(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 988 189 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
05.11.2008 Bulletin 2008/45

(21) Application number: **07713636.4**

(22) Date of filing: **18.01.2007**

(51) Int Cl.:
C23C 22/12 *(2006.01)* ***C23C 22/78*** *(2006.01)*

(86) International application number:
PCT/JP2007/050650

(87) International publication number:
WO 2007/097139 (30.08.2007 Gazette 2007/35)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR

(30) Priority: **20.02.2006 JP 2006043099**
20.02.2006 JP 2006043105

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(54) PROCESS FOR PRODUCING HOT-DIP GALVANIZED STEEL SHEET WITH ZINC PHOSPHATE COAT

(57) The present invention provides a method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating which is possible to keep the composition balance of the treatment agent constant, to reduce the manufacturing cost, and to minimize the burden to the environment. It also provides a galvanized steel sheet having phosphate coating which exhibits excellent lubricity and adhesiveness by the above method.

The invention is a method for continuously manufacturing hot-dip galvanized steel sheet having zinc phosphate coating comprising the steps of: a surface conditioning agent supply process for supplying a surface conditioning agent to a surface of hot-dip galvanized steel sheet; a pre-drying process for drying the surface conditioning agent in a post-process of the surface conditioning agent supply process; and a treatment agent supply process for supplying treatment agent containing zinc phosphate solution to the surface of the hot-dip galvanized steel sheet in a post-process of the pre-drying process.

Printed by Jouve, 75001 PARIS (FR)

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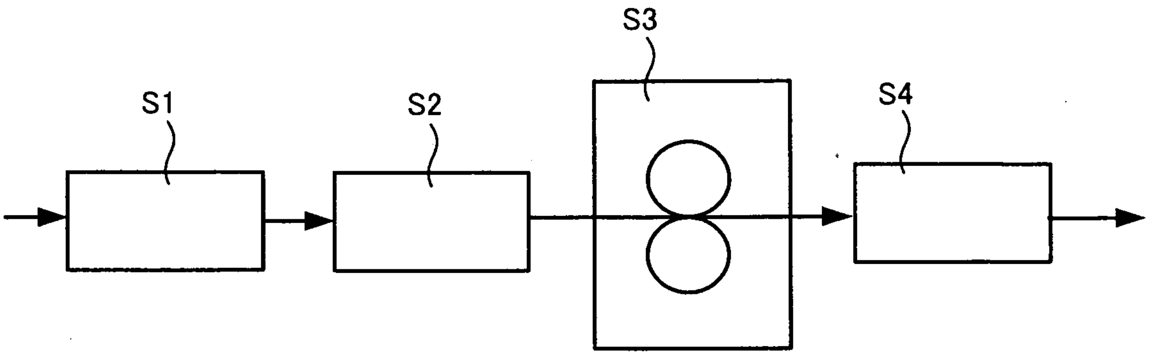
FIG. 1



Description

Technical Field

[0001] The present invention relates to a method for manufacturing a hot-dip galvanized steel sheet which is used in a field of automotive manufacturing and so on to enhance press formability and exhibits excellent in lubricity and/or adhesiveness. More specifically, the invention relates to a method for manufacturing a hot-dip galvanized steel sheet having zinc phosphate coating which is capable to enhance productivity such as operatability of manufacturing for hot-dip galvanized steel sheet having the above properties in a continuous hot-dip galvanized steel sheet manufacturing-line.

Background Art

[0002] In recent years, as a rust preventive measure for steel sheets for automotive manufacturing and so on, a hot-dip galvanized steel sheet has been used. In most automotive applications, press forming is given to the galvanized steel sheet. However, compared with a cold-rolled steel sheet, the galvanized steel sheet is known to be inferior in press formability. About an electrogalvanized (EG) steel sheet or a hot-dip galvanized (GI) steel sheet, since zinc in the plating surface is soft, the zinc may cause seizing with dies at a time of scraping; or about a hot-dip galvanized steel sheet, soft eta-phase may remain, these factors lower the slidability. Also, about galvannealed (GA) steel sheet, as soft alloy layer like zeta-phase is formed on the plating surface at a time of alloying, which same as above lower the slidability.

