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(54) **METHOD FOR PRODUCING RUST-PROOF MEMBER**

(57) A reactive chemical conversion treatment liquid capable of forming a Si-containing chemical conversion film is provided. The chemical conversion treatment liquid contains colloidal silica, a trivalent chromium-containing water-soluble substance, and a high pKa organic acid-containing water-soluble substance such as a hydroxymonocarboxylic acid and may further contain a film-formable metal-containing water-soluble substance in a preferred embodiment, and the pH of the chemical conversion treatment liquid is 3.0 or more.

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Description

[Technical Field]

[0001] The present invention relates to a method for producing a rust-proof member.

[Background Art]

[0002] Patent Document 1 describes a corrosion-resistant base material including a substrate to be treated, a zinc or zinc-alloy plating layer formed on the substrate, and a chemical conversion film formed atop the plating layer by one-liquid treatment, wherein the chemical conversion film has a two-layered structure composed of a lower layer containing Cr and an upper layer containing SiO_2.

[Prior Art Documents]

[Patent Documents]

[0003] [Patent Document 1] JP3620510B

[Disclosure of the Invention]

[Problems to be solved by the Invention]

[0004] An object of the present invention is to provide a reactive chemical conversion treatment liquid capable of forming a chemical conversion film containing Si as described in Patent Document 1 and a method for producing a rust-proof member using the chemical conversion treatment liquid.

[Means for solving the Problems]

[0005] In one aspect, the present invention provided to solve the above problems is a method for producing a rust-proof member, comprising a chemical conversion treatment step of forming a chemical conversion film on a member to be treated containing zinc on its surface. The chemical conversion treatment step includes bringing a chemical conversion treatment liquid into contact with the member to be treated and then washing the member. The chemical conversion treatment liquid contains colloidal silica, a trivalent chromium-containing water-soluble substance that is an ionic substance containing trivalent chromium, and a high pKa organic acid-containing water-soluble substance that is a water-soluble substance containing a high pKa organic acid. The high pKa organic acid is an organic acid having a lowest pKa of 3.5 or more. The chemical conversion treatment liquid has a pH of 3.0 or more and 4.5 or less in a state before contacting with the member to be treated. The high pKa organic acid contains glycolic acid (except for a case of containing at least one selected from allylamine, polyallylamine, aromatic sulfonic acid, aromatic sulfonic acid-formaldehyde condensate, and derivatives thereof). That is, the above chemical conversion treatment liquid does not contain allylamine, polyallylamine, aromatic sulfonic acid, aromatic sulfonic acid-formaldehyde condensate, or a derivative thereof as an active ingredient.

[0006] In the above production method, the chemical conversion treatment liquid may satisfy at least one of the following requirements.

- The colloidal silica content is 2 g/L or more and 25 g/L or less.
- The trivalent chromium equivalent content of the trivalent chromium-containing water-soluble substance is 1 g/L or more and 6 g/L or less.
- The molar ratio of the high pKa organic acid equivalent content of the high pKa organic acid-containing water-soluble substance to the trivalent chromium equivalent content of the trivalent chromium-containing water-soluble substance is 0.2 or more and 2 or less.
- The chemical conversion treatment liquid further contains a film-formable metal-containing water-soluble substance that is a water-soluble substance containing metal ions capable of forming a film by interacting with oxygen.
- The ratio of the colloidal silica content (unit: g/L) to the high pKa organic acid equivalent content (unit: g/L) of the high pKa organic acid-containing water-soluble substance (colloidal silica/high pKa organic acid) is within a range of 0.5 to 10.
- The chemical conversion treatment liquid further contains a low pKa organic acid-containing water-soluble substance that is a water-soluble substance containing a low pKa organic acid that is an organic acid having a lowest pKa of

1.27 or more and less than 3.5, and the molar ratio of the low pKa organic acid equivalent content of the low pKa organic acid-containing water-soluble substance to the high pKa organic acid equivalent content of the high pKa organic acid-containing water-soluble substance is 1 or less.

[0007] In the above production method, the member to be treated is preferably obtained by forming a zinc-based plating layer on a base material.

[0008] In the above production method, the base material may be a cast product.

[Effect of the Invention]

[0009] According to the present invention, there are provided a reactive chemical conversion treatment liquid capable of forming a chemical conversion film containing Si and a method for producing a rust-proof member using the chemical conversion treatment liquid.

[Best Modes for Carrying out the Invention]

[0010] Hereinafter, one or more embodiments of the present invention will be described.

[0011] The chemical conversion treatment liquid according to one embodiment of the present invention contains colloidal silica, a trivalent chromium-containing water-soluble substance, a film-formable metal-containing water-soluble substance, and a high pKa organic acid-containing water-soluble substance, and the pH of the chemical conversion treatment liquid is 3.0 or more. The chemical conversion treatment liquid according to the present embodiment preferably further contains a film-formable metal-containing water-soluble substance.

[0012] The colloidal silica is silica that is dispersed as colloid in the chemical conversion treatment liquid and typically has a primary particle diameter of sub-nm order to sub-μm order. In the chemical conversion treatment liquid according to the present embodiment, as will be described later, a high pH region in which the pH tends to be high is generated in the vicinity of the surface of a member to be treated. Therefore, the colloidal silica contained in the chemical conversion treatment liquid in the vicinity of the surface of the member to be treated gels easily. In this region containing the gel in the vicinity of the surface of the member to be treated, the colloidal silica gels thereby to reduce mass transfer with the bulk region, and therefore the high pH state of the chemical conversion treatment liquid tends to be maintained. Hence, the zinc dissolved from the member to be treated is less likely to diffuse into the bulk region and likely to remain in the high pH region. Thus, in the chemical conversion treatment liquid according to the present embodiment, the zinc dissolved from the member to be treated tends to be a constituent element of the chemical conversion film as a hydroxide.

