



**EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 153(4) EPC

(43) Date of publication:

**20.09.2017 Bulletin 2017/38**

(51) Int Cl.:

**C23C 22/78** (2006.01) **C23C 28/00** (2006.01)  
**C23G 1/20** (2006.01)

(21) Application number: **15858294.0**

(86) International application number:

**PCT/JP2015/005583**

(22) Date of filing: **09.11.2015**

(87) International publication number:

**WO 2016/075920 (19.05.2016 Gazette 2016/20)**

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB  
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO  
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

**BA ME**

Designated Validation States:

**MA MD**

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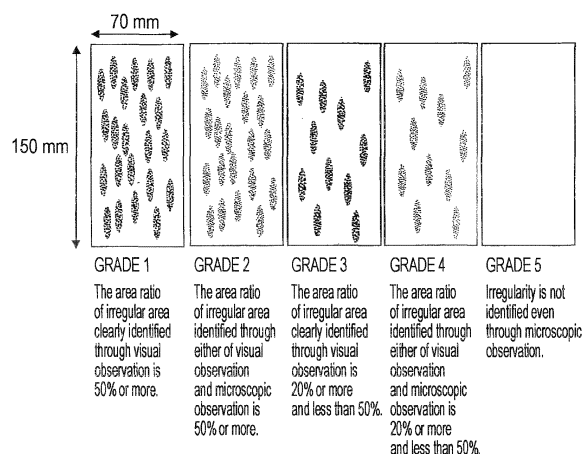
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(54) **METHOD FOR MANUFACTURING GALVANIZED STEEL SHEET**

(57) Provided is a method for manufacturing a steel sheet coated with a zinc-based coating layer with which it is possible to remove an oxide on the surface of a zinc-based coating layer through contact with an alkaline aqueous solution and with which it is possible to prevent a problem related to surface appearance due to precipitates generated in an alkaline aqueous solution.

The method for manufacturing a steel sheet coated with a zinc-based coating layer of the first invention to solve the problems described above is a method for manufacturing a steel sheet coated with a zinc-based coating layer having a reaction layer on the surface of the steel sheet, the method including: the method including bringing the steel sheet coated with a zinc-based coating layer into contact for 1.0 second or more with an alkaline aqueous solution containing one or more chelating agents selected from among sodium gluconate, sodium glucoheptonate, sodium citrate, tartaric acid, arabonic acid, galactonic acid, sorbit, mannite, glycerin, EDTA, and sodium tripolyphosphate in a total amount of 0.050 mass% or more and having a pH of 10.0 or more as a pre-treatment before a formation of the reaction layer, and forming the reaction layer being an oxide layer containing a crystal-structured substance expressed by  $\text{Zn}_4(\text{SO}_4)_{1-x}(\text{CO}_3)_x(\text{OH})_6 \cdot n\text{H}_2\text{O}$ .

FIG. 1



**Description**

## Technical Field

5 **[0001]** The present invention relates to a method for manufacturing a steel sheet coated with a zinc-based coating layer having a reaction layer.

## Background Art

10 **[0002]** A steel sheet coated with a zinc-based coating layer has been used in a wide range of applications mainly in automobile bodies, domestic electrical appliances, and building materials. There is a known technique in which properties such as press formability, corrosion resistance, and surface appearance quality of a steel sheet coated with a zinc-based coating layer used in such applications are improved by forming a reaction layer on the surface of the steel sheet.

15 **[0003]** However, conventionally, a steel sheet coated with a zinc-based coating layer before a reaction layer is formed thereon has an unnecessary layer having a thickness of less than 10 nm composed of oxides of, for example, Zn and Al, which are impurity chemical elements, in the outermost surface layer thereof. Since such an unnecessary oxide layer decreases the reactivity of a chemical conversion treatment such as a zinc phosphate treatment or a chromate treatment, it is necessary to set a long reaction time in order to form a sufficient amount of the reaction layer.

20 **[0004]** An increase in reaction time is accompanied by an increase in equipment cost, line length, and running cost for, for example, electricity and gas.

**[0005]** In response to such a problem, there is a known technique in which a reaction time is decreased by bringing the surface layer of a steel sheet coated with a zinc-based coating layer into contact with an alkaline aqueous solution in order to remove an unnecessary oxide layer existing on the surface layer of the steel sheet before a reaction layer is formed.

25 **[0006]** Patent Literature 1 describes a technique in which a galvanized steel sheet is treated by using a  $\text{SiO}_2$ -containing chromate solution after the steel sheet has been brought into contact with an alkaline aqueous solution.

**[0007]** Also, there is a known technique in which an oxide film is intentionally formed after a treatment has been performed by using an alkaline aqueous solution.

30 **[0008]** Patent Literature 2 and Patent Literature 3 describe techniques in which an oxide layer is formed after the surface of a galvanized steel sheet has been brought into contact with an alkaline aqueous solution.

**[0009]** Patent Literature 4 describes a technique in which an oxide layer is formed after the surface of a galvanized steel sheet has been brought into contact with an alkaline aqueous solution.

35 **[0010]** Patent Literature 5 describes a technique in which an oxide layer containing a crystal-structured substance expressed by  $\text{Zn}_4(\text{SO}_4)_{1-x}(\text{CO}_3)_x(\text{OH})_6 \cdot n\text{H}_2\text{O}$  is formed after the surface of a galvanized steel sheet has been brought into contact with an alkaline aqueous solution.

## Citation List

## Patent Literature

40

**[0011]**

PTL 1: Japanese Unexamined Patent Application Publication No. 5-279868

PTL 2: Japanese Unexamined Patent Application Publication No. 2006-183074

45 PTL 3: Japanese Unexamined Patent Application Publication No. 2006-233280

PTL 4: Japanese Unexamined Patent Application Publication No. 2005-97741

PTL 5: Japanese Patent Application No. 2015-530230

## Summary of Invention

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## Technical Problem

**[0012]** In the case of the techniques according to Patent Literature 1 through Patent Literature 5, it is possible to decrease the reaction time required to form a reaction layer through contact with an alkaline aqueous solution. However, 55 in the case of ordinarily used continuous treatment equipment, since pressing flaws occur on the surface of a steel sheet due to precipitates of Zn and Al generated in the alkaline aqueous solution adhering to deflecting rolls and supporting rolls, there is a case where problems related to surface appearance such as an irregularity in surface appearance occurs after a reaction layer has been formed.

**[0013]** The present invention has been completed in view of the situation described above. An object of the present invention is to provide a method for manufacturing a steel sheet coated with a zinc-based coating layer in which it is possible to remove an unnecessary oxide layer on the surface of the zinc-based coating layer through contact with an alkaline aqueous solution and in which it is possible to prevent a problem related to surface appearance due to precipitates generated in an alkaline aqueous solution. Solution to Problem

**[0014]** The present inventors diligently conducted investigations in order to solve the problems described above, and, as a result, found that it is possible to solve the problems described above by adding a specific chelating agent to an alkaline aqueous solution which is used before a reaction layer is formed, resulting in the completion of the present invention. More specifically, the present invention provides the following.