[0003] As a means for solving these problems, Patent Document 1 discloses a technique to enhance the lubricity by providing iron-zinc alloy electroplated coating over the galvanized coating; this technique is widely and practically used. Nevertheless, by this technique, electroplating equipment is needed, which results in a large increase of manufacturing cost.

[0004] Moreover, in view of reduction of manufacturing cost, Patent Document 2 discloses a technique to produce hot-dip galvanized steel sheet which exhibits excellent lubricity by making zinc phosphate coating as an upper layer, instead of using plated coating described in Patent Document 1. This means that the invention having the zinc phosphate coating configures, for example, a zinc-containing metal-plated steel sheet complex excellent in high-speed press formability at a time of coach-building.

[0005] However, in the manufacturing process of steel sheet having the zinc phosphate coating, since a desired performance cannot be obtained without imparting pretreatment to a steel sheet to be coated, it needs various pretreatments. For instance, in the above Patent Document 2 and Patent Document 3, when steel sheets are produced in the continuous hot-dip galvanized steel sheet manufacturing line, in order to prevent a pretreatment agent from being brought into a zinc phosphate aqueous solution, water rinsing process is required.

[0006] In addition, Patent Documents 4 and 5 disclose methods, wherein, before a contact with zinc phosphate aqueous solution, a base material is rinsed and then dipped in the surface conditioning agent such as titanium-colloid aqueous solution for surface treatment. On the other hand, a technique which imparts organic solid lubricant coating like wax and fat to a galvanized surface is conventionally disclosed (Japanese Patent No. 3006455, etc.); chaff produced by press adheres to the dies at a time of press forming, occurrence of defect of press products attributed to the chaff, and odor problem at a time of welding connection (organic substance is decomposed by heat of welding that exert a harmful influence in the working environment.).

[0007] Accordingly, in response to the request of a manufacturing cost reduction, instead of having the above Fe-Zn electroplated coating, expansion of applications of the so-called "inorganic lubricant coating", which is obtained by imparting galvanized upper layer with phosphoric acid coating (Current Advances in Materials and Processes, Vol. 11 (1998), p.546), Mn-P oxide coating (Current Advances in Materials and Processes, Vol.6 (1993), p.1545), and Ni-series coating (Current Advances in Materials and Processes, Vol.11 (1998), p.384), etc., has been developing.

[0008] The inorganic lubricant coating is characterizing in that it does not cause problems like unusual odor at a time of welding connection and it is capable to impart stable formability to the material to be formed. Particularly, phosphoric-acid series coating is conventionally used, and this has proposed various techniques. For example, Patent Document 6 discloses that Mg-containing zinc phosphate coating is provided on the galvanized surface and this coated material is suitably used for automotive body.

[0009] However, this inorganic lubricant coating has a problem in adhesiveness with other parts. A galvanized steel sheet having the inorganic lubricant coating is often adhered with other parts to build up a product; therefore adhesiveness has been a very important issue. Studies about adhesiveness of steel sheet having this inorganic lubricant coating have proceeded. For instance, Patent Document 7 and Patent Document 8 disclose that forming ZnO oxide on the surface of plated layer and forming Mn-Zn-OH-P series crystalline oxide over the surface make it possible to obtain a galvanized steel sheet which exhibits excellent lubricity, chemical conversion treatability, and adhesive compatibility.

[0010] Moreover, Patent Document 9 discloses a steel sheet having an inorganic lubricant coating which has sufficient adhesiveness with various adhesives including Mastic-type adhesive.

[0011] Further, in the galvanized steel sheet having inorganic lubricant coating, specifically, zinc phosphate coating, it is necessary to secure the even coating-condition and various properties for rust-proof steel sheet for automotive use. Not only improvement of the slidability and lubricity, but also other properties such as weldability and adhesiveness are also required to attain an equivalent degree or more. From this point of view, a method for manufacturing galvanized steel sheet having zinc phosphate coating requires complex and highly accurate manufacturing process.

