conversion treating liquid was prepared by mixing an aqueous solution containing 20 g/liter, in terms of $PO_4$, of phosphoric acid, 3 g/liter, in terms of $NO_3$, of nitric acid and 1.5 g/liter, in terms of fluorine ions, of hydrofluoric acid with zinc oxide in an amount of 1.3 g/liter in terms of zinc ions; by adjusting the total acidity/free acidity ratio of the resultant aqueous solution to a level of 21:1 by using sodium carbonate; and then adding sodium nitrite in an amount of 0.3 g/liter in terms of nitrite ions to the solution.

[Comparative treating liquid G]

A comparative cathodic electrolysis treating liquid was prepared by mixing an aqueous solution containing 5 g/liter, in terms of $PO_4$, of phosphoric acid, and 2 g/liter, in terms of $NO_3$, of nitric acid with zinc oxide in an amount of 1.0 g/liter in terms of zinc ions.

[Comparative treating liquid H]

A comparative first chemical conversion treating liquid was prepared by mixing an aqueous solution containing 4 g/liter, in terms of $PO_4$, of phosphoric acid, 16 g/liter, in terms of $NO_3$, of nitric acid and 1.5 g/liter, in terms of fluorine ions, of hydrofluoric acid with zinc oxide in an amount of 1.3 g/liter in terms of zinc ions, and nickel nitrate in an amount of 0.04 g/liter in terms of nickel ions; by adjusting the total acidity/free acidity ratio of the resultant aqueous solution to a level of 21:1 by using sodium carbonate; and then adding sodium nitrite in an amount of 0.3 g/liter in terms of nitrite ions to the solution.

Table 1 also shows the compositions of the treating liquids A to H.

## Example 1

The GA material surface-cleaned by the treatment described in item 2.1 above was employed as a substrate. The surface activating treatment I was applied to the GA substrate. The surface activated GA substrate was immersed in the treating liquid for a first chemical conversion treatment A at a temperature of 45°C for one second, taken up from the treating liquid, washed with water and then dried. A zinc phosphate composite coating layer having the composition and the amount indicated in Table 3 were formed on the substrate.

The resultant intermediate composite material was subjected to a second phosphate chemical conversion treatment comprising the following steps 1 to 7, to produce a zinc-plated composite steel strip.

### Second chemical conversion treatment

1 Degreasing step

The surface of the intermediate composite steel strip was degreased with a sodium phosphate-containing degreasing agent (available under the trademark of Fine Cleaner L4480, from Nihon Parkerizing

Co.) under the following conditions.

[Degreasing conditions]
Concentration of degreasing agent: 18 g/liter
Treating temperature: 45°C
Treating time: 120 seconds
Procedure: spraying

2 Water-rinsing step

An alkaline substance derived from the degreasing step and remaining on the degreased strip surface was removed by rinsing with tap water under the following conditions, to clean the intermediate composite strip surface.

[Conditions]
Treating temperature: room temperature
Treating time: 20 seconds
Procedure: spraying

3 Surface-conditioning step

The intermediate composite strip was surface-conditioned with a weak alkaline surface-conditioning agent (available under the trademark of prepalene-ZTH, from Nihon Parkerizing Co.) containing titanium colloid, under the following conditions.

[Conditions]
Concentration of surface-conditioning agent: 1.5 g/liter
Treating temperature: room temperature
Treating time: 20 seconds
Procedure: spraying

4 Chemical conversion step

The surface-conditioned intermediate composite strip was chemical conversion-treated with a phosphate-treating agent (available under the trademark of Palbond-L3080, from Nihon Parkerizing Co.) under the following conditions.

[Conditions]
Concentration of phosphate-treating agent: 48 g/liter
Treating temperature: 43°C
Treating time: 120 seconds
Procedure: dipping
Free acidity: 1 point (determined by sampling 10 ml of the treating liquid, and titrating with a 0.1N aqueous sodium hydroxide solution in the presence of a Bromphenol Blue indicator)
Total acidity: 23 points (determined by sampling 10 ml of the treating liquid and titrating with a 0.1N aqueous sodium hydroxide solution in the presence of a Phenolphthalein indicator)
Concentration of reaction accelerator: 3 points (determined by Saccharometer method)

5 Water-rinsing step

The residual chemical conversion treating liquid on the composite steel strip was removed by rinsing with tap water under the following conditions.