**[0015]** The method for manufacturing a steel sheet coated with a zinc-based coating layer of the first invention in order to solve the problems described above is a method for manufacturing a steel sheet coated with a zinc-based coating layer having a reaction layer on the surface of the steel sheet, the method including:

bringing a steel sheet coated with a zinc-based coating layer into contact for 1.0 second or more with an alkaline aqueous solution containing one or more chelating agents selected from among sodium gluconate, sodium glucoheptonate, sodium citrate, tartaric acid, arabonic acid, galactonic acid, sorbit, mannite, glycerin, EDTA, and sodium tripolyphosphate in a total amount of 0.050 mass% or more and having a pH of 10.0 or more as a pre-treatment before a formation of the reaction layer, and

forming the reaction layer being an oxide layer containing a crystal-structured substance expressed by  $\text{Zn}_4(\text{SO}_4)_{1-x}(\text{CO}_3)_x(\text{OH})_6 \cdot n\text{H}_2\text{O}$ .

**[0016]** The method for manufacturing a steel sheet coated with a zinc-based coating layer of the second invention in order to solve the problems described above is the method for manufacturing a steel sheet coated with a zinc-based coating layer according to the first invention, wherein pH of the alkaline aqueous solution is 12.6 or more.

#### Advantageous Effects of Invention

**[0017]** According to the present invention, it is possible to effectively remove oxides on the surface of a zinc-based coating layer through contact with an alkaline aqueous solution. In addition, in an alkaline treatment which is performed in order to decrease the time required to form a reaction layer, since it is possible to decrease the amount of, for example, precipitates of Al and Zn, it is possible to obtain a steel sheet coated with a zinc-based coating layer having a reaction layer and having good surface appearance.

#### Brief Description of Drawing

**[0018]** [Fig. 1] Fig. 1 is a schematic diagram illustrating evaluation criteria for an irregularity in surface appearance.

#### Description of Embodiments

**[0019]** Hereafter, the embodiments of the present invention will be described. Here, the present invention is not limited to the embodiments described below. In the present invention, the term "a steel sheet coated with a zinc-based coating layer" refers to a steel sheet having a coating film containing mainly zinc on the surface thereof regardless of its manufacturing method, and the meaning of the term includes a zinc-coated steel sheet, a zinc-alloy-coated steel sheet, a steel sheet coated with a coating layer containing particles dispersed in zinc, and so forth. That is, the meaning of the term "a zinc-based coating layer" includes a zinc coating layer, a zinc-alloy coating layer, a coating layer containing particles dispersed in zinc, and so forth.

**[0020]** The present invention is a method for manufacturing a steel sheet coated with a zinc-based coating layer, the steel sheet having a reaction layer, that is, an oxide layer containing a crystal-structured substance expressed by  $\text{Zn}_4(\text{SO}_4)_{1-x}(\text{CO}_3)_x(\text{OH})_6 \cdot n\text{H}_2\text{O}$ , with which it is possible to effectively remove an unnecessary oxide layer existing on the surface of the zinc-based coating layer. The present invention includes, for example, a process in which zinc-based coating is performed, a process in which the steel sheet is brought into contact with an alkaline aqueous solution, and a process in which an oxide layer containing a crystal-structured substance expressed by  $\text{Zn}_4(\text{SO}_4)_{1-x}(\text{CO}_3)_x(\text{OH})_6 \cdot n\text{H}_2\text{O}$  is formed. Hereafter, each of the processes will be described.

**[0021]** Process in which zinc-based coating is performed

**[0022]** First, a process in which zinc-based coating is performed will be described. In the process in which zinc-based coating is performed, there is no particular limitation on the method used for forming a zinc-based coating layer, and a commonly used method such as a galvanizing method or an electro-galvanizing method may be used. In addition, there is no particular limitation on the conditions used for performing an electro-galvanizing treatment or a galvanizing treatment,

and preferable conditions may be used appropriately. Here, in the case where galvanizing is performed, it is preferable that Al be added to the galvanizing bath from the viewpoint of a countermeasure against dross. In this case, there is no particular limitation on constituent chemical elements other than Al. That is, even in the case where Pb, Sb, Si, Sn, Mg, Mn, Ni, Ti, Li, Cu, and the like are contained in addition to Al, there is no decrease in the effects of the present invention.

**[0023]** Here, there is no particular limitation on the grade of steel sheet on which zinc coating is performed, and a steel sheet of any steel grade such as low-carbon steel, ultralow-carbon steel, IF steel, or a high-strength steel sheet, in which various alloy chemical elements are added, may be used. In addition, the steel sheet may be any of a hot-rolled steel sheet and a cold-rolled steel sheet. There is no particular limitation on the thickness of the steel sheet. Here, it is preferable that the thickness be 0.4 mm to 5.0 mm from the viewpoint of applications such as automobile bodies, domestic electrical appliances, and building materials.

**[0024]** Moreover, in a process in which zinc-based coating is performed, after a galvanizing treatment is performed, a galvanized steel sheet may be manufactured by performing an alloying treatment. In the present invention, there is no particular limitation on the conditions for performing an alloying treatment, and preferable conditions may be used appropriately.

**[0025]** Process in which a steel sheet is brought into contact with an alkaline aqueous solution

**[0026]** After zinc-based coating has been performed, a contact treatment is performed by using an alkaline aqueous solution. The alkaline aqueous solution which is used in this contact treatment has a pH of 10.0 or more. In the case where the pH is less than 10.0, an insufficient amount of oxide layer is removed. It is preferable that the pH be 12.6 or more, because it is possible to effectively decrease the contact time with the alkaline aqueous solution.

**[0027]** On the other hand, it is preferable that the pH be 14.0 or less from the viewpoint of preventing the dissolution of the zinc-based coating layer and the blackening of surface appearance.

**[0028]** Specific chelating agents are contained in the alkaline aqueous solution in a total amount of 0.050 mass% or more. In the case where there is an increase in the amount of, for example, precipitates of Al and Zn in the alkaline aqueous solution, the solution has a suspension-like appearance. In the present invention, 0.050 mass% or more of chelating agents are added to the alkaline aqueous solution in order to decrease the amounts of, for example, the precipitates of Al and Zn.

**[0029]** The chelating agents described above are one or more selected from among sodium gluconate, sodium glucoheptonate, sodium citrate, tartaric acid, arabonic acid, galactonic acid, sorbit, mannite, glycerin, EDTA, and sodium tripolyphosphate. It is preferable to use sodium gluconate as the chelating agent described above, because it is capable of chelating Al and Zn and inexpensive.