[0012] Specifically, the technique forming these phosphoric-acid series coating is called "reactive surface chemical-conversion treatment". It is a technique such that a treatment agent containing a primary phosphoric acid, Zn, Ni, Mn, Mg, nitric acid, nitrous acid, fluorine compound, and so on is contacted with a surface of galvanized steel sheet and reacts thereon to form a coating. More specifically, the treatment agent is supplied by spray and the like to the galvanized surface, meanwhile coating reaction is proceeded together with etching of galvanizing. At this phase, zinc resolved out by the etching exists in the treatment agent as Zn ion; when Zn ion concentration increases, pH of the treatment agent rises, which results in a prevention of the etching reaction. So, in order to maintain the even coating condition, it is necessary to supply phosphoric acid and so on into the whole treatment agent and to keep pH and Zn concentration at a constant level.

[0013] Usually, capacity of tank and the like for storing the treatment agent is limited; so as to keep the raised Zn concentration and pH constant, a method such as adding supplement liquid while discharging a part of the treatment agent as a drain is often adopted.

Patent Document 1: Japanese Patent Application Laid-Open (JP-A) No. 01-319661
Patent Document 2: JP-A No. 07-138764
Patent Document 3: JP-A No. 2001-098383
Patent Document 4: JP-A No. 2005-054202
Patent Document 5: JP-A No. 2005-054203
Patent Document 6: JP-A No. 11-315386
Patent Document 7: Japanese Patent No. 3153097
Patent Document 8: Japanese Patent No. 3199980
Patent Document 9: JP-A No. 2002-053974

Disclosure of the Invention

Problems to be solved by the Invention

[0014] Nevertheless, in the manufacturing method described in Patent Documents 1 to 4, when rinsed by water, water is taken into the process for supplying zinc phosphate solution; when rinsed without water, liquid such as surface conditioning agent is taken into the process for supplying zinc phosphate solution. These vary the composition balance of zinc phosphate solution as a treatment agent. Moreover, when rinsed without water, as the steel sheet is activated by surface conditioning agent and so on, this encourages the reaction with treatment liquid used in the post-process. Consequently, galvanized coating, especially zinc portion is unignorably resolved out from the steel sheet, which enlarges change of composition balance of the treatment liquid. Usually, capacity of tank and the like for storing the treatment agent is limited; so as to keep the varying composition balance of the treatment agent constant, a method such as adding supplement liquid while discharging a part of the treatment agent as a drain is often adopted. Thus, supplement cost of zinc phosphate solution and emission facility are required; in addition to this, phosphorous waste solution rises, drain facility and so on are also required to be installed.

[0015] Further, considering recent years' environmental concern, it is socially requested to produce phosphorous waste solution as less as possible. Also, conventionally, in the water-system treatment, it is normally known that surface of the rinsed steel is not dried. If the surface is dried, the surface is oxidized and this lowers the reactivity; thereby drying has been thought to deteriorate the performance of the final product.

[0016] Furthermore, about adhesiveness of the galvanized steel sheet having inorganic lubricant coating, according to the inventions described in Patent Documents 7 and 8, identified type of adhesive is the only one, it is not necessarily compatible in the current coach-building process using various kind of submaterials.

[0017] And, in a steel sheet having the inorganic lubricant coating described in Patent Document 9, when the coating is amorphous phosphate coating, particularly, there is a fear of insufficient performance in the formability and sliding tests where the coating is exposed under high surface pressure especially at a time of processing. Hence, a galvanized steel sheet having inorganic lubricant coating, which is capable to secure sufficient adhesiveness with various adhesives and to have sufficient slidability and formability, has not exist.

[0018] Accordingly, an object of the present invention is to provide a method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating which is possible to keep the composition balance of the treatment agent constant, to reduce the manufacturing cost, and to minimize the burden to the environment. Another object of the invention is to provide a galvanized steel sheet having zinc phosphate coating which exhibits excellent lubricity and adhesiveness by the above method.

Means for Solving the Problems

[0019] The present inventors have been conducted serious studies in order to solve the above problems. As a result, the present inventors have acquired following ideas and developed a method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating of the present invention.