[0013] In addition, the colloidal silica that has diffused and moved from the bulk region to the high pH region rapidly gels to lower the mobility due to the high pH in the high pH region, and therefore, by using the reactive chemical conversion treatment liquid according to the present embodiment, a thick chemical conversion film is likely to be formed. The thickness of a chemical conversion film formed by using a general reactive chemical conversion treatment liquid is less than 100 nm, but the chemical conversion film according to the present embodiment easily has a thickness of 200 nm or more, and it is also possible to grow the film to a thickness of about 1 μm by adjusting the contact time between the member to be treated and the chemical conversion treatment liquid.

[0014] The content of the colloidal silica in the chemical conversion treatment liquid according to the present embodiment is preferably 2 g/L or more and 25 g/L or less. If the content of the colloidal silica is unduly low, there is concern that the rate of formation of the chemical conversion film will slow down and/or the corrosion resistance of the chemical conversion film will deteriorate. If the content of the colloidal silica is unduly high, there is concern that the viscosity of the chemical conversion treatment liquid will increase and/or the life of the chemical conversion treatment liquid will be shortened. From the viewpoint of ensuring the corrosion resistance of the chemical conversion film while ensuring the stability of the chemical conversion treatment liquid, the content of the colloidal silica in the chemical conversion film may be preferably 4 g/L or more and 20 g/L or less and more preferably 6 g/L or more and 20 g/L or less.

[0015] The trivalent chromium-containing water-soluble substance is an ionic substance containing trivalent chromium (Cr^{3+}). The trivalent chromium equivalent content of the trivalent chromium-containing water-soluble substance (referred to as a "trivalent chromium content," hereinafter) is preferably 1 g/L or more and 6 g/L or less. If the trivalent chromium content is unduly low, there is concern that the rate of formation of the chemical conversion film will slow down and/or the corrosion resistance of the chemical conversion film will deteriorate. If the trivalent chromium content is unduly high, there is concern that the viscosity of the chemical conversion treatment liquid will increase and/or the life of the chemical conversion treatment liquid will be shortened. From the viewpoint of ensuring the corrosion resistance of the chemical conversion film while ensuring the stability of the chemical conversion treatment liquid, the trivalent chromium content in the chemical conversion film may be preferably 1 g/L or more and 5 g/L or less and more preferably 1.2 g/L or more and 4.1 g/L or less.

[0016] The high pKa organic acid-containing water-soluble substance is a water-soluble substance containing an organic acid having a lowest pKa of 3.5 or more (high pKa organic acid) and contains the high pKa organic acid, its ion, and a complex containing the ion. The high pKa organic acid-containing water-soluble substance has a high pH buffering area due to its high pKa, and therefore the chemical conversion treatment liquid located in the region in the vicinity of the surface of the member to be treated can relatively easily maintain the pH rise caused by the dissolution of the member to be treated. This is one of the reasons why the high pH region is formed when the chemical conversion treatment liquid according to the present embodiment is used. Specifically, in the high pH region, the chemical conversion treatment liquid may have a pH of about 6 or higher at which the colloidal silica gels easily. From the viewpoint of enhancing the stability of the chemical conversion treatment liquid, the lowest pKa of the high pKa organic acid may be preferably 4.5 or less and more preferably 4.0 or less.

[0017] In addition, the high pKa organic acid-containing water-soluble substance has a high pKa, and it is therefore difficult to form a complex with zinc ions generated by dissolution of the member to be treated. For this reason, the zinc ions generated in the chemical conversion treatment liquid in the vicinity of the surface of the member to be treated are less likely to be complexed and easily exist in the form of zinc hydrated ions. In the chemical conversion treatment using the chemical conversion treatment liquid according to the present embodiment, therefore, the zinc ions generated by dissolution of the member to be treated tend to become hydroxides to be constituent elements of the chemical conversion film.

[0018] Specific examples of the high pKa organic acid related to the high pKa organic acid-containing water-soluble substance include hydroxymonocarboxylic acids such as glycolic acid (3.83), lactic acid (3.86), (±)-3-hydroxybutyric acid (4.70), and glyceric acid (3.64). The high pKa organic acid or acids related to the high pKa organic acid-containing water-soluble substance may be of one type or two or more types. Considering the difficulty of interacting with zinc ions, the organic acid related to the high pKa organic acid-containing water-soluble substance preferably contains lactic acid or glycolic acid.

[0019] The content of the high pKa organic acid-containing water-soluble substance in the chemical conversion treatment liquid according to the present embodiment is set in accordance with the type of the high pKa organic acid, the desired film properties (corrosion resistance, film appearance, film formation rate), etc. As a non-limiting example, the molar ratio of the high pKa organic acid equivalent content of the high pKa organic acid-containing water-soluble substance to the trivalent chromium content (high pKa organic acid/trivalent chromium) may be preferably is 0.2 or more and 2 or less, more preferably 0.25 or more and 2 or less, and particularly preferably 0.5 or more and 1.2 or less. When glycolic acid is contained as the high pKa organic acid, the glycolic acid equivalent content of the high pKa organic acid-containing water-soluble substance composed of glycolic acid is preferably 1 g/L or more and 10 g/L or less, more preferably 2 g/L or more and 7 g/L or less, and particularly preferably 3 g/L or more and 6 g/L or less. Also in this case, the high pKa organic acid-containing water-soluble substance may contain a high pKa organic acid other than glycolic acid (examples include lactic acid).