**[0030]** In the case where the total content of chelating agents in the alkaline aqueous solution is less than 0.050 mass%, there is an insufficient increase in the solubility of Al and Zn in the alkaline aqueous solution. It is preferable that the content of chelating agents in the alkaline aqueous solution be 0.100 mass% or more from the viewpoint of decreasing the amount of precipitates in the alkaline aqueous solution. On the other hand, it is preferable that the content of chelating agents in the alkaline aqueous solution be 10.0 mass% or less from the viewpoint of chemical cost.

**[0031]** It is preferable that the temperature of the alkaline aqueous solution be in the range of 20°C to 70°C, or more preferably 40°C to 70°C, in order to decrease the contact time between the alkaline aqueous solution and a steel sheet.

**[0032]** There is no limitation on the kind of an alkaline builder. Here, it is preferable to use a chemical such as NaOH from the viewpoint of cost. In order to achieve the desired pH of the alkaline aqueous solution, the amount of the alkaline builder is appropriately controlled. In addition, the alkaline aqueous solution may contain substances and chemical components other than chemical elements such as Zn, Al, and Fe, which are contained in a zinc-based coating solution.

**[0033]** There is no particular limitation on the method used for bringing the alkaline aqueous solution into contact with a steel sheet coated with a zinc-based coating layer (in particular, an oxide layer on the surface thereof), and examples of the method include one in which the steel sheet coated with a zinc-based coating layer is dipped in the alkaline aqueous solution and one in which the steel sheet coated with a zinc-based coating layer is sprayed with the alkaline aqueous solution.

**[0034]** A time during which the steel sheet coated with a zinc-based coating layer is brought into contact with the alkaline aqueous solution is 1.0 second or more. In the case where the contact time is less than 1.0 second, since an insufficient amount of oxides is removed from the surface of the zinc-based coating layer, there is an insufficient decrease in reaction time during which a reaction layer is formed. It is preferable that the time during which the steel sheet coated with a zinc-based coating layer is brought into contact with the alkaline aqueous solution be 10.0 seconds or less from the viewpoint of equipment cost and productivity.

**[0035]** In the present invention, a skin pass rolling may be performed after the process in which zinc-based coating is performed and before or after the treatment is performed by using an alkaline aqueous solution. There is an increase in reactivity in a portion of a steel sheet which has been brought into contact with rolls for skin pass rolling, because an unnecessary oxide layer of Al and Zn is removed from the surface of the zinc-based coating layer through the contact with the rolls.

**[0036]** Process in which a reaction layer is formed

**[0037]** Usually, after the process in which a steel sheet is brought into contact with the alkaline aqueous solution, and then rinsing with water and drying are performed, a treatment is performed in order to form a reaction layer, that is, an oxide layer containing a crystal-structured substance expressed by  $\text{Zn}_4(\text{SO}_4)_{1-x}(\text{CO}_3)_x(\text{OH})_6 \cdot n\text{H}_2\text{O}$ .

**[0038]** In the present invention, the term "an oxide layer containing a crystal-structured substance expressed by  $\text{Zn}_4(\text{SO}_4)_{1-x}(\text{CO}_3)_x(\text{OH})_6 \cdot n\text{H}_2\text{O}$ " refers to the layer of a reaction product which is formed on the surface of a steel sheet through a chemical reaction which occurs as a result of contact between a zinc-based coating layer and a chemical treatment solution. An example of a treatment for forming an oxide layer containing a crystal-structured substance expressed by  $\text{Zn}_4(\text{SO}_4)_{1-x}(\text{CO}_3)_x(\text{OH})_6 \cdot n\text{H}_2\text{O}$  includes an oxide-layer-forming process in which a steel sheet coated with a zinc-based coating layer is brought into contact with an acid solution containing sulfate ions, then held for 1 second to 60 seconds, and then washed with water and a neutralizing treatment process in which the surface of the oxide layer formed in the oxide-layer-forming process described above is kept in contact with an alkaline aqueous solution for 0.5 seconds or more, then washed with water, and then dried. The alkaline aqueous solution may contain P ions in an amount of 0.01 g/L or more in terms of P concentration and carbonate ions in an amount of 0.1 g/L or more in terms of carbonate ion concentration. The present invention is not limited to such a treatment method as long as a crystal-structured substance expressed by  $\text{Zn}_4(\text{SO}_4)_{1-x}(\text{CO}_3)_x(\text{OH})_6 \cdot n\text{H}_2\text{O}$  exists on the surface of a steel sheet.

#### EXAMPLE 1

**[0039]** Hereafter, the present invention will be described on the bases of examples. The scope of the present invention is not limited to the examples described below.

**[0040]** A skin pass rolling was performed on steel sheets which had been prepared by performing a galvanizing treatment on cold-rolled steel sheets having a thickness of 0.7 mm and a width of 1100 mm. Subsequently, the steel sheets were subjected to a treatment for removing an oxide layer in which the steel sheets were kept in contact with the alkaline aqueous solutions prepared under the conditions given in Tables 1-1 and 1-2 over the specified times, then washed with water, and then dried.

**[0041]** Also, steel sheets which had been prepared by performing a galvanizing treatment followed by an alloying treatment and skin pass rolling on a cold-rolled steel sheets having a thickness of 0.7 mm and a width of 1100 mm and steel sheets which had been prepared by performing an electro-galvanizing treatment on cold-rolled steel sheets having a thickness of 0.7 mm and a width of 1100 mm were kept in contact with the alkaline aqueous solutions in the same procedures as those described above, then washed with water, and then dried.

**[0042]** On the steel sheets coated with a zinc-based coating layer obtained as described above, determination of the thickness of an unnecessary oxide layer on the surface of the zinc-based coating layer after a treatment had been performed by using an alkaline aqueous solution and evaluation of the irregularity in surface appearance after a reaction layer had been formed were performed, and determination of suspended solids (SS) contained in the alkaline aqueous solutions was performed. Here, the pH of the alkaline aqueous solution was determined by using commercially available glass electrodes.

**[0043]** Subsequently, a treatment for forming an oxide layer containing a crystal-structured substance expressed by  $\text{Zn}_4(\text{SO}_4)_{1-x}(\text{CO}_3)_x(\text{OH})_6 \cdot n\text{H}_2\text{O}$  was performed by dipping the steel sheets in a sulfuric acid solution containing 30 g/L of sodium acetate trihydrate and having a pH of 1.5, then squeezing the steel sheets by using rolls, and then holding the steel sheets for 10 seconds. Then, after having performed washing with water, drying was performed. Subsequently, a neutralizing treatment was performed by using a treatment solution containing 9.8 g/L of sodium pyrophosphate and 0.48 g/L of sodium carbonate decahydrate.

#### (1) Determination of the thickness of an unnecessary oxide layer

**[0044]** After the contact with the alkaline aqueous solution, an X-ray fluorescence spectrometer was used for determining the thickness of an unnecessary oxide layer formed on the surface of the steel sheet coated with a zinc-based coating layer. It is judged that a case where the thickness of the oxide layer (thickness of an oxide film) is 4 nm or less as a case where there is a decrease in reaction time required to form a reaction layer. It is judged that a case where the thickness of an oxide film is 2 nm or less as a case where there is a further decrease in reaction time.