(a) By drying the surface conditioning agent before the process supplying zinc phosphate solution, it is capable to prevent zinc phosphate solution from being brought into the surface conditioning agent. This means that if the surface conditioning agent is dried, it is possible to inhibit activation of galvanized surface. The wording "surface conditioning agent" means an aqueous liquid containing crystal nucleating agent for zinc phosphate; the examples include: an aqueous liquid wherein Ti-colloid is dispersed in a sodium pyrophosphate aqueous solution, and an aqueous liquid wherein zinc phosphate particles are dispersed.

(b) In the above surface conditioning agent, by using the aqueous liquid wherein zinc phosphate particles are dispersed and drying the aqueous liquid, it is possible to control the change of composition balance of the treatment agent. This means that if the aqueous liquid containing zinc phosphate particles is dried, without aggregating, zinc phosphate particles can be absorbed to the hot-dip galvanized surface while maintaining the particle size and can maintain the particle form. Further, it is capable to inhibit oxidation reaction in the steel sheet surface before the treatment agent process by a protective-coating-like effect, thereby it is possible to make the galvanized surface reacts in the following dry process. On the other hand, in case of the aqueous liquid wherein Ti-colloid is dispersed in the sodium pyrophosphate aqueous solution, there is a possibility of drying-aggregation of the crystal nucleating agent.

[0020] In addition, with respect to the obtained galvanized steel sheet, the following ideas were found; accordingly, the inventors completed the present invention.

(c) In the steel sheet surface, if P-O bond orientation of zinc phosphate formed over the surface of the galvanized steel sheet has larger number of vertical orientation to the steel sheet surface, it is capable to improve adhesiveness while maintaining excellent lubricity. This is assumed that interaction between P-O bond and C-O bond of an adhesive (mainly resin) is increased. P-O bond orientation of zinc phosphate can be determined by a spectrum obtained by an absorption spectrum measuring method for measuring an infrared light which is incoming from a direction at an angle of 60° to a normal line of the steel sheet and absorbed from the surface using ratio of integrated absorption strength between a p-polarized light (a vertical component of a polarized light to the steel sheet surface) and a s-polarized light (a horizontal component of a polarized light to steel sheet surface) in the absorption of P-O bond stretching vibration.

(d) In order to know the P-O bond orientation in further detail, focusing on absorption of a particular P-O bond and obtaining a ratio of absorbance to the p-polarized light and s-polarized light allow accurate determination. In the spectrum absorption of crystalline zinc phosphate of the galvanized steel sheet surface of the present invention, the spectrum has a characteristic absorption band within the wavelength ranges of 8.4 to 9.2 μm and 10.2 to 11.0 μm. Accordingly, with respect to the absorption band within the ranges, by measuring ratio of absorbance of p-polarized light to that of s-polarized light, it is possible to determine the adhesiveness in further detail. Namely, raising the ratio of absorbance between p-polarized light and s-polarized light of the absorption band makes it possible to obtain a galvanized steel sheet having zinc phosphate coating which exhibits more excellent lubricity and adhesiveness.

[0021] The present invention has been completed based on the above ideas. It is described in detail as follows. The first aspect of the present invention is a method for continuously manufacturing hot-dip galvanized steel sheet having zinc phosphate coating comprising the steps of: a surface conditioning agent supply process for supplying a surface conditioning agent to a surface of hot-dip galvanized steel sheet; a pre-drying process for drying the surface conditioning agent in a post-process of the surface conditioning agent supply process; and a treatment agent supply process for supplying a treatment agent containing zinc phosphate solution to the surface of the hot-dip galvanized steel sheet in a post-process of the pre-drying process, so as to solve the problems.

[0022] The wording "hot-dip galvanized steel sheet" is a concept including not only "hot-dip galvanized steel sheet" itself but also "galvannealed steel sheet". Also, the wording "galvanized steel sheet" is a generic name including "electrogalvanized steel sheet", "hot-dip galvanized steel sheet" and "galvannealed steel sheet".

[0023] Moreover, the wording "zinc phosphate" of "zinc phosphate coating" means a crystalline zinc phosphate (Zn_3

$(PO_4)_2 \cdot 4H_2O$) which shows Hopeite diffraction in a normal X-ray diffraction analysis.

[0024] The second aspect of the invention is the method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to the first aspect of the invention, wherein the surface conditioning agent used in the surface conditioning agent supply process is an aqueous liquid containing zinc phosphate particles.