[0020] The ratio of the colloidal silica content (unit: g/L) to the high pKa organic acid equivalent content (unit: g/L) of the high pKa organic acid-containing water-soluble substance (colloidal silica/high pKa organic acid) is preferably within a range of 0.5 to 10 and more preferably within a range of 0.6 to 9. If this ratio is unduly large, it may possibly be difficult to obtain the effect of containing the high pKa organic acid-containing water-soluble substance. If this ratio is unduly small, the rate of formation of the chemical conversion film will slow down, and the film thickness may become thin.

[0021] The chemical conversion treatment liquid according to the present embodiment may contain, in addition to the high pKa organic acid-containing water-soluble substance, a low pKa organic acid-containing water-soluble substance that is a water-soluble substance containing a low pKa organic acid. The low pKa organic acid is an organic acid having a lowest pKa of less than 3.5. By containing the low pKa organic acid-containing water-soluble substance, it may be possible to adjust the appearance (in particular, the degree of gloss) of the chemical conversion film. Examples of the low pKa organic acid related to the low pKa organic acid-containing water-soluble substance include oxalic acid (lowest pKa: 1.27), succinic acid (lowest pKa: 3.09), and malic acid (lowest pKa: 3.4). The molar ratio of the low pKa organic acid equivalent content of the low pKa organic acid-containing water-soluble substance to the high pKa organic acid equivalent content of the high pKa organic acid-containing water-soluble substance (organic acid molar ratio) is preferably 3 or less. From the viewpoint of stably enhancing the corrosion resistance, the organic acid molar ratio is preferably 1 or less, more preferably 1/2 or less, further preferably 1/3 or less, and particularly preferably 1/10 or less.

[0022] The film-formable metal-containing water-soluble substance is a water-soluble substance that contains ions of a metal (film-formable metal) capable of forming a film, such as by interacting with oxygen. Specifically, examples of the film-formable metal include Ti, Al, V, Nb, Ta, W, and Zr. Ti and Al are exemplified as more preferred film-formable metals. The film-formable metal or metals constituting the film-formable metal-containing water-soluble substance contained in the chemical conversion treatment liquid may be of one type or two or more types.

[0023] The content of the film-formable metal-containing water-soluble substance in the chemical conversion treatment liquid according to the present embodiment is set in accordance with the type of the film-formable metal, the desired film properties (such as corrosion resistance, film appearance, and film formation rate). As a non-limiting example, when the film-formable metals are Ti and Al, the Ti equivalent content of the film-formable metal-containing water-soluble substance containing Ti is preferably 0.03 g/L or more and 0.45 g/L or less, more preferably 0.05 g/L or more and 0.30 g/L or less, and particularly preferably 0.06 g/L or more and 0.20 g/L or less. In this case, the Al equivalent content of the film-formable metal-containing water-soluble substance containing Al is preferably 2 mg/L or more and 50 mg/L or less, more preferably 3 mg/L or more and 30 mg/L or less, and particularly preferably 4 mg/L or more and 15 mg/L or less.

[0024] The chemical conversion treatment liquid according to the present embodiment may contain one or more following optional additive components in addition to the above essential components. Examples of such an optional additive component include a film-formable element-containing substance that contains one or more elements selected from the group consisting of P, B, C, S, Li, Ca, Mg, Fe, Ni, Co, Cu, Si, Zn, Al, Sn, and Bi and lanthanoids. The element equivalent content of the film-formable element-containing substance is appropriately set within a range in which the purpose of containing the element is achieved.

[0025] The pH of the chemical conversion treatment liquid according to the present embodiment is 3.0 or higher. The pH of the chemical conversion treatment liquid is relatively high and it contains a high pKa organic acid-containing water-soluble substance having a high pH buffering area as previously described; therefore, in the chemical conversion treatment liquid according to the present embodiment, a high pH region is likely to be formed in the vicinity of the surface of the member to be treated. Hence, the colloidal silica contained in the chemical conversion treatment liquid according to the present embodiment gels easily in the vicinity of the surface of the member to be treated, and a thick chemical conversion film is likely to be formed.

[0026] The adjustment of the pH of the chemical conversion treatment liquid according to the present embodiment can be performed, for example, by using inorganic acids such as hydrochloric acid and nitric acid, organic acids such as acetic acid, inorganic bases such as sodium hydroxide and potassium hydroxide, or organic bases such as amines. The upper limit of the pH of the chemical conversion treatment liquid according to the present embodiment is not set, provided that it serves as a chemical conversion treatment liquid. From the viewpoint of ensuring the ease of generating the chemical conversion film and the stability of the chemical conversion treatment liquid, the pH of the chemical conversion treatment liquid according to the present embodiment may be preferably 4.5 or less and more preferably 4.0 or less.

[0027] The method for producing a rust-proof member according to one embodiment of the present invention uses the above chemical conversion treatment liquid according to the present embodiment and includes a plating step and a chemical conversion treatment step, which will be described below.