**[0045]** At the time of the determination, by setting the voltage and current of a tube to be respectively 30 kV and 100 mA, and by setting a dispersive crystal to be TAP, an O-K $\alpha$  ray was detected. At the time of the determination of an O-K $\alpha$  ray, intensity was determined at a peak position and a background position in order to calculate the net intensity of an O-K $\alpha$  ray. Here, the integration time at each of the peak position and the background position was 20 seconds.

**[0046]** In addition, silicon wafers which were cleaved into an appropriate size and whose surface were respectively covered with silicon oxide films having a film thickness of 96 nm, 54 nm, and 24 nm were set on the sample stage with these series of samples so that it was possible to calculate the intensity of an O-K $\alpha$  ray of each of such silicon oxide films. A calibration curve is prepared to determine the relationship between the thickness of an oxide layer and the

intensity of an O-K $\alpha$  ray by using such data. The thickness of the oxide layer of the sample is calculated as the thickness of the oxide layer in terms of the thickness of a silicon oxide film.

(2) Evaluation of the irregularity in surface appearance and determination of the thickness of an oxide film after a surface oxidation treatment has been performed

**[0047]** After having performed a treatment for forming an oxide layer on the surface of each of galvanized steel sheets, galvanized steel sheets, and electro-galvanized steel sheets which had been subjected to a contact treatment by using an alkaline aqueous solution, an irregularity in surface appearance was evaluated by performing visual observation and microscopic observation. That is, by preparing a solution containing 5.0 g/L of ferrous sulfate and 50 g/L of sodium acetate heptahydrate which was adjusted so as to have a pH of 2.0 by using sulfuric acid, by applying the prepared treatment solution to each of the various kinds of the coated steel sheets which had been subjected to a contact treatment by using an alkaline aqueous solution so that the thickness of the solution was 3  $\mu$ m, by holding the coated steel sheet for 10 seconds, by then washing the coated steel sheet with water, and by then drying the coated steel sheet, a treatment for forming an oxide layer was performed. Here, the observation area was 70 mm  $\times$  150 mm. With reference to the surface appearance samples illustrated in Fig. 1, evaluation was performed on a scale of one to five. Grade 4 indicates a satisfactory case, and grade 5 indicates a more satisfactory case.

(3) Determination of suspended solids (SS)

**[0048]** The alkaline aqueous solution which had been used for the treatment of 100 tons or more of a steel sheet coated with a zinc-based coating layer was collected and subjected to suction filtration by using a membrane filter having a pore size of 1  $\mu$ m. After having dried the material retained on the filter at a temperature of 110°C, the weight of the dried material was determined, and the weight was expressed in units of mg/L. The amount of production for which the determined value was more than 10 mg/L was recorded. A case where the amount of steel sheets treated for which the determined value was more than 10 mg/L was 3000 tons or more was judged as satisfactory from the viewpoint of productivity. In addition, a case where the determined value was not more than 10 mg/L even after 5000 tons of steel sheets had been treated was judged as a case of no suspended solids (represented by "> 5000" in Tables 1-1 and 1-2). In the case of Nos. 1, 54, and 56 where a treatment was not performed by using an alkaline aqueous solution, such determination was not performed.

**[0049]** The results obtained as described above are given in Tables 1-1 and 1-2. Here, the conditions on which the tests of No. 15 and No. 41 were performed were same, and the conditions on which the tests of No. 20 and No. 28 were performed were same.

[Table 1-1]

| Contact Treatment Condition with Alkaline Treatment Solution |                        |                           |                  |                       |             |      |                |              |                        |                                    |                                                                       |                     | Result              |                       | Note |
|--------------------------------------------------------------|------------------------|---------------------------|------------------|-----------------------|-------------|------|----------------|--------------|------------------------|------------------------------------|-----------------------------------------------------------------------|---------------------|---------------------|-----------------------|------|
| No.                                                          | Material for Sample    | Alkaline Aqueous Solution |                  |                       |             |      |                |              | Thicknes of Oxide Film | Irregularity in Surface Appearance | Amount of Production for More than 10 mg of Suspended Solid Generated | Comparative Example |                     |                       |      |
|                                                              |                        | Alkaline Builder          | Chelating Agent  |                       | Temperature | pH   | Contact Method | Contact Time |                        |                                    |                                                                       |                     |                     |                       |      |
|                                                              |                        |                           | Kind of Chemical | Concentration (mass%) |             |      |                |              |                        |                                    |                                                                       |                     | Kind of Chemical    | Concentration (mass%) |      |
| 1                                                            | Galvanized Steel Sheet | None                      | -                | -                     | -           | -    | -              | -            | 8                      | 5                                  | -                                                                     | Comparative Example |                     |                       |      |
| 2                                                            |                        | Sodium Hydrate            | 0.01             | -                     | 50          | 10.0 | Dip            | 3.0          | 3                      | 1                                  | 500                                                                   | Comparative Example |                     |                       |      |
| 3                                                            |                        |                           | 0,5              | -                     |             | 12.6 |                |              | 2                      | 1                                  | 200                                                                   | Comparative Example |                     |                       |      |
| 4                                                            |                        | Sodium Hydrate            | 0.01             | Sodium Gluconate      | 0.005       | 50   | 10.0           | Dip          | 3.0                    | 3                                  | 4                                                                     | 1500                | Comparative Example |                       |      |
| 5                                                            |                        |                           |                  |                       | 0.050       |      |                |              | 3                      | 5                                  | >5000                                                                 | Example             |                     |                       |      |
| 6                                                            |                        |                           |                  | 0.100                 |             |      |                |              | 3                      | 5                                  | >5000                                                                 | Example             |                     |                       |      |
| 7                                                            |                        |                           |                  | 0.500                 |             |      |                |              | 3                      | 5                                  | >5000                                                                 | Example             |                     |                       |      |
| 8                                                            |                        |                           |                  | 1.0                   |             |      |                |              | 3                      | 5                                  | >5000                                                                 | Example             |                     |                       |      |
| 9                                                            |                        |                           |                  | 2.0                   |             |      |                |              | 3                      | 5                                  | >5000                                                                 | Example             |                     |                       |      |
| 10                                                           |                        |                           |                  | 3.0                   |             |      |                |              | 3                      | 5                                  | >5000                                                                 | Example             |                     |                       |      |
| 11                                                           |                        | Sodium Hydrate            | 0.5              | Sodium Gluconate      | 0.005       | 50   | 12.6           | Dip          | 3.0                    | 2                                  | 4                                                                     | 1500                | Comparative Example |                       |      |
| 12                                                           |                        |                           |                  | 0.050                 |             |      |                |              | 2                      | 5                                  | >5000                                                                 | Example             |                     |                       |      |
| 13                                                           |                        |                           |                  | 0.100                 |             |      |                |              | 2                      | 5                                  | >5000                                                                 | Example             |                     |                       |      |
| 14                                                           |                        |                           |                  | 0.500                 |             |      |                |              | 2                      | 5                                  | >5000                                                                 | Example             |                     |                       |      |
| 15                                                           |                        |                           |                  | 1.0                   |             |      |                |              | 2                      | 5                                  | >5000                                                                 | Example             |                     |                       |      |