[0025] The third aspect of the invention is the method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to the second aspect of the invention, wherein average diameter of the zinc phosphate particles contained in the surface conditioning agent of the surface conditioning agent supply process is 10 μm or less.

[0026] The fourth aspect of the invention is the method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to the second aspect of the invention, wherein average diameter of the zinc phosphate particles contained in the surface conditioning agent of the surface conditioning agent supply process is 10 μm or less, and pH of the surface conditioning agent is 5 or more.

[0027] The fifth aspect of the invention is the method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to any one of the first to fourth aspects of the invention, wherein the surface conditioning agent used in the surface conditioning agent supply process contains more than 0 mol/L and 0.5 mol/L or less of zinc phosphate particles, and contains a total of 0.3 mol/L or less of one element selected from a group consisting of Li, Na, K, Be, Mg, and Ca.

[0028] The sixth aspect of the invention is the method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to any one of the first to fifth aspects of the invention, wherein the treatment agent used in the treatment agent supply process contains 0.001 to 0.7 mol/L of phosphate root and contains 0.7 or less of.Zn ion in mole ratio to the phosphate root.

[0029] The seventh aspect of the invention is the method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to any one of the first to sixth aspects of the invention, wherein zinc phosphate solution of the treatment agent used in the treatment agent supply process contains Zn ion and phosphate root, has a pH of 4 or less, and contains one element, other than the Zn ion and the phosphate root, selected from a group of strong electrolyte anion consisting of 0.2 or less of nitrate root, 0.2 or less of nitrous root, 0.1 or less of hydrofluoric root, and 0.05 or less of sulfuric root in mole ratio to 1 mole of the phosphate root.

[0030] The eighth aspect of the invention is the method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to any one of the first to seventh aspects of the invention, wherein phosphorus adhered to a hot-dip galvanized surface by the surface conditioning agent supply process and the treatment agent supply process is prepared to be 30 to 500 mg/m^2 in phosphorus equivalent.

[0031] Phosphorus adhesion quantity with regard to "phosphorus equivalent" can be calculated by measurement associated with chemical dissolution or fluorescent X-ray. The method by chemical dissolution is the one to dissolve a galvanized layer of galvanized steel sheet having a predetermined area with predetermined amount of strong acid (e.g., hydrochloric acid) and to measure the phosphorus concentration in the above solution by ICP (inductively-coupled plasma emission spectrometry) to calculate phosphorus equivalent. On the other hand, the method associated with fluorescent X-ray is the one to obtain fluorescent X-ray strength by making various phosphorus adhesion quantity, measuring fluorescent X-ray strength attributing to PKα in the fluorescent X-ray method, calculating the phosphorus adhesion quantity by the method of the above chemical dissolution, and producing an analytical curves. According to the fluorescent X-ray method, it is capable to obtain the phosphorus adhesion quantity without breaking the galvanized layer of galvanized steel sheet, in a same method for the following samples.

[0032] The ninth aspect of the invention is the method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to the second aspect of the invention, wherein pH of the surface conditioning agent used in the surface conditioning agent supply process is 5 or more, and average diameter of the zinc phosphate particles is 0.1 to 3 μm.

[0033] The 10th aspect of the invention is the method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to the second or ninth aspect of the invention, wherein 0.01 to 5 mg/m^2 of the zinc phosphate particles in phosphorus equivalent is adhered to a surface of galvanized steel sheet which has come through the surface conditioning agent supply process and the pre-drying process.

[0034] The 11th aspect of the invention is the method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to any one of the second, ninth, and 10th aspects of the invention, wherein the treatment agent used in the treatment agent supply process contains Zn and phosphate root, has a pH of 4 or less, and contains one element, other than the zinc and phosphate root, selected from a group of strong electrolyte anion consisting of 0.2 or less of nitrate root, 0.2 or less of nitrous root, 0.1 or less of hydrofluoric root, 0.05 or less of sulfuric root in mole ratio to 1 mole of phosphate root.