[Conditions]
Treating temperature: room temperature
Treating time: 20 seconds
Procedure: spraying

6 Deionized water-rinsing step

The water rinsed composite steel strip was further rinsed with deionized water under the following conditions, to remove impurity ions contained in the residual rinsing water on the composite steel strip surface.

[Conditions]
Treating temperature: room temperature
Treating time: 20 seconds
Procedure: spraying

7 Drying step

The residual water on the composite steel strip surface was removed by drying with hot air blast under the following conditions.

[Conditions]
Treating temperature: 100°C
Treating time: 120 seconds

Example 2

The same first chemical conversion treatment as in Example 1 was carried out except that the GA material was replaced by an EG material and the resultant zinc phosphate composite coating layer formed on the EG material had the composition and amount indicated in Table 3. The same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to produce a zinc-plated composite steel strip.

Example 3

The GA material cleaned by the cleaning step described in item 2.1 above was used as a substrate, and the surface-activating treatment II was applied to the surface-cleaned GA material.

The surface-activated GA material was immersed in the treating liquid B at a temperature of 45°C for 6 seconds, rinsed with water and dried. The resultant zinc phosphate composite coating layer had the composition and amount indicated in Table 3.

Then the same second chemical conversion treatment as in Example 1 was applied onto the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Example 4

The same first chemical conversion treatment as in Example 3, except that the GA material was replaced by an EG material and the resultant zinc phosphate composite coating layer formed on the EG material had the composition and amount indicated in Table 3. The same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Example 5

The GA material was cleaned by the cleaning step described in item 2.1 above was used as a substrate. The substrate was subjected to a cathodic electrolytic treatment in the treating liquid C at a temperature of 40°C at a current density of 9 A/dm$^2$ for 2 seconds by using the substrate as a cathode and a carbon plate as an anode, rinsed with water and dried.

The resultant zinc phosphate composite coating layer had the composition and amount indicated in Table 3.

Then, the same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Example 6

The same cathodic electrolysis treatment as in Example 5 was carried out except that the GA material was replaced by the EG material and the resultant zinc phosphate composite coating layer had the composition and amount as indicated in Table 3. The same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Example 7

The GA material cleaned by the cleaning step described in item 2.1 above was used as a substrate, and the surface-activating treatment III was applied to the surface-cleaned GA material.

The surface-activated GA material was immersed in the treating liquid D at a temperature of 50°C for 1 second, rinsed with water and dried. The resultant zinc phosphate composite coating layer had the composition and amount indicated in Table 3.

Then the same second chemical conversion treatment as in Example 1 was applied onto the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Example 8

The same first chemical conversion treatment as in Example 7 was carried out except that the GA material was replaced by an EG material and the resultant zinc phosphate composite coating layer formed on the EG material had the composition and amount indicated in Table 3. The same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Example 9

The GA material was cleaned by the cleaning step described in item 2.1 above was used as a substrate. The substrate was subjected to a cathodic electrolysis treatment in the treating liquid E at a temperature of 50°C at a current density of 6 A/dm$^2$ for 6 seconds by using the substrate as a cathode and a carbon plate as an anode, rinsed with water and dried.

The resultant zinc phosphate composite coating layer had the composition and amount indicated in Table 3.

Then, the same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Example 10

The same cathodic electrolysis treatment as in Example 9 was carried out except that the GA material was replaced by the EG material and the resultant zinc phosphate composite coating layer had the composition and amount as indicated in Table 3. The same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Example 11

The GA material cleaned by the cleaning step described in item 2.1 above was used as a substrate.

The surface-cleaned GA material was immersed in the treating liquid A at a temperature of 50°C for 3 seconds, rinsed with water and dried. The resultant zinc phosphate composite coating layer had the composition and amount indicated in Table 3.