(continued)

| Contact Treatment Condition with Alkaline Treatment Solution |                     |                           |                       |                  |                       |                   |      |                |              |                               |                                             |                                                                              |                     |  |  |  |
|--------------------------------------------------------------|---------------------|---------------------------|-----------------------|------------------|-----------------------|-------------------|------|----------------|--------------|-------------------------------|---------------------------------------------|------------------------------------------------------------------------------|---------------------|--|--|--|
|                                                              |                     | Alkaline Aqueous Solution |                       |                  |                       |                   |      |                |              |                               |                                             | Result                                                                       |                     |  |  |  |
| No.                                                          | Material for Sample | Alkaline Builder          |                       | Chelating Agent  |                       | Temperature<br>°C | pH   | Contact Method | Contact Time | Thickness of Oxide Film<br>nm | Irregularity in Surface Appearance<br>grade | Amount of Production for More than 10 mg of Suspended Solid Generated<br>ton | Note                |  |  |  |
|                                                              |                     | Kind of Chemical          | Concentration (mass%) | Kind of Chemical | Concentration (mass%) |                   |      |                |              |                               |                                             |                                                                              |                     |  |  |  |
| 16                                                           |                     |                           |                       |                  | 2.0                   |                   |      |                |              | 2                             | 5                                           | >5000                                                                        | Example             |  |  |  |
| 17                                                           |                     |                           |                       |                  | 3.0                   |                   |      |                |              | 2                             | 5                                           | >5000                                                                        | Example             |  |  |  |
| 18                                                           |                     |                           |                       |                  | 10.0                  |                   |      |                |              | 2                             | 5                                           | >5000                                                                        | Example             |  |  |  |
| 19                                                           |                     | Sodium Hydrate            | 0.01                  | Sodium Gluconate | 1.0                   | 50                | 10.0 | Dip            | 0.5          | 7                             | 5                                           | >5000                                                                        | Comparative Example |  |  |  |
| 20                                                           |                     |                           |                       |                  |                       |                   |      |                | 1.0          | 4                             | 5                                           | >5000                                                                        | Example             |  |  |  |
| 21                                                           |                     |                           |                       |                  |                       |                   |      |                | 5.0          | 2                             | 5                                           | >5000                                                                        | Example             |  |  |  |
| 22                                                           |                     |                           |                       |                  |                       |                   |      |                | 10.0         | 1                             | 5                                           | >5000                                                                        | Example             |  |  |  |
| 23                                                           |                     | Sodium Hydrate            | 0.5                   | Sodium Gluconate | 1.0                   | 50                | 12.6 | Dip            | 0.5          | 6                             | 5                                           | >5000                                                                        | Comparative Example |  |  |  |
| 24                                                           |                     |                           |                       |                  |                       |                   |      |                | 1.0          | 2                             | 5                                           | >5000                                                                        | Example             |  |  |  |
| 25                                                           |                     |                           |                       |                  |                       |                   |      |                | 5.0          | 1                             | 5                                           | >5000                                                                        | Example             |  |  |  |
| 26                                                           |                     |                           |                       |                  |                       |                   |      |                | 10.0         | 0                             | 5                                           | >5000                                                                        | Example             |  |  |  |
| 27                                                           |                     | Sodium Hydrate            | 0.001                 | Sodium Gluconate | 1.0                   | 50                | 9.0  | Dip            | 1.0          | 7                             | 5                                           | >5000                                                                        | Comparative Example |  |  |  |
| 28                                                           |                     |                           |                       |                  |                       |                   |      |                | 0.01         | 4                             | 5                                           | >5000                                                                        | Example             |  |  |  |
| 29                                                           |                     |                           |                       |                  |                       |                   |      |                | 0.05         | 4                             | 5                                           | >5000                                                                        | Example             |  |  |  |
| 30                                                           |                     |                           |                       |                  |                       |                   |      |                | 0.1          | 3                             | 5                                           | >5000                                                                        | Example             |  |  |  |
| 31                                                           |                     |                           |                       |                  |                       |                   |      |                | 10           | 2                             | 5                                           | >5000                                                                        | Example             |  |  |  |



(continued)

| Contact Treatment Condition with Alkaline Treatment Solution |                     |                           |                       |                  |                       |                   |      |                |              |                         |                                    |                                                                       |                     |  |  |
|--------------------------------------------------------------|---------------------|---------------------------|-----------------------|------------------|-----------------------|-------------------|------|----------------|--------------|-------------------------|------------------------------------|-----------------------------------------------------------------------|---------------------|--|--|
| No.                                                          | Material for Sample | Alkaline Aqueous Solution |                       |                  |                       |                   |      |                |              |                         |                                    | Result                                                                |                     |  |  |
|                                                              |                     | Alkaline Builder          |                       | Chelating Agent  |                       | Temperature<br>°C | pH   | Contact Method | Contact Time | Thickness of Oxide Film | Irregularity in Surface Appearance | Amount of Production for More than 10 mg of Suspended Solid Generated | Note                |  |  |
|                                                              |                     |                           |                       |                  |                       |                   |      |                |              |                         |                                    |                                                                       |                     |  |  |
|                                                              |                     |                           |                       |                  |                       |                   |      |                |              |                         |                                    |                                                                       |                     |  |  |
| 32                                                           |                     | Kind of Chemical          | Concentration (mass%) | Kind of Chemical | Concentration (mass%) |                   | 13.5 |                |              | 1                       | 5                                  | >5000                                                                 | Example             |  |  |
| 33                                                           |                     |                           | 98                    |                  |                       |                   | 14.0 |                |              | 0                       | 5                                  | >5000                                                                 | Example             |  |  |
| 34                                                           |                     | Sodium Hydrate            | 0.001                 | Sodium Gluconate | 1.0                   | 50                | 9.0  | Dip            | 3.0          | 7                       | 5                                  | >5000                                                                 | Comparative Example |  |  |
| 35                                                           |                     |                           | 0.05                  |                  |                       |                   | 11.0 |                |              | 3                       | 5                                  | >5000                                                                 | Example             |  |  |
| 36                                                           |                     |                           | 0.1                   |                  |                       |                   | 12.0 |                |              | 3                       | 5                                  | >5000                                                                 | Example             |  |  |
| 37                                                           |                     |                           | 10                    |                  |                       |                   | 13.0 |                |              | 2                       | 5                                  | >5000                                                                 | Example             |  |  |
| 38                                                           |                     |                           | 70                    |                  |                       |                   | 13.5 |                |              | 1                       | 5                                  | >5000                                                                 | Example             |  |  |
| 39                                                           |                     |                           | 98                    |                  |                       |                   | 14.0 |                |              | 0                       | 5                                  | >5000                                                                 | Example             |  |  |