[0035] The 12th aspect of the invention is the method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to any one of the second, ninth to 11th aspects of the invention, wherein the method further comprising a post-drying process for drying the treatment agent after the treatment agent supply process, and the zinc phosphate coating is adhered at an amount of 30 to 250 mg/m^2 in phosphorus equivalent after the post-drying process.

[0036] The 13th aspect of the invention is the method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to any one of the first to 12th aspects of the invention, wherein either one of or both of supplying methods for the surface conditioning agent in the surface conditioning agent supply process and for the treatment agent in the treatment agent supply process is roll coating method.

[0037] The 14th aspect of the invention is a hot-dip galvanized steel sheet having crystalline zinc phosphate coating formed on the surface thereof manufactured in accordance with the methods described in any one of the ninth to 13th aspects of the invention, the hot-dip galvanized steel sheet is characterizing in that: an absorption spectrum obtained by a reflected light of infrared light incoming from a direction at an angle of 60° to a normal line of the zinc phosphate coating surface has a plurality of absorption bands within a wavelength range of 8 to 12 μm; further, ratio of integrated absorption strength of a s-polarized light to a p-polarized light within the wavelength range is 1.2 or more.

[0038] The wording "p-polarized light" means a vertical component of polarized light to the surface; while "s-polarized light" means a horizontal component of polarized light to the surface. Also, "ratio of integrated absorption strength" means ratio of integrated absorption strength of the absorption spectrum of p-polarized light and s-polarized light.

[0039] The 15th aspect of the invention is a hot-dip galvanized steel sheet having crystalline zinc phosphate coating formed on the surface thereof manufactured in accordance with the methods described in any one of the ninth to 13th aspects of the invention, the hot-dip galvanized steel sheet is characterizing in that: an absorption spectrum obtained from the reflected light of infrared light incoming from a direction at an angle of 60° to a normal line of the phosphate coating has a plurality of absorption bands within a wavelength range of 8 to 12 μm; a p-polarized light absorbance within a wavelength of 8.4 to 9.2 μm of the absorption spectrum is twice as much as a s-polarized light absorbance; and the p-polarized light absorbance within wavelength range of 10.2 to 11.0 μm is twice as much as the s-polarized light absorbance.

Effects of the Invention

[0040] According to the first aspect of the present invention, since surface conditioning agent in liquid condition is not brought into the treatment agent supply process, the surface conditioning agent does not contaminate the treatment agent; thereby composition balance of the treatment agent can be maintained for a long time. As a result, it is possible to obtain effects such as reduction of manufacturing cost, reduction of treatment agent's make-up volume and waste solution discharge, and improvement of productivity. Also, this invention makes it possible to manufacture the hot-dip galvanized steel sheet having zinc phosphate coating in consideration of the environment. Hence, decreased treatment agent is a portion which adhered to the sheet, the manufacturing process is simply established by supplying the decreased treatment agent. Therefore, zinc phosphate coating can be formed in a continuous hot-dip galvanized steel sheet line in the closed-system.

[0041] According to the second aspect of the invention, as crystal nucleating agent contained in the surface conditioning agent is not dried and aggregated, it is capable to furthermore steadily form a zinc phosphate coating to be coated.

[0042] According to the third aspect of the invention, it is capable to enhance operatability and stability of the surface conditioning agent.

[0043] According to the fourth aspect of the invention, it is capable to enhance operatability and stability of the surface conditioning agent more.

[0044] According to the fifth aspect of the invention, it is possible to enhance stability of the surface conditioning agent and to homogenize the reaction in the sheet surface in the pre-drying process.

[0045] According to the sixth aspect of the invention, it is capable to enhance operatability and stability of the treatment agent.

[0046] According to the seventh aspect of the invention, it is capable to enhance stability of the treatment agent more and to enhance homogeneity of the coating.

[0047] According to the eighth aspect of the invention, since phosphorus is supplied from two sources, the preparation is easy; therefore it is capable to accurately prepare a suitable amount of phosphorus.

[0048] According to the ninth aspect of the invention, it is possible to enhance stability of the surface conditioning agent furthermore; in view of cost and environment, a furthermore advantageous method for manufacturing the hot-dip galvanized steel sheet having zinc phosphate coating can be provided. In addition, by this aspect of the invention, the provided zinc phosphate particles can be more evenly supplied to the galvanized surface.