Then the same second chemical conversion treatment as in Example 1 was applied onto the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Example 12

The same first chemical conversion treatment as in Example 11 was carried out except that the GA material was replaced by the EG material and the resultant zinc phosphate composite coating layer had the composition and amount as indicated in Table 3. The same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Example 13

The GA material that was cleaned by the cleaning step described in item 2.1 above was used as a substrate. The substrate was subjected to a cathodic electrolytic treatment in the treating liquid C at a temperature of 35°C at a current density of 3 A/dm$^2$ for 9 seconds by using the substrate as a cathode and a carbon plate as an anode, rinsed with water and dried.

The resultant zinc phosphate composite coating layer had the composition and amount indicated in Table 3.

Then, the same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Example 14

The same cathodic electrolysis treatment as in Example 13 was carried out except that the GA material was replaced by the EG material and the resultant zinc phosphate composite coating layer had the composition and amount as indicated in Table 3. The same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Example 15

The GA material was cleaned by the cleaning step described in item 2.1 above was used as a substrate. The substrate was subjected to a cathodic electrolysis treatment in the treating liquid E at a temperature of 45°C at a current density of 15 A/dm$^2$ for 2 seconds by using the substrate as a cathode and a carbon plate as an anode, rinsed with water and dried.

The resultant zinc phosphate composite coating layer had the composition and amount indicated in Table 3.

Then, the same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Example 16

The same cathodic electrolysis treatment as in Example 15 was carried out except that the GA material was replaced by the EG material and the resultant zinc phosphate composite coating layer had the composition and amount as indicated in Table 3. The same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Example 17

The same GA material cleaned by the cleaning step described in item 2.1 above was used as a substrate, and the surface-activating treatment IV was applied to the surface-cleaned GA material.

The surface-activated GA material was immersed in the treating liquid A at a temperature of 45°C for 1 second, rinsed with water and dried. The resultant zinc phosphate composite coating layer had the composition and amount indicated in Table 3.

Then the same second chemical conversion treatment as in Example 1 was applied onto the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Example 18

The same first chemical conversion treatment as in Example 17 was carried out except that the GA material was replaced by the EG material and the resultant zinc phosphate composite coating layer had the composition and amount as indicated in Table 3. The same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Comparative Example 1

The GA material cleaned by the cleaning step described in item 2.1 above was used as a substrate, and the surface-activating treatment I was applied to the surface-cleaned GA material.

The surface-activated GA material was immersed in the comparative treating liquid F at a temperature of 50°C for 3 seconds, rinsed with water and dried. The resultant zinc phosphate composite coating layer had the composition and amount indicated in Table 3.

Then the same second chemical conversion treatment as in Example 1 was applied onto the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

Comparative Example 2

The GA material was cleaned by the cleaning step described in item 2.1 above was used as a substrate. The substrate was subjected to a cathodic electrolysis treatment in the comparative treating liquid G at a temperature of 45°C at a current density of 15 A/dm$^2$ for 2 seconds by using the substrate as a cathode and a carbon plate as an anode, rinsed with water and dried.

The resultant zinc phosphate composite coating layer had the composition and amount indicated in Table 3.

Then, the same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

## Comparative Example 3

The GA material cleaned by the cleaning step described in item 2.1 above was used as a substrate, and the surface-activating treatment III was applied to the surface-cleaned GA material.

The surface-activated GA material was immersed in the comparative treating liquid H at a temperature of 45°C for 6 seconds, rinsed with water and dried. The resultant zinc phosphate composite coating layer had the composition and amount indicated in Table 3.

Then the same second chemical conversion treatment as in Example 1 was applied onto the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

## Comparative Example 4

The same first chemical conversion treatment as in Comparative Example 1 was carried out except that the GA material was replaced by the EG material and the resultant zinc phosphate composite coating layer had the composition and amount as indicated in Table 3. The same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

## Comparative Example 5

The same cathodic electrolysis treatment as in Comparative Example 2 was carried out except that the GA material was replaced by the EG material and the resultant zinc phosphate composite coating layer had the composition and amount as indicated in Table 3. The same second chemical conversion treatment as in Example 1 was applied to the zinc phosphate composite coating layer to provide a zinc-plated composite steel strip.

## Comparative Example 6

The GA material was surface-cleaned by the procedure described in item 2.1 above, and then the surface-cleaned GA material was directly subjected to the same second chemical conversion treatment as in Example 1.

## Comparative Example 7

The EG material was surface-cleaned by the procedure described in item 2.1 above, and then the surface-cleaned EG material was directly subjected to the same second chemical conversion treatment as in Example 1.