[0028] In the plating step, a zinc-based plating layer is formed on a base material to obtain a member to be treated that includes the base material and the zinc-based plating layer. In the present specification, the "zinc-based plating" means a general term for zinc plating and zinc alloy plating. The base material is composed, for example, of an iron-based material, is produced by rolling, casting, extrusion, etc., and is shape-formed by machining such as rolling, cutting, or pressing, molding, etc. The zinc-based plating layer may be formed by electroplating or may also be formed by other methods.

[0029] The chemical conversion film formed from the chemical conversion treatment liquid according to the present embodiment is less susceptible to the shape (such as steps or irregularities) and surface properties (such as surface roughness) of the base material. The chemical conversion treatment liquid according to the present embodiment has a relatively high pH as previously described, and the weight loss of the zinc-based plating layer is therefore smaller than that in the case of using a general chemical conversion treatment liquid having a pH of less than 3 (specifically, 2.0 to 2.5). For this reason, even when the variation of the surface properties of the base material is large, such as when the base material has a stepped shape or the surface roughness is high, and accordingly the member to be treated has a thin portion of the zinc-based plating layer, it is possible to stably form the chemical conversion film. Specific examples of such a base material include a cast product. When the thickness of the zinc-based plating layer is 10 μm or more, the possibility of local deterioration in the corrosion resistance can be stably avoided. When the thickness of the zinc-based plating layer is 5 μm or more, local deterioration in the corrosion resistance can be suppressed.

[0030] Thus, the chemical conversion film formed from the chemical conversion treatment liquid according to the present embodiment is less susceptible to the influence (thickness, composition) of the zinc-based plating and is therefore less likely to be affected by the composition of the plating liquid for forming the zinc-based plating. When forming the zinc-based plating, a gloss agent (primary gloss agent, secondary gloss agent) is added to the plating liquid from the viewpoint of adjusting the film thickness and surface properties (such as the degree of gloss) of the formed zinc-based plating layer. The concentration of the gloss agent in the plating liquid constantly varies because the gloss agent is consumed when the plating liquid is used. To suppress the variation range, the plating liquid is used while periodically adding the gloss agent to the plating liquid. The chemical conversion film according to the present embodiment is less susceptible to the composition of the plating liquid, and it is therefore not necessary to provide a strict management width for the gloss agent concentration.

[0031] In the chemical conversion treatment step, the member to be treated is brought into contact with the chemical conversion treatment liquid according to the present embodiment, and then the member to be treated is washed to form a chemical conversion film on the member to be treated. Examples of the method of contacting the chemical conversion treatment liquid and the member to be treated include immersing the member to be treated into the chemical conversion treatment liquid and spraying the chemical conversion treatment liquid onto the member to be treated.

[0032] In a reactive chemical conversion treatment, there is generally no remarkable tendency that the fluidity of the chemical conversion treatment liquid in the vicinity of the surface of the member to be treated deteriorates due to the dissolution of zinc from the surface of the member to be treated. Therefore, interdiffusion between the chemical conversion treatment liquid in the vicinity of the surface of the member to be treated and the bulk chemical conversion treatment liquid continuously occurs through the chemical conversion treatment. Hence, even if zinc dissolves from the surface of the member to be treated and the pH of the chemical conversion treatment liquid in the vicinity of the surface thereby rises, the bulk chemical conversion treatment liquid diffuses into the vicinity of the surface, and the rise in the pH of the chemical conversion treatment liquid in the vicinity of the surface is thus restricted.

[0033] On the other hand, in the chemical conversion treatment liquid according to the present embodiment, as previously described, gelification of the colloidal silica occurs due to the dissolution of zinc from the surface of the member to be treated, and the fluidity of the chemical conversion treatment liquid therefore deteriorates in the vicinity of the surface of the member to be treated. Moreover, the bulk chemical conversion treatment liquid comes into contact with the colloidal silica caused to gel, and the colloidal silica contained in the bulk chemical conversion treatment liquid thereby further gels. Hence, in the reactive chemical conversion treatment liquid according to the present embodiment, the thickness of the chemical conversion film tends to increase as the treatment time increases. This point is significantly different from the general reactive chemical conversion treatment liquid. As the thickness of the chemical conversion film increases, the corrosion resistance of the rust-proof member tends to improve, and therefore, when the chemical conversion treatment liquid according to the present embodiment is used, the corrosion resistance can be controlled by adjusting the treatment time.

[0034] The chemical conversion treatment temperature when the chemical conversion treatment liquid is brought into contact with the member to be treated may be set within a range of 20°C to 60°C. The above temperature range allows a rust-proof member having good corrosion resistance to be stably produced because the chemical conversion treatment liquid of the present embodiment is less likely to be affected by the treatment temperature. If the temperature of the chemical conversion treatment liquid is unduly low, there is concern that the liquid viscosity will decrease to increase the workload such as stirring. If the temperature of the chemical conversion treatment liquid is unduly high, there is concern that the amount of volatilization of water, which is a solvent, will increase to increase the workload (water injection, stirring) for stabilizing the composition and viscosity of the chemical conversion treatment liquid. When the chemical conversion treatment temperature is within a range of 30°C to 55°C, it is possible to suppress the deterioration of the workability in the chemical conversion treatment step, and when the chemical conversion treatment temperature is within a range of 35°C to 50°C, it is possible to stably realize the production of a rust-proof member having good corrosion resistance while ensuring good workability in the chemical conversion treatment step.