[0049] According to the 10th aspect of the invention, it is capable to enhance stability of the surface conditioning agent and also capable to easily prepare a total amount of phosphorus adhesion quantity at a time of treatment agent supply, further, lubricity thereof can be enhanced.

[0050] According to the 11th aspect of the invention, stability of the treatment agent can be enhanced; in view of cost and environment, a furthermore advantageous method for manufacturing the hot-dip galvanized steel sheet having zinc phosphate coating can be provided.

[0051] According to the 12th aspect of the invention, lubricity thereof can be enhanced.

[0052] According to the 13th aspect of the invention, as supply of the surface conditioning agent and/or supply of the treatment agent are carried out by roll coater, there is no need to refill these agents of which concentration is unnecessarily high, and the refill itself requires less quantity. In view of cost and environment, a furthermore advantageous method for manufacturing the hot-dip galvanized steel sheet having zinc phosphate coating can be provided.

[0053] According to the 14th aspect of the invention, it is capable to provide a hot-dip galvanized steel sheet having zinc phosphate coating, which exhibits excellent adhesiveness and lubricity.

[0054] According to the 15th aspect of the invention, it is capable to provide a hot-dip galvanized steel sheet having zinc phosphate coating, which can maintain the slidability and further exhibits excellent adhesiveness.

Brief Description of the Drawings

[0055]

FIG. 1 shows a view showing a frame format of a flow of manufacturing method for a galvanized steel sheet having zinc phosphate coating of the present invention;
FIG. 2 shows a graph showing an example of relation between wavelengths and absorbance obtained by infrared absorption spectrum;
FIG. 3 shows a schematic view of T-peeling testing method; and
FIG. 4 shows a schematic view of shear-tensile test method.

Description of the reference numerals

[0056]

1	galvanized steel sheet
2	adhesive
3	galvanized steel sheet
4	adhesive
S1	surface conditioning agent supply process
S2	pre-drying process
S3	treatment agent supply process
S4	post-drying process

Best Mode for Carrying Out the Invention

[0057] Hereinafter, a method for manufacturing a galvanized steel sheet having zinc phosphate coating of the present invention will be described. FIG. 1 shows a flow of an embodiment of the manufacturing method for galvanized steel sheet having zinc phosphate coating of the invention. The manufacturing method includes: a surface conditioning agent supply process (S1) for supplying a surface conditioning agent to a base material; a pre-drying process (S2) for drying the surface conditioning agent; a treatment agent supply process (S3) for supplying a treatment agent; and a pre-drying process (S4) for drying the treatment agent after the treatment agent supply process (S3). Each process will be described in detail as follows. The wording "Base material" is a galvanized steel sheet having a base metal as a steel sheet and a galvanized layer coating on the base metal surface.

[0058] The surface conditioning agent supply process (S1) is a process to supply surface conditioning agent containing a crystal nucleating agent to the galvanized steel sheet. The method for supplying the surface conditioning agent of the surface conditioning agent supply process (S1) is not particularly limited. The examples include: roll coater, spray coating, in addition, post-spray air knife, post-spray wringer roll, and post-spray squeezing roll. In view of operatability, roll coater and post-spray squeezing roll are preferable. Further, among these, roll coater is preferable as it requires shorter contact time between galvanizing and the surface conditioning agent than other methods does. This method needs no troublesome component preparation and pH control for the surface conditioning agent, but it just needs addition of a surface conditioning agent having exactly the same component to refill the decreased portion of the surface conditioning agent. Control of component of surface conditioning agent, concentration thereof, and pH thereof of one component is only necessary. Further, as change of component of the surface conditioning agent is controlled, discharge of the surface conditioning agent becomes unnecessary; in view of reduction of cost and environmental burden, it is preferable.