The treatments in Examples 1 to 18 and Comparative Examples 1 to 7 are also outlined in Table 2.

## Test

The zinc-plated composite steel strips produced in Examples 1 to 18 and Comparative Examples 1 to 7 were subjected to the following tests.

### 3.1 Properties of coating layer

### 3.1.1. Weight of zinc phosphate composite coating layer

An original weight (W1 in g) of a test piece was measured by using a precision balance. The test piece was immersed in an aqueous solution prepared by dissolving 20 g/liter of ammonium bichromate and 490 g/liter of a 25% aqueous ammonia solution in deionized water, at room temperature for 15 minutes to remove the zinc phosphate composite coating layer.

The test piece was rinsed with water to remove residual aqueous ammonium bichromate solution thereon, and then dried.

The weight (W2 in g) of the resultant test piece was measured by the precision balance. From the weight difference W1 - W2, the weight of the zinc phosphate composite coating layer per unit area was calculated.

Further, the amounts of zinc ions and iron ions contained in the aqueous ammonium bichromate used for the measurement of the coating layer weight were measured by an atomic-absorption spectroscopic analysis and from the measurement results, the amounts of zinc and iron contained in the zinc phosphate composite coating layer per unit area were calculated.

3.1.2. Composition of zinc phosphate composite coating layer

Contents in mg/m$^2$ of the other component elements than zinc and iron in the zinc phosphate composite coating layer were respectively determined by a fluorescent X-ray analysis.

3.1.3. Size of phosphate crystals in phosphate chemical conversion layer

The secondary electron beam images of the phosphate chemical conversion layer were observed and the phosphate crystal size was determined from the images.

3.2 Paint-coating test

3.2.1 Preparation of test piece

In each of Examples 1 to 18 and Comparative Examples 1 to 7, a piece of the resultant zinc-plated composite steel strip was paint-coated to provide a test piece.

a) Electrodeposition paint-coating

The test piece was paint-coated with a cationic electrodeposition paint (available under the trademark of EL-2000, from Kansai Paint Co.) for motorcars under the following conditions.

[Conditions]
Treating temperature: 30°C
Established voltage: 200V
Treating time: 3 minutes
Thickness of paint layer: 20 μm

b) Baking

The coated paint layer was baked by a hot air-drying method under the following conditions.

[Conditions]
Treating temperature: 170°C
Treating time: 20 minutes

c) Intermediate paint-coating

The above-mentioned test piece was paint-coated with an intermediate paint (available under the trademark of TP-37, from Kansai Paint Co.) under the following conditions.

[Conditions]
Treating temperature: room temperature
Procedure: spraying
Paint layer thickness: 40 μm

d) Baking

The intermediate paint layer was baked by a hot air drying method under the following conditions.

[Conditions]
Treating temperature: 140°C
Treating time: 30 minutes

e) Finish paint-coating

The intermediate paint-coated test piece was further coated with a finish paint (available under the trademark of Neo 6000, from Kansai Paint Co.) under the following conditions.

[Conditions]
Treating temperature: room temperature
Procedure: spraying
Paint layer thickness: 40μm

f) Baking

The finish paint layer was baked by a hot air drying method under the following conditions.

[Conditions]
Treating temperature: 140°C
Treating time: 30 minutes

3.2.2. Corrosion resistance test for electrodeposition paint-coated test piece

After the electrodeposition paint-coating, the resultant test piece was subjected to a cross-cutting by using an NT cutter. The cross-cut test piece was immersed in 5% aqueous NaCl solution at a temperature of 55°C for 10 days. Blisters formed on the cross-cut portions were peeled out by an adhesive tape and one side maximum width in mm of the blisters was measured.

3.2.3. Water resistance and secondary adhesion test of finish paint coating

After the finish paint-coating, the resultant paint-coated test piece was immersed in deionized water at a temperature of 40°C for 10 days, cross-cut at intervals of 1 mm by a NT cutter. Then, a peeling treatment with an adhesive tape was applied to the cross-cut test piece. The number of the removed cut layers was counted.