[Table 1-2]

| Contact Treatment Condition with Alkaline Treatment Solution |                     |                             |                       |                            |                       |                |              |       |                   |                |              |         | Result            |                 | Note |                        |                                    |                                                                            |                 |
|--------------------------------------------------------------|---------------------|-----------------------------|-----------------------|----------------------------|-----------------------|----------------|--------------|-------|-------------------|----------------|--------------|---------|-------------------|-----------------|------|------------------------|------------------------------------|----------------------------------------------------------------------------|-----------------|
| No.                                                          | Material for Sample | Alkaline Aqueous Solution   |                       |                            |                       |                |              |       |                   | Contact Method | Contact Time | pH      | Temperature<br>°C | Chelating Agent |      | Thickess of Oxide Film | Irregularity in Surface Appearance | Amount of Production for More than 10 mg of Suspend-<br>ed Solid Generated |                 |
|                                                              |                     | Kind of Chemical            | Concentration (mass%) | Kind of Chemical           | Concentration (mass%) | Contact Method | Contact Time | pH    | Temperature<br>°C |                |              |         |                   |                 |      |                        |                                    |                                                                            | Chelating Agent |
|                                                              |                     |                             |                       |                            |                       |                |              |       |                   |                |              |         |                   |                 |      |                        |                                    |                                                                            |                 |
| 40                                                           |                     | Sodium Hydrate              | 0.5                   | Sodium Gluco-<br>nate      | 1.0                   | 20             | 12.6         | Dip   | 3.0               | 3              | 5            | >5000   | Example           |                 |      |                        |                                    |                                                                            |                 |
| 41                                                           |                     |                             |                       |                            |                       | 50             |              |       |                   | 2              | 5            | >5000   | Example           |                 |      |                        |                                    |                                                                            |                 |
| 42                                                           |                     |                             |                       |                            |                       | 70             |              |       |                   | 1              | 5            | >5000   | Example           |                 |      |                        |                                    |                                                                            |                 |
| 43                                                           |                     | Sodium Hydrate              | 0.5                   | Sodium Gluco-<br>nate      | 1.0                   | 50             | 12.6         | Spray | 3.0               | 2              | 5            | >5000   | Example           |                 |      |                        |                                    |                                                                            |                 |
| 44                                                           |                     | Sodium Hydrate              | 0.5                   | Sodium Gluco-<br>heptonate | 1.0                   | 50             | 12.6         | Dip   | 3.0               | 2              | 5            | >5000   | Example           |                 |      |                        |                                    |                                                                            |                 |
| 45                                                           |                     |                             |                       | Sodium Citrate             |                       |                |              |       |                   | 2              | 5            | >5000   | Example           |                 |      |                        |                                    |                                                                            |                 |
| 46                                                           |                     |                             |                       | Tartaric Acid              |                       |                |              |       |                   | 2              | 5            | >5000   | Example           |                 |      |                        |                                    |                                                                            |                 |
| 47                                                           |                     |                             |                       | Arabonic Acid              |                       |                |              |       |                   | 2              | 5            | >5000   | Example           |                 |      |                        |                                    |                                                                            |                 |
| 48                                                           |                     |                             |                       | Galactonic Acid            |                       |                |              |       |                   | 2              | 5            | >5000   | Example           |                 |      |                        |                                    |                                                                            |                 |
| 49                                                           |                     |                             |                       | Sorbit                     |                       |                |              |       |                   | 2              | 5            | >5000   | Example           |                 |      |                        |                                    |                                                                            |                 |
| 50                                                           |                     |                             |                       | Mannite                    |                       |                |              |       |                   | 2              | 5            | >5000   | Example           |                 |      |                        |                                    |                                                                            |                 |
| 51                                                           |                     | Glycerin                    |                       |                            |                       |                |              |       | 2                 | 5              | >5000        | Example |                   |                 |      |                        |                                    |                                                                            |                 |
| 52                                                           |                     | EDTA                        |                       |                            |                       |                |              |       | 2                 | 5              | >5000        | Example |                   |                 |      |                        |                                    |                                                                            |                 |
| 53                                                           |                     | Sodium Triphospho-<br>phate |                       |                            |                       |                |              |       | 2                 | 5              | >5000        | Example |                   |                 |      |                        |                                    |                                                                            |                 |

(continued)

| Contact Treatment Condition with Alkaline Treatment Solution |                                |                           |                       |                    |     |                   |      |                |              |                         |                                    |                                                                       | Result              |  | Note |
|--------------------------------------------------------------|--------------------------------|---------------------------|-----------------------|--------------------|-----|-------------------|------|----------------|--------------|-------------------------|------------------------------------|-----------------------------------------------------------------------|---------------------|--|------|
| No.                                                          | Material for Sample            | Alkaline Aqueous Solution |                       |                    |     |                   |      |                |              | Thickness of Oxide Film | Irregularity in Surface Appearance | Amount of Production for More than 10 mg of Suspended Solid Generated | ton                 |  |      |
|                                                              |                                | Alkaline Builder          |                       | Chelating Agent    |     | Temperature<br>°C | pH   | Contact Method | Contact Time |                         |                                    |                                                                       |                     |  |      |
|                                                              |                                |                           |                       |                    |     |                   |      |                |              |                         |                                    |                                                                       |                     |  |      |
|                                                              |                                |                           |                       |                    |     |                   |      |                |              |                         |                                    |                                                                       |                     |  |      |
| Kind of Chemical                                             | Concentration (mass%)          | Kind of Chemical          | Concentration (mass%) |                    |     |                   |      |                | nm           | grade                   |                                    |                                                                       |                     |  |      |
| 54                                                           | Galvannealed Steel Sheet       | None                      | -                     | -                  | -   | -                 | -    | -              | -            | 10                      | 5                                  | -                                                                     | Comparative Example |  |      |
| 55                                                           |                                | Sodium Hydrate            | 0.5                   | Sodium Glucosinate | 1.0 | 50                | 12.6 | Dip            | 3.0          | 2                       | 5                                  | >5000                                                                 | Example             |  |      |
| 56                                                           | Electro-galvanized Steel Sheet | None                      | -                     | -                  | -   | -                 | -    | -              | -            | 7                       | 5                                  | -                                                                     | Comparative Example |  |      |
| 57                                                           |                                | Sodium Hydrate            | 0.5                   | Sodium Glucosinate | 1.0 | 50                | 12.6 | Dip            | 3.0          | 1                       | 5                                  | >5000                                                                 | Example             |  |      |

[0050] From Tables 1-1 and 1-2, the following facts are clarified.

[0051] Surface analysis was performed on Nos. 1 through 57 after unnecessary oxide layer had been removed by using an alkaline aqueous solution.