[0035] After the contact between the chemical conversion treatment liquid and the member to be treated is completed, the chemical conversion treatment liquid remaining on the surface of the member is washed off and dried. Although the washing method is not limited, generally, rinsing with stored water followed by rinsing with flowing water is performed. Drying conditions are set as appropriate. It is expected that the stability of the chemical conversion film will be enhanced by increasing the drying temperature and the drying time. As a non-limiting example, the drying temperature is preferably 40°C or higher, more preferably 50°C or higher, and particularly preferably 70°C or higher. The drying time may be set in relation to the drying temperature. As a non-limiting example, when the drying temperature is 40°C, the drying time can be 20 minutes, when the drying temperature is 50°C, the drying time can be 10 minutes, and when the drying temperature is 70°C, the drying time can be 5 minutes.

[0036] The chemical conversion treatment forms a substance that constitutes the chemical conversion film due to the pH rise of the chemical conversion treatment liquid in the vicinity of the surface, which occurs when zinc dissolves from the surface of the member to be treated, and therefore zinc-containing substances (such as zinc ions and zinc complex ions) are inevitably dissolved in the chemical conversion treatment liquid during its use. The zinc equivalent concentration of the zinc-containing substances affects the process of dissolving zinc from the member to be treated and can affect the thickness and quality of the chemical conversion film. Fortunately, however, in the chemical conversion treatment liquid according to the present embodiment, as previously described, the colloidal silica gels in the high pH region to reduce the fluidity of the chemical conversion treatment liquid and also reduce the mass transfer with the chemical conversion treatment liquid in the bulk region. For this reason, the zinc equivalent concentration of the zinc-containing substances in the chemical conversion treatment liquid located in the high pH region is higher than the zinc equivalent concentration of the zinc-containing substances in the bulk chemical conversion treatment liquid. Hence, as a result, in the chemical conversion treatment liquid according to the present embodiment, the zinc equivalent concentration of the zinc-containing substances is less likely to affect the properties (such as the film thickness and composition) of the chemical conversion film. That is, the chemical conversion treatment liquid according to the present embodiment has high robustness against the zinc contamination.

[0037] Likewise, iron-containing substances (such as iron ions and iron complex ions) derived from the base material and the like are dissolved in the chemical conversion treatment liquid during its use. The content of the ion-containing substances tends to increase as the usage time increases. In the chemical conversion treatment liquid according to the present embodiment, as described above, the region in which the chemical conversion film is formed in the vicinity of the surface of the member to be treated is less susceptible to the composition of the bulk chemical conversion treatment liquid, and the chemical conversion treatment liquid thus has high robustness against the iron contamination.

[0038] The embodiments heretofore explained are described to facilitate understanding of the present invention and are not described to limit the present invention. Therefore, the elements disclosed in the above embodiments also include all design modifications and equivalents belonging to the technical scope of the present invention. For example, the chemical conversion film may contain an organic binder component. In this case, the chemical conversion treatment liquid may contain a component that gives the organic binder component, and a region that can be positioned as an organic-based overcoat for the above inorganic-based chemical conversion film may be formed on a Si-rich region.

[0039] The present invention includes the following aspects.

(1) A chemical conversion treatment liquid containing colloidal silica, a trivalent chromium-containing water-soluble substance, and a high pKa organic acid-containing water-soluble substance, wherein the pH of the chemical conversion treatment liquid is 3.0 or more.

(2) The chemical conversion treatment liquid described in the above (1), wherein the colloidal silica content is 2 g/L or more and 25 g/L or less, the trivalent chromium equivalent content of the trivalent chromium-containing water-soluble substance is 1 g/L or more and 6 g/L or less, and the molar ratio of the high pKa organic acid equivalent content of the high pKa organic acid-containing water-soluble substance to the trivalent chromium equivalent content of the trivalent chromium-containing water-soluble substance is 0.2 or more and 2 or less.

(3) The chemical conversion treatment liquid described in the above (1) or the above (2), wherein the high pKa organic acid contained in the high pKa organic acid-containing water-soluble substance contains a hydroxymonocarboxylic acid.

(4) The chemical conversion treatment liquid described in any one of the above (1) to the above (3), further containing a film-formable metal-containing water-soluble substance.

(5) The chemical conversion treatment liquid described in any one of the above (1) to the above (4), wherein the ratio of the colloidal silica content (unit: g/L) to the high pKa organic acid equivalent content (unit: g/L) of the high pKa organic acid-containing water-soluble substance (colloidal silica/high pKa organic acid) is within a range of 0.5 to 10.

(6) The chemical conversion treatment liquid described in any one of the above (1) to the above (5), further containing a low pKa organic acid-containing water-soluble substance, wherein the molar ratio of the low pKa organic acid equivalent content of the low pKa organic acid-containing water-soluble substance to the high pKa organic acid equivalent content of the high pKa organic acid-containing water-soluble substance is 3 or less.

(7) The chemical conversion treatment liquid described in any one of the above (1) to the above (6), wherein it is of a reactive type.

(8) A method for producing a rust-proof member, comprising: a plating step of forming the zinc-based plating layer on the base material to obtain a member to be treated comprising the base material and the zinc-based plating layer; and a chemical conversion treatment step of forming the chemical conversion film on the member to be treated, wherein the chemical conversion treatment step includes bringing the member to be treated into contact with the chemical conversion treatment liquid described in the above (7) and then washing the member.

(9) The method for producing a rust-proof member described in the above (8), wherein the base material is a cast product.

[Examples]

[0040] The effects of the present invention will be described below based on examples, but the present invention is not limited thereto.