3.2.4. High speed cylindrical deep drawing test

After the zinc phosphate composite coating layer was formed on the zinc-plated steel strip, the resultant intermediate composite steel strip was cut to provide a circular test piece having a diameter of 115 mm. A rust-preventing oil containing, as a principal component, a mineral oil was applied in an amount of 1.5 g/m$^2$ to the test piece. The oil-coated test piece was subjected to a high speed cylindrical deep drawing test at a punch diameter of 50 mm, at a punch speed of 30 m/min. at a drawing ratio of 2.3.

Under the above-mentioned conditions, a blank holder load (t) was changed stepwise. A limiting blank holder load (t), at which the test piece could be draw-formed at the maximum level, was measured.

The test results are shown in Table 3.

Table 1

Treating liquid compositions & contents
Treating method & conditions

| Treatment | Composition & Contents | Treating conditions |
|---|---|---|
| Activation I | PL-Z: 1.5 g/l | Room temp. 2 sec, spray |
| Activation II | Ni sulfate: 20 g/l | 60°C 2 sec, spray |
| Activation III | Nitric acid (67.5%): 29.6 g/l | Room temp. 3 sec, dip |
| Activation IV | Co sulfate: 30 g/l | 60°C 2 sec, spray |
| Treating liquid A | $PO_4$:20 g/l, $NO_3$:3 g/l, F:1.5 g/l, Zn:1.3 g/l, Ni:0.5 g/l, Mn:0.5 g/l, $NO_2$:0.3 g/l, AR:21 | Chemical conversion treatment |
| Treating liquid B | $PO_4$:20 g/l, $NO_3$:3 g/l, F:1.5 g/l, Zn:2.0 g/l, Ni:2.5 g/l, Mn:0.5 g/l, $NO_2$:0.3 g/l, AR:17 | Chemical conversion treatment |
| Treating liquid C | $PO_4$:6 g/l, $NO_3$:1 g/l, Zn:2.0 g/l, Ni:0.5 g/l | Cathodic electrolysis treatment |
| Treating liquid D | $PO_4$:30 g/l, $NO_3$:8 g/l, F:2.5 g/l, Zn:1.3 g/l, Mn:0.5 g/l, Ca:0.4 g/l, $NO_2$:0.7 g/l, AR:9 | Chemical conversion treatment |
| Treating liquid E | $PO_4$:5 g/l, $NO_3$:2 g/l, Zn:1.0 g/l, Co:0.5 g/l, Fe:0.1 g/l | Cathodic electrolysis treatment |
| Comparative liquid F | $PO_4$:20 g/l, $NO_3$:3 g/l, F:1.5 g/l, Zn:1.3 g/l, $NO_2$:0.3 g/l, AR:21 | Chemical conversion treatment |
| Comparative liquid G | $PO_4$:5 g/l, $NO_3$:2 g/l, Zn:1.0 g/l | Cathodic electrolysis treatment |
| Comparative liquid H | $PO_4$:4 g/l, $NO_3$:16 g/l, F:1.5 g/l, Zn:1.3 g/l, Ni:0.04 g/l, $NO_2$:0.3 g/l, AR:21 | Chemical conversion treatment |

Note: AR ... Total acidity/free acidity ratio (point/point)