[0052] In the case of comparative examples Nos. 1, 54 and 56 where a contact treatment was not performed by using an alkaline aqueous solution, the thickness of an oxide layer was 7 nm to 10 nm, which means that insufficient amount of oxide layer was removed.

[0053] In the case of Nos. 2 and 3, although a contact treatment was performed by using an alkaline aqueous solution, these cases are deficient examples (comparative example) on the point that a chelating agent was not added to the alkaline aqueous solution. It was possible to remove sufficient amount of oxide layer. However, since suspended solids were generated in the alkaline aqueous solution as the amount of production of steel sheets increased, there was a deterioration in surface appearance.

[0054] In the case of Nos. 4 and 11, although a contact treatment was performed by using an alkaline aqueous solution containing a chelating agent, these cases are examples of an insufficient concentration of chelating agent (comparative examples). It was possible to remove sufficient amount of oxide layer. However, suspended solids were generated in the alkaline aqueous solution as the amount of production of steel sheets increased.

[0055] In the case of Nos. 19 and 23, although a contact treatment was performed by using an alkaline aqueous solution containing a chelating agent, these cases are examples of a short contact time (comparative examples). The thickness of an oxide layer was 6 nm to 7 nm, which means that insufficient amount of oxide layer was removed.

[0056] In the case of Nos. 27 and 34, although a contact treatment was performed by using an alkaline aqueous solution containing a chelating agent, these cases are examples of a low pH (comparative examples). The thickness of an oxide layer was 7 nm, which means that insufficient amount of oxide layer was removed.

[0057] Nos. 24 and 28 through 33 are the examples of the present invention in which the effect of pH was clarified by performing a contact treatment with a contact time of 1.0 second. In the case where pH was 12.6 or more, since it was possible to decrease the thickness of an oxide film to 2 nm or less even with a contact time of 1.0 second, it was possible to decrease a reaction time required to form a reaction layer to a higher degree.

## EXAMPLE 2

[0058] Analysis was performed on the oxide layer containing a crystal-structured substance expressed by  $\text{Zn}_4(\text{SO}_4)_{1-x}(\text{CO}_3)_x(\text{OH})_6 \cdot n\text{H}_2\text{O}$  of Nos. 2 through 53, 55, and 57.

### (4) Confirmation of $\text{Zn}_4(\text{SO}_4)_{1-x}(\text{CO}_3)_x(\text{OH})_6 \cdot n\text{H}_2\text{O}$

[0059] By brushing the surface of the oxide layer containing a crystal-structured substance expressed by  $\text{Zn}_4(\text{SO}_4)_{1-x}(\text{CO}_3)_x(\text{OH})_6 \cdot n\text{H}_2\text{O}$  by using a stainless brush having bristles having a diameter of 0.15 mm and a length of 45 mm and ethanol, and by suction filtering of the obtained ethanol solution, the components of the film were taken in the form of powder. Quantitative analysis of C was performed by programmed temperature gas chromatography on the components of the film taken in the form of powder components by using a gas chromatography mass spectrometer. A pyrolytic furnace was connected to the front part of the gas chromatography mass spectrometer. By charging about 2 mg of the taken powder sample into the pyrolytic furnace, and by transporting a gas generated in the pyrolytic furnace in which the temperature was increased from 30°C to 500°C at an increasing rate of 5°C/min to the gas chromatography mass spectrometer with helium, the composition of the gas was analyzed. The column temperature at the time of GC/MS analysis was set to be 300°C.

### Existence form of C

[0060] By using the components of the film taken in the form of powder by using the same method as that described above, and by performing gas chromatography mass spectrometry, the existence form of C was analyzed.

### Existence forms of Zn, S, O, and H

[0061] By using an X-ray photoelectron spectrometer, the existence forms of S, Zn, and O were analyzed. By using an Al-K $\alpha$  monochrome radiation source, narrow measurement of spectra corresponding to Zn-LMM and S-2p was performed.

### Existence form of P

[0062] By using an X-ray-absorption fine-structure spectrometer, the existence form of P was analyzed. By using beam

line BL27A of Photon Factory, High Energy Accelerator Research Organization, the observation of an X-ray absorption fine structure (ZAFS) was performed at room temperature. By irradiating the surface of a degreased sample with a monochrome radiation beam, the spectrum of an X-ray absorption near-edge structure (XANES) of P-K shell was observed by using a total electron yield method (TEY) by performing sample absorption current measurement.

Quantitative determination of crystallization water

**[0063]** By using a differential thermogravimetric analyzer, the amount of decrease in weight at a temperature of 100°C or lower was determined. About 15 mg of powder sample was used for the determination. After having charging the sample into the analyzer, by increasing the temperature from room temperature (about 25°C) to 1000°C at an increasing rate of 10°C/min, a change in weight while the temperature was being increased was recorded.

Identification of crystal structure

**[0064]** By performing X-ray diffractometry on the components of the film taken in the form of powder by using the same method as that described above, the crystal structure was presumed. The determination was performed with Cu being used as the target under the conditions of an acceleration voltage of 40 kV, a tube current of 50 mA, a scanning speed of 4 deg/min, and a scanning range of 2° to 90°.

**[0065]** Hereafter, the obtained results regarding Nos. 2 through 38, 40 through 53, 55, and 57 will be described.

**[0066]** From the results obtained by performing gas chromatography mass spectrometry, it was clarified that, since CO<sub>2</sub> emission was observed in a temperature range of 150°C to 500°C, C existed in the form of carbonates.

**[0067]** From the results of the analysis using an X-ray photoelectron spectrometer, it was clarified that, since a peak corresponding to Zn-LMM was observed in the vicinity of 987 eV, Zn existed in the form of zinc hydroxide. Similarly, it was clarified that, since a peak corresponding to S-2p was observed in the vicinity of 171 eV, S existed in the form of sulfates.

**[0068]** From the results of the analysis using an X-ray-absorption fine-structure spectrometer, it was clarified that, since peaks were observed in the vicinity of each of 2153 eV, 2158 eV, and 2170 eV, P existed in the form of pyrophosphates.

**[0069]** From the results of the analysis using a differential thermogravimetric analyzer, it was clarified that, since a decrease in weight by 11.2% was observed in a temperature range of 100°C or lower, crystallization water was contained.

**[0070]** From the results obtained by performing X-ray diffractometry, diffraction peak was observed in the vicinity of each of the positions respectively corresponding to 8.5°, 15.0°, 17.4°, 21.3°, 23.2°, 26.3°, 27.7°, 28.7°, 32.8°, 34.1°, 58.6°, and 59.4° in terms of 2θ.

**[0071]** From the results described above, the composition ratios, and the charge balance, it was clarified that a crystal-structured substance expressed by  $\text{Zn}_4(\text{SO}_4)_{0.95}(\text{CO}_3)_{0.05}(\text{OH})_6 \cdot 3.3\text{H}_2\text{O}$  was contained.