(Example 1 to Example 4)

[0041] Rust-proof members were produced under the following conditions:

(1) base material: iron-based cast member (100 mm×50 mm, thickness 8.0 mm);

(2) zinc-based plating layer: electrogalvanization ("FZ-77A1 (primary gloss agent)/GC1 (secondary gloss agent)" available from YUKEN INDUSTRY CO., LTD.), plating thickness 10 μm;

(3) chemical conversion treatment liquid: composition listed in Table 1; and

(4) chemical conversion treatment: immersed in a chemical conversion treatment liquid at 45°C for 40 seconds while

bubbling (air agitation) (for only Example 1, further immersed for 30 seconds after stopping the bubbling), washed with water (rinsing with stored water followed by washing with flowing water), dried (80°C, 10 minutes).

[Table 1]

		Example 1	Example 2	Example 3	Example 4
Content (g/L)	Cr equivalent concentration	1.8	1.8	3.6	3.0
	High pKa organic acid	2.6	2.6	5.2	4.4
	Ti equivalent concentration	None	0.10	0.19	0.16
	Al equivalent concentration	None	0.006	0.012	0.010
	Colloidal silica	20.0	20.0	14.0	10.0
Treatment liquid	pH	3.5	3.5	3.3	3.3
Treatment conditions	Treatment time	40 sec→30 sec	40 sec	40 sec	40 sec
	Temperature	45°C	45°C	45°C	40°C
Film evaluation	Treated appearance	White, no gloss	White, weak gloss	Blue, weak gloss	White, gloss
Note		Example of present invention	Example of present invention	Example of present invention	Example of present invention

[0042] In the preparation of the chemical conversion treatment liquid, chromium chloride was used as the chromium source, titanium tetrachloride was used as the titanium source, aluminum chloride was used as the aluminum source, glycolic acid was used as the high pKa organic acid, and the pH was adjusted by using hydrochloric acid, sodium hydroxide, and potassium hydroxide. As listed in Table 1, regarding the treated appearance, gloss was not significant in any of the examples, and the appearance color was white to blue. This appearance was able to be adjusted by varying the content of the film-formable metal-containing water-soluble substance including Ti and Al. Specifically, by increasing the content of the film-formable metal-containing water-soluble substance containing Ti and Al, it was possible to make the treated appearance blue.

[0043] The rust-proof member was subjected to the neutral salt spray test (SST) described in JIS Z2371: 2015, visually observed at predetermined time intervals, and the time until white rust occurred (white rust occurrence time) was measured. Specifically, the surface of the rust-proof member was visually observed every 12 hours from the start of the test, and when white rust was recognized in 1% or more of the measurement area, the test time related to the observation was adopted as the white rust occurrence time. The measurement results are listed in Table 2. Comparative Example 1 refers to a rust-proof member obtained by immersing the same base material (iron-based cast member subjected to electrogalvanizing) as in Example 1 in a general reactive chemical conversion treatment liquid ("YFA-S/30HR" available from YUKEN INDUSTRY CO., LTD.) under standard conditions for 40 seconds.

[Table 2]

	White rust occurrence time (hours)
Example 1	504
Example 2	360
Example 3	240
Example 4	240
Comparative Example 1	96

(Example 5)

[0044] Using the chemical conversion treatment liquid according to Example 1, the robustness of the chemical conversion treatment was evaluated.

[0045] The rust-proof member was subjected to the neutral salt spray test described in JIS Z2371: 2015, and after 480 hours of testing, the rust-proof member was visually observed and evaluated in accordance with the following criteria.

A: No white rust was recognized in the measurement area.
B: The area ratio of white rust occurrence in the measurement area was less than 5%.
C: The area ratio of white rust occurrence in the measurement area was 5% or more.

(Example 5-1) Plating Film Thickness

[0046] The film thickness of electrogalvanizing was varied. The results are listed in Table 3.

[Table 3]

Plating film thickness (μm)	Evaluation result
5	B
10	A
20	A
30	A

(Example 5-2) Gloss Agent Concentration

[0047] The compounding of the gloss agent in the plating liquid for electrogalvanizing was varied. The results are listed in Table 4. The display in the column of "gloss agent ratio" in Table 4 means "addition amount of primary gloss agent (unit: mL/L)/addition amount of secondary gloss agent (unit: mL/L)."

[Table 4]

Gloss agent ratio	Evaluation result
50/1	B
80/2	A
100/1	A
70/0.5	A
70/1.5	A

(Example 5-3) Chemical Conversion Treatment Time

[0048] The treatment time of the chemical conversion treatment was varied. The results are listed in Table 5.

[Table 5]

Treatment time (seconds)	Evaluation result
20	B
30	B
40	A
60	A

(Example 5-4) Chemical Conversion Treatment Temperature

[0049] The treatment temperature of the chemical conversion treatment was varied. The results are listed in Table 6.

[Table 6]

Treatment temperature (°C)	Evaluation result
35	A
45	A
50	A

(Example 5-5) pH of Chemical Conversion Treatment Liquid

[0050] The pH of the chemical conversion treatment liquid was varied. The results are listed in Table 7.

[Table 7]

pH	Evaluation result
3.0	B
3.5	A
4.0	A

(Example 5-6) Drying Temperature

[0051] The drying temperature after the chemical conversion treatment was varied. The results are listed in Table 8.