Table 2

| Item<br>Example No. | | Substrate | Surface Activation | Formation of zing phosphate composite coating layer | | | |
|---|---|---|---|---|---|---|---|
| | | | | Treating liquid | Treating temp. | Treating conditions | Type of treatment |
| Example | 1 | GA | I | A, | 45°C, | 1 sec, dip | C.C.T. |
| | 2 | EG | I | A, | 45°C, | 1 sec, dip | " |
| | 3 | GA | II | B, | 45°C, | 6 sec, dip | " |
| | 4 | EG | II | B, | 45°C, | 6 sec, dip | " |
| | 5 | GA | - | C, | 40°C, | 9 A/dm$^2$, 2 sec, | C.E.T. |
| | 6 | EG | - | C, | 40°C, | 9 A/dm$^2$, 2 sec, | " |
| | 7 | GA | III | D, | 50°C, | 1 sec, dip | C.C.T. |
| | 8 | EG | III | D, | 50°C, | 1 sec, dip | " |
| | 9 | GA | - | E, | 50°C, | 6 A/dm$^2$, 6 sec, | C.E.T. |
| | 10 | EG | - | E, | 50°C, | 6 A/dm$^2$, 6 sec, | " |
| | 11 | GA | - | A, | 50°C, | 3 sec, dip | C.C.T. |
| | 12 | EG | - | A, | 50°C, | 3 sec, dip | " |
| | 13 | GA | - | C, | 35°C, | 3 A/dm$^2$, 9 sec, | C.E.T. |
| | 14 | EG | - | C, | 35°C, | 3 A/dm$^2$, 9 sec, | " |
| | 15 | GA | - | E, | 45°C, | 15 A/dm$^2$, 2 sec, | " |
| | 16 | EG | - | E, | 45°C, | 15 A/dm$^2$, 2 sec, | " |
| | 17 | GA | IV | A, | 45°C, | 1 sec, dip | C.C.T. |
| | 18 | EG | IV | A, | 45°C, | 1 sec, dip | " |
| Comparative example | 1 | GA | I | F, | 50°C, | 3 sec, dip | " |
| | 2 | GA | - | G, | 45°C, | 15 A/dm$^2$, 2 sec, | C.E.T. |
| | 3 | GA | III | H, | 45°C, | 6 sec, dip | C.C.T. |
| | 4 | EG | I | F, | 50°C, | 3 sec, dip | " |
| | 5 | EG | - | G, | 45°C, | 15 A/dm$^2$, 2 sec, | C.E.T. |
| | 6 | GA | - | - | - | -- | |
| | 7 | EG | - | - | - | -- | |

Note: Dip ... Immersion treatment
C.C.T. ... Chemical conversion treatment
C.E.T. ... Cathodic electrolysis treatment

Table 3

| Item<br>Example No. | | Zinc phosphate composite coating layer | | | | | | | | Phosphate crystal size (μm) in phosphate chemical conversion layer | Paint-coating performance | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Weight of coating layer (g/m²) | Zn/P weight ratio | Ni content (%) | Mn content (%) | Fe content (%) | Co content (%) | Ca content (%) | Limiting blank holder load (t) | | One side maximum blister width (mm) | Secondary paint-bonding property removed (lager number) |
| Example | 1 | 0.4 | 3.129 | 0.06 | 0.5 | - | - | - | - | 5 - 10 | 3.6 | 0 |
| | 2 | 0.7 | 2.889 | 1.0 | 2.8 | - | - | - | - | 3 - 8 | 3.7 | 0 |
| | 3 | 1.0 | 2.948 | 3.0 | - | - | - | - | 7 | 5 - 6 | 3.0 | 0 |
| | 4 | 2.1 | 2.881 | 3.9 | - | - | - | - | 6 | 2 - 4 | 3.1 | 0 |
| | 5 | 1.5 | 2.793 | 3.0 | - | - | - | - | - | 4 - 7 | 2.9 | 0 |
| | 6 | 2.0 | 2.785 | 3.3 | - | - | - | - | - | 2 - 3 | 3.5 | 0 |
| | 7 | 1.1 | 2.905 | - | 1.8 | - | - | 1.8 | - | 6 - 12 | 3.7 | 0 |
| | 8 | 0.9 | 2.881 | - | 2.2 | - | - | 1.7 | - | 4 - 9 | 4.1 | 0 |
| | 9 | 2.6 | 3.066 | - | - | 0.9 | 1.1 | - | - | 7 - 10 | 4.0 | 0 |
| | 10 | 3.0 | 3.022 | - | - | 0.6 | 1.4 | - | - | 2 - 5 | 4.3 | 0 |
| | 11 | 1.4 | 2.756 | 2.6 | 3.0 | - | - | - | 5.5 | 5 - 9 | 3.2 | 0 |
| | 12 | 1.7 | 2.733 | 2.8 | 3.1 | - | - | - | 6.5 | 2 - 5 | 3.5 | 0 |
| | 13 | 2.2 | 2.926 | 3.3 | - | - | - | - | - | 3 - 8 | 2.8 | 0 |
| | 14 | 2.4 | 3.074 | 3.1 | - | - | - | - | - | 3 - 4 | 3.2 | 0 |
| | 15 | 2.7 | 2.867 | - | - | 2.2 | 1.9 | - | - | 5 - 11 | 3.9 | 0 |
| | 16 | 3.0 | 2.852 | - | - | 2.3 | 2.0 | - | - | 4 - 8 | 4.3 | 0 |
| | 17 | 1.1 | 2.504 | 2.6 | 2.7 | - | 3.7 | - | - | 3 - 8 | 2.8 | 0 |
| | 18 | 1.3 | 2.540 | 2.6 | 2.9 | - | 3.0 | - | - | 2 - 6 | 3.7 | 0 |
| Comparative Example | 1 | 0.3 | 3.170 | - | - | - | - | - | 1.0 | 13 - 16 | 4.5 | 5 |
| | 2 | 3.3 | 3.170 | - | - | - | - | - | 1.5 | 14 - 16 | 4.4 | 8 |
| | 3 | 0.9 | 3.167 | 0.05 | - | - | - | - | - | 13 - 15 | 4.6 | 10 |
| | 4 | 0.2 | 3.170 | - | - | - | - | - | - | 13 - 14 | 5.3 | 16 |
| | 5 | 3.9 | 3.170 | - | - | - | - | - | - | 13 - 14 | 5.6 | 45 |
| | 6 | - | -- | - | - | - | - | - | 1.0 | 14 - 18 | 4.8 | 7 |
| | 7 | - | -- | - | - | - | - | - | 1.5 | 13 - 14 | 6.2 | 8 |