**[0072]** Close analysis of film was performed on No. 39.

**[0073]** From the results obtained by performing gas chromatography mass spectrometry, it was clarified that, since CO<sub>2</sub> emission was observed in a temperature range of 150°C to 500°C, C existed in the form of carbonates.

**[0074]** From the results of the analysis using an X-ray photoelectron spectrometer, it was clarified that, since a peak corresponding to Zn-LMM was observed in the vicinity of 987 eV, Zn existed in the form of zinc hydroxide. Similarly, it was clarified that, since a peak corresponding to S-2p was observed in the vicinity of 171 eV, S existed in the form of sulfates.

**[0075]** From the results of the analysis using an X-ray-absorption fine-structure spectrometer, it was clarified that, since peaks were observed in the vicinity of each of 2153 eV, 2158 eV, and 2170 eV, P existed in the form of pyrophosphates.

**[0076]** From the results of the analysis using a differential thermogravimetric analyzer, it was clarified that, since a decrease in weight by 9.4% was observed in a temperature range of 100°C or lower, crystallization water was contained.

**[0077]** From the results obtained by performing X-ray diffractometry, diffraction peak was observed in the vicinity of each of the positions respectively corresponding to 8.8°, 15.0°, 17.9°, 21.3°, 23.2°, 27.0°, 29.2°, 32.9°, 34.7°, and 58.9° in terms of 2θ.

**[0078]** From the results described above, the composition ratios, and the charge balance, it was clarified that a crystal-structured substance expressed by  $\text{Zn}_4(\text{SO}_4)_{0.8}(\text{CO}_3)_{0.2}(\text{OH})_6 \cdot 2.7\text{H}_2\text{O}$  was contained.

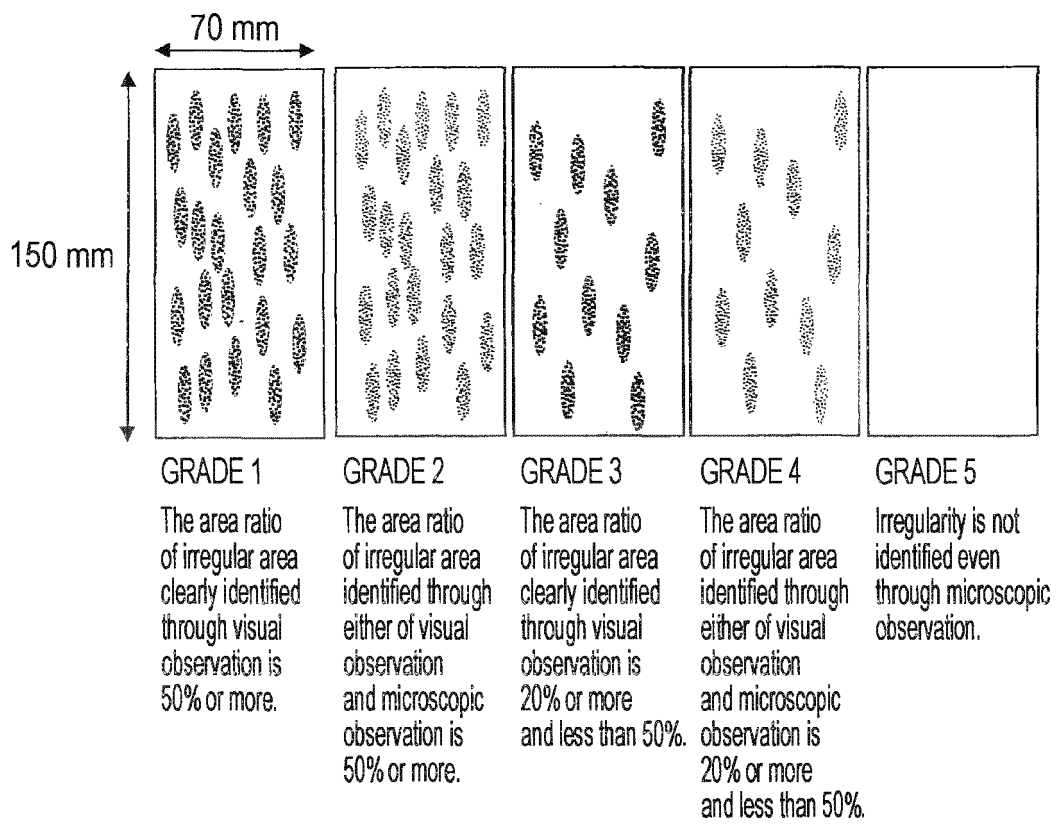
## Claims

1. A method for manufacturing a steel sheet coated with a zinc-based coating layer having a reaction layer on the surface of the steel sheet, the method comprising:

bringing a steel sheet coated with a zinc-based coating layer into contact for 1.0 second or more with an alkaline aqueous solution containing one or more chelating agents selected from among sodium gluconate, sodium glucoheptonate, sodium citrate, tartaric acid, arabonic acid, galactonic acid, sorbit, mannite, glycerin, EDTA, and sodium tripolyphosphate in a total amount of 0.050 mass% or more and having a pH of 10.0 or more as a pre-treatment before a formation of the reaction layer, and forming the reaction layer being an oxide layer containing a crystal-structured substance expressed by  $Zn_4(SO_4)_{1-x}(CO_3)_x(OH)_6 \cdot nH_2O$ .

2. The method for manufacturing a steel sheet coated with a zinc-based coating layer according to Claim 1, wherein pH of the alkaline aqueous solution is 12.6 or more.

FIG. 1



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/005583

## A. CLASSIFICATION OF SUBJECT MATTER

C23C22/78(2006.01)i, C23C28/00(2006.01)i, C23G1/20(2006.01)i

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)

C23C22/78, C23C28/00, C23G1/20

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2016

Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                             | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| P, Y      | WO 2015/129283 A1 (JFE Steel Corp.),<br>03 September 2015 (03.09.2015),<br>paragraphs [0046] to [0049], [0081]<br>(Family: none)                                                               | 1, 2                  |
| Y         | JP 2007-169772 A (Nippon Denro Mfg. Co., Ltd.),<br>05 July 2007 (05.07.2007),<br>paragraph [0011]<br>(Family: none)                                                                            | 1, 2                  |
| Y         | JP 63-213682 A (Nisshin Steel Co., Ltd.),<br>06 September 1988 (06.09.1988),<br>claims; page 2, lower right column, lines 6 to<br>9; page 3, upper left column, lines 3 to 8<br>(Family: none) | 1, 2                  |

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Date of mailing of the international search report

16 February 2016 (16.02.16)

Name and mailing address of the ISA/

Japan Patent Office

3-4-3, Kasumigaseki, Chiyoda-ku,

Tokyo 100-8915, Japan

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**Patent documents cited in the description**

- JP 5279868 A [0011]
- JP 2006183074 A [0011]
- JP 2006233280 A [0011]
- JP 2005097741 A [0011]
- JP 2015530230 A [0011]