[Table 8]

Drying temperature (°C)	Evaluation result
50	B
60	B
70	A
80	A
100	A

(Example 5-7) Zinc Concentration of Chemical Conversion Treatment Liquid

[0052] When preparing the chemical conversion treatment liquid, zinc chloride was added to vary the zinc equivalent concentration of the zinc-containing substance in the chemical conversion treatment liquid. The results are listed in Table 9.

[Table 9]

Zinc equivalent concentration (g/L)	Evaluation result
0	A
3	A
5	A
10	A

(Example 5-8) Iron Concentration of Chemical Conversion Treatment Liquid

[0053] When preparing the chemical conversion treatment liquid, iron chloride was added to vary the iron equivalent concentration of the iron-containing substance in the chemical conversion treatment liquid. The results are listed in Table 10.

[Table 10]

Iron equivalent concentration (ppm)	Evaluation result
0	A
50	A
100	B
200	B

(Example 6) Composition of Chemical Conversion Treatment Liquid

[0054] With reference to the composition of Example 4, the content of components other than colloidal silica (Cr, Ti, Al, high pKa organic acid) and the content of colloidal silica were varied as listed in Table 11 to prepare a number of chemical conversion treatment liquids (Treatment Liquid 4-1 to Treatment Liquid 4-36). The composition of Treatment Liquid 4-22 was the same as that of the chemical conversion treatment liquid according to Example 4, and the pH of all the treatment liquids was 3.3. The same chemical conversion treatment as in Example 4 was performed, and the SST was carried out on the obtained rust-proof members. The rust-proof members were visually observed at test times of 72 hours, 168 hours, and 264 hours and the white rust occurrence area ratio (unit: %) was measured. The measurement results of the white rust occurrence area ratio are listed in Table 11.

[Table 11]

Treatment liquid	Other than silica	Silica	72 h	168 h	264 h
4-1	×0.4	×0.4	0	3	15
4-2	×0.4	×0.6	0	1	8
4-3	×0.4	×0.8	0	1	8
4-4	×0.4	×1	0	0	5
4-5	×0.4	×1.2	0	0	2
4-6	×0.4	×1.4	0	0	1
4-7	×0.6	×0.4	0	3	15
4-8	×0.6	×0.6	0	1	10
4-9	×0.6	×0.8	0	0	2
4-10	×0.6	×1	0	0	0
4-11	×0.6	×1.2	0	0	0
4-12	×0.6	×1.4	0	1	1
4-13	×0.8	×0.4	0	1	20
4-14	×0.8	×0.6	0	1	5
4-15	×0.8	×0.8	0	0	10
4-16	×0.8	×1	0	0	2
4-17	×0.8	×1.2	0	0	1
4-18	×0.8	×1.4	0	0	2
4-19	×1	×0.4	0	1	5
4-20	×1	×0.6	0	1	4

(continued)

Treatment liquid	Other than silica	Silica	72 h	168 h	264 h
4-21	×1	×0.8	0	0	2
4-22	×1	×1	0	1	1
4-23	×1	×1.2	0	0	1
4-24	×1	×1.4	0	0	1
4-25	×1.2	×0.4	0	2	10
4-26	×1.2	×0.6	0	2	5
4-27	×1.2	×0.8	0	0	3
4-28	×1.2	×1	0	0	2
4-29	×1.2	×1.2	0	1	7
4-30	×1.2	×1.4	0	0	3
4-31	×1.4	×0.4	0	5	30
4-32	×1.4	×0.6	0	2	8
4-33	×1.4	×0.8	0	0	5
4-34	×1.4	×1	0	1	5
4-35	×1.4	×1.2	0	0	4
4-36	×1.4	×1.4	0	1	3

[0055] As listed in Table 11, it has been confirmed that, up to 168 hours of the test time, the rust-proof member formed using any of the treatment liquids has a white rust occurrence area ratio of 5% or less and also has good corrosion resistance.

[0056] The results of the test time of 264 hours are listed in a matrix (Table 12). In Table 12, the region in which the white rust occurrence area ratio is 5% or less is enclosed by a thick line. In this region, there were results that the white rust occurrence area ratio was more than 5% and 10% or less only in two cells. In Table 12, these results are illustrated in two-dot chain frames.

[Table 12]

		Other than colloidal silica					
		×0.4	×0.6	×0.8	×1	×1.2	×1.4
Colloidal silica	×0.4	15	15	20	5	10	30
	×0.6	8	10	5	4	5	8
	×0.8	8	2	10	2	3	5
	×1	5	0	2	1	2	5
	×1.2	2	0	1	1	7	4
	×1.4	1	1	2	1	3	3

[0057] It has been confirmed that as the colloidal silica content becomes relatively high, a rust-proof film excellent in the corrosion resistance can be stably obtained even when the content of components other than the colloidal silica varies to some extent.

(Example 7) Effect of Organic Acid Type

[0058] As listed in Table 13, for the chemical conversion treatment liquid according to Example 4, a part of the high pKa organic acid was replaced with oxalic acid (lowest pKa is 1.27), which is a type of low pKa organic acid, and Chemical

Conversion Treatment Liquids 4-37 to 4-40 were prepared. In addition, a chemical conversion treatment liquid according to Comparative Example 2 was prepared by replacing all of the high pKa organic acids in the chemical conversion treatment liquid according to Example 4 with oxalic acid. The row of "Organic acid molar ratio" in Table 13 lists the molar ratio of the low pKa organic acid equivalent content of the low pKa organic acid-containing water-soluble substance to the high pKa organic acid equivalent content of the high pKa organic acid-containing water-soluble substance (low pKa organic acid/high pKa organic acid). As listed in Table 13, Chemical Conversion Treatment Liquids 4-37 to 4-40 are made different from the chemical conversion treatment liquid according to Example 4 in the organic acid molar ratio within the range of 0.1 to 3.