Table 3 clearly indicates that the composite steel strips produced in Examples 1 to 18 in accordance with the present invention exhibited an excellent corrosion resistance after the electrodeposition paint-coating and an excellent water resistance and secondary paint-bonding property after the finish paint-coating. In Comparative Examples 1 to 7, however, the resultant products exhibited at least one unsatisfactory test result, especially a poor water-resistance and secondary paint-bonding property after the finish paint-coating.

In the zinc-containing metal-plated composite steel article of the present invention, the combination of the specific zinc phosphate composite coating layer with the phosphate chemical conversion layer formed on the composite coating layer effectively enhances the paint-coating property of the resultant composite steel article and the corrosion resistance of the paint-coated composite steel article even under wetted corrosive conditions.

The method of the present invention enables the zinc-containing metal-plated composite steel article having the above-mentioned advantageous performance to be produced at a high efficiency at a low cost.

The zinc-containing metal-plated composite steel article of the present invention has a high recycle-ability and can be utilized in various uses.

## Claims

1. A zinc-containing metal-plated composite steel article comprising

    a substrate comprising a steel article plated on at least one surface thereof with a plating later consisting essentially of a zinc-containing metal;

    a zinc phosphate composite coating layer formed on the at least one plated surface of the zinc-containing metal-plated steel article and comprising zinc and phosphorus in a weight ratio of zinc to phosphorus of 2.504:1 to 3.166:1, and 0.06 to 9.0% by weight of at least one additional metal selected from the group consisting of iron, cobalt, nickel, calcium, magnesium and manganese; and

    a phosphate chemical conversion layer comprising fine phosphate crystals and formed on the surface of the zinc phosphate composite coating layer.

2. A zinc-containing metal-plated composite steel article as claimed in claim 1, wherein the zinc phosphate composite coating layer contains 1.0 to 9.0% by weight of at least one additional metal selected from the group consisting of nickel and manganese.

3. A zinc-containing metal-plated composite steel article as claimed in claim 1 or 2, wherein the zinc phosphate composite coating layer is present in an amount of 0.3 to 3.0 g/m$^2$.

4. A zinc-containing metal-plated composite steel article as claimed in any of claims 1 to 3, wherein the plating layer consists essentially of a member selected from the group consisting of zinc and alloys of zinc with at least one metal selected from the group consisting of nickel, iron, aluminium, manganese, chromium, lead and antimony.

5. A zinc-containing metal-plated composite steel article as claimed in any of claims 1 to 4, wherein the phosphate crystals of the phosphate chemical conversion layer have a size of 1 to 12 $\mu$m.

6. A zinc-containing metal-plated composite steel article as claimed in any of claims 1 to 5, which is in the form of a strip.

7. A zinc-containing metal-plated composite steel article as claimed in any of claims 1 to 5, which is in a press-worked form.

8. A method of producing a zinc-containing metal-plated composite steel article as claimed in claim 1, comprising:

    applying a cathodic electrolysis treatment to a substrate comprising a steel strip plated on at least one surface thereof with zinc-containing metal, at the at least one plated surface thereof, with an aqueous electrolytic plating liquid comprising:

    (1) 5 to 30 g/liter of phosphate ions,
    (2) 1.0 to 15 g/liter of nitrate ions,
    (3) 0.1 to 8.0 g/liter of zinc ions,
    (4) 0.1 to 8.0 g/liter of ions of at least one additional metal selected from the group consisting of iron, nickel, manganese, cobalt, calcium and magnesium,

the weight ratio of the zinc ions to the total additional metal ions being 1:10 to 10:1, to form a zinc phosphate composite layer; and

subjecting the zinc phosphate composite layer surface to a phosphate chemical conversion treatment to form a phosphate chemical conversion layer comprising fine phosphate crystals.

**9.** A method as claimed in claim 8, wherein the cathodic electrolysis treatment is carried out at an electric current density of 0.2 to 30 A/dm$^2$.

**10.** A method of producing a zinc-containing metal-plated steel article as claimed in claim 1, comprising:

applying a first chemical conversion treatment to a substrate comprising a steel article plated on at least one surface thereof with zinc-containing metal, at the at least one plated surface thereof, with an aqueous treating liquid comprising:

(1) 5 to 30 g/liter of phosphate ions,
(2) 1.0 to 15 g/liter of nitrate ions,
(3) 0.1 to 8.0 g/liter of zinc ions,
(4) 0.1 to 8.0 g/liter of ions of at least one additional metal selected from the group consisting of iron, nickel, cobalt, calcium, magnesium, and manganese,

the weight ratio of the zinc ions to the total additional metal ions being 1:10 to 10:1; and

(5) 0.01 to 8.0 g/liter of a reaction accelerator comprising at least one member selected from the group consisting of peroxides, fluoride ions, fluoride complex ions and nitrous acid, the amounts of the fluoride ions and the fluoride complex ions being indicated in terms of fluoride ions, to form a zinc-phosphate composite coating layer; and

subjecting the zinc phosphate composite layer surface to a second phosphate chemical conversion treatment to form a phosphate chemical conversion layer comprising fine phosphate crystals.

**11.** A method as claimed in claim 10, wherein the aqueous treating liquid for the first chemical conversion treatment has a ratio of total acidity to free acidity of 8:1 to 30:1.

**12.** A method as claimed in claim 10 or 11, wherein the first chemical conversion treatment is carried out at a temperature of 30 to 70°C.

**13.** A method as claimed in any of claims 8 to 12, wherein the fine phosphate crystals in the phosphate chemical conversion layer have a size of 1 to 12 $\mu$m.

**14.** A method as claimed in any of claims 8 to 13, wherein before the cathodic electrolysis treatment or the chemical conversion treatment, as the case may be, the zinc-containing metal-plated surface of the substrate is surface-activated with (i) an aqueous treating liquid containing ions of at least one metal selected from the group consisting of nickel and cobalt to cause the at least one metal to deposit in an amount of 0.2 to 50 mg/m$^2$ on the zinc-containing metal-plated surface of the substrate; or (ii) an aqueous titanium colloidal solution; or (iii) an aqueous etching solution to remove metal oxides from the zinc-containing metal-plated surface of the substrate.

**15.** A method as claimed in any of claims 8 to 14, wherein the cathodic electrolysis treated strip or the first chemical conversion treated strip, as the case may be,is press-worked, and the press-worked article is subjected to the phosphate chemical conversion treatment or the second phosphate chemical conversion treatment, as the case may be.

**16.** A method as claimed in claim 15, wherein, before the press-working, the surface of the zinc phosphate composite coating layer of the treated strip is coated with a lubricant to form a lubricant layer.

**17.** A method as claimed in claim 16, wherein the lubricant comprises at least one member selected from the group consisting of mineral oils, natural fats, synthetic ester oils and waxes.

**18.** A method as claimed in claim 16 or 17, wherein the lubricant layer is present in an amount of 0.2 to 2 g/m$^2$.