[Table 13]

		Unit	Example 4	4-37	4-38	4-39	4-40	Comparative Example 2
Content	Cr equivalent concentration	g/L	3.0	3.0	3.0	3.0	3.0	3.0
	High pKa organic acid	g/L	4.4	4.0	3.3	2.2	1.1	0.0
		mmol/L	57.9	52.6	43.4	28.9	14.5	0.0
	Low pKa organic acid	g/L	0.0	0.47	1.3	2.6	3.9	5.2
		mmol/L	0.0	5.2	14.4	28.9	43.3	57.8
	Organic acid molar ratio		0.0	0.1	0.33	1.0	3.0	-
	Ti equivalent concentration	g/L	0.16	0.16	0.16	0.16	0.16	0.16
	Al equivalent concentration	g/L	0.010	0.010	0.010	0.010	0.010	0.010
	Colloidal silica	g/L	10.0	10.0	10.0	10.0	10.0	10.0
Treatment liquid	pH		3.3	3.3	3.3	3.3	3.3	3.3
Treatment conditions	Treatment time	seconds	40	40	40	40	40	40
	Temperature	°C	40	40	40	40	40	40

[0059] Rust-proof members were produced using these chemical conversion treatment liquids. The same test as in Example 6 was performed on the obtained rust-proof members. Table 14 lists the measurement results of the white rust occurrence area ratio (unit: %) at each measurement time.

[Table 14]

Treatment liquid	72 h	168 h	264 h
Example 4	0	1	1
4-37	0	0	1
4-38	0	1	3
4-39	0	1	5
4-40	1	3	10
Comparative Example 2	2	5	30

[0060] The white rust occurrence area ratio of the rust-proof member produced using the chemical conversion treatment liquid according to Comparative Example 2 was 2% after 72 hours.

Claims

1. A method for producing a rust-proof member, comprising

   a chemical conversion treatment step of forming a chemical conversion film on a member to be treated containing zinc on its surface, the chemical conversion treatment step including bringing a chemical conversion treatment liquid into contact with the member to be treated and then washing the member,
   the chemical conversion treatment liquid containing colloidal silica, a trivalent chromium-containing water-soluble substance that is an ionic substance containing trivalent chromium, and a high pKa organic acid-containing water-soluble substance that is a water-soluble substance containing a high pKa organic acid that is an organic acid having a lowest pKa of 3.5 or more,
   the chemical conversion treatment liquid having a pH of 3.0 or more and 4.5 or less in a state before contacting with the member to be treated,
   the high pKa organic acid containing glycolic acid (except for a case of containing at least one selected from allylamine, polyallylamine, aromatic sulfonic acid, aromatic sulfonic acid-formaldehyde condensate, and derivatives thereof).

2. The method for producing a rust-proof member according to claim 1, wherein in the chemical conversion treatment liquid,

   the colloidal silica has a content of 2 g/L or more and 25 g/L or less,
   the trivalent chromium-containing water-soluble substance has a trivalent chromium equivalent content of 1 g/L or more and 6 g/L or less, and
   a molar ratio of a high pKa organic acid equivalent content of the high pKa organic acid-containing water-soluble substance to the trivalent chromium equivalent content of the trivalent chromium-containing water-soluble substance is 0.2 or more and 2 or less.

3. The method for producing a rust-proof member according to claim 1 or 2, wherein the chemical conversion treatment liquid further contains a film-formable metal-containing water-soluble substance that is a water-soluble substance containing metal ions capable of forming a film by interacting with oxygen.

4. The method for producing a rust-proof member according to any one of claims 1 to 3, wherein in the chemical conversion treatment liquid, a ratio of a content of the colloidal silica (unit: g/L) to a high pKa organic acid equivalent content (unit: g/L) of the high pKa organic acid-containing water-soluble substance (colloidal silica/high pKa organic acid) is within a range of 0.5 to 10.

5. The method for producing a rust-proof member according to any one of claims 1 to 4, wherein the chemical conversion treatment liquid further contains a low pKa organic acid-containing water-soluble substance that is a water-soluble substance containing a low pKa organic acid that is an organic acid having a lowest pKa of 1.27 or more and less than 3.5, and a molar ratio of a low pKa organic acid equivalent content of the low pKa organic acid-containing water-soluble substance to a high pKa organic acid equivalent content of the high pKa organic acid-containing water-soluble substance is 1 or less.

6. The method for producing a rust-proof member according to any one of claims 1 to 5, wherein the member to be treated is obtained by forming a zinc-based plating layer on a base material.

7. The method for producing a rust-proof member according to claim 6, wherein the base material is a cast product.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2021/030556

A. CLASSIFICATION OF SUBJECT MATTER

C23C 22/30(2006.01)i
FI: C23C22/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C22/30

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2021
Registered utility model specifications of Japan 1996-2021
Published registered utility model applications of Japan 1994-2021

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 3246429 A1 (ATOTECH DEUTSCHLAND GMBH) 22 November 2017 (2017-11-22) entire text	1-7

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Date of the actual completion of the international search	Date of mailing of the international search report
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Japan Patent Office (ISA/JP) **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2021/030556

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