[0059] A crystal nucleating agent contained in the surface conditioning agent is not particularly limited to; an agent normally used for the base-coating treatment process of automotive body can be used. The examples include: an aqueous liquid wherein Ti-colloid is dispersed in a sodium pyrophosphate aqueous solution and an aqueous liquid in which zinc phosphate particles are dispersed. In the examples, the aqueous liquid in which zinc phosphate particles are dispersed is particularly preferable. Because, even if this aqueous liquid is supplied and dried in the below-mentioned pre-drying process (S2), without aggregating, zinc phosphate particles can be absorbed to the galvanized surface while maintaining the particle size. On the other hand, if the Ti-colloid by itself or the like is used, the crystal nucleating agent may possibly be dried and aggregated in the pre-drying process (S2).

[0060] Adhesion quantity of the surface conditioning agent is preferably less than 30 mg/m^2. This is because, in the range of 30 mg/m^2 or more, spots in the base treatment occur and the appearance is sometimes damaged. It is preferably 15 mg/m^2 or less, and more preferably 10 mg/m^2 or less. Meanwhile, even if more than 30 mg/m^2 of the surface conditioning agent is applied, effect as the base treatment is saturated, it may rather affect the treatment agent in the post-process; thus the above upper limit is preferable.

[0061] Moreover, in case of a below-mentioned galvanized steel sheet which exhibits excellent adhesiveness, supply of the aqueous liquid in which zinc phosphate particles are dispersed is preferably 0.01 to 5 mg/m^2 in phosphorus equivalent in the zinc phosphate at a time of drying. If it is less than 0.01 mg/m^2, sufficient adhesiveness cannot be obtained; meanwhile if it is over 5 mg/m^2, the effect becomes saturated. It is preferably 0.1 to 2 mg/m^2. Further, concentration of zinc phosphate may be 0.05 to 5 mol/L. This is because, in the range less than 0.05 mol/L, wet-film layer thickness becomes too thick to obtain predetermined adhesion quantity; thereby coating unevenness tends to occur. On the other hand, in the range over 5 mol/L, viscosity of the surface conditioning agent becomes excessively high; thereby, in the same way, coating unevenness tends to occur.

[0062] Also, zinc phosphate particles used for crystalline nucleation may be crystalline, amorphous, or mixture thereof. Whether or not it is crystalline can be determined by a general X-ray diffraction analysis.

[0063] pH of the surface conditioning agent is preferably 5 or more. If pH is less than 5, when the surface conditioning agent is supplied to a galvanized sheet surface, zinc liquates out from the sheet surface. Further, aqueous liquid in which zinc phosphate particles are dispersed itself may slightly cause dissolution reaction of zinc phosphate particles, stability of the particles may possibly be deteriorated. The pH of the agent is further preferably in the range of 7 to 10. If pH is more than 10, dissolution reaction of zinc phosphate itself is set off. Moreover, buffer solution for controlling pH may be added to the surface conditioning agent. Examples of the buffer solution include a buffer solution consisting of K_2HPO_4 and NaOH. Concentration of the buffer solution in the surface conditioning agent is preferably 0.1 to 2 g/L. If the concentration is less than 0.1 g/L, the desired provision is hard to be obtained; if it is over 2 g/L, it might affects to the homogenous supply.

[0064] Particle diameter of the dispersed zinc phosphate particles is preferably 10 μm or less. Because, if the diameter becomes over 10 μm, dispersing element becomes unstable, this may deteriorates life of the aqueous liquid. It is preferably 5 μm or less, and more preferably 3 μm or less. Lower limit of the particle diameter is not particularly limited to; in view of viscosity of the aqueous liquid, it is preferably 0.1 μm or more. With regard to the below-mentioned galvanized steel sheet also showing excellent adhesiveness, the particle diameter is preferably 3 μm or less. It is further more preferably 1 μm or less. The particle diameter can be measured in a state of dispersed aqueous liquid by a laser diffractometer.

[0065] Content of the zinc phosphate particles is 0.5 mol/L or less. This is because, when concentration of the zinc phosphate particles becomes over 0.5 mol/L, content of the dispersing element becomes too high, which may deteriorates life of the aqueous liquid. In view of stability of the aqueous liquid, it is preferably 0.3 mol/L or less. The content of the zinc phosphate particles can be converted from atomic weight as $Zn_3(PO_4)_2$ by measuring zinc concentration.

[0066] Into the aqueous liquid, at least one or more kinds selected from: alkali metal of Li, Na, and K; and alkali earth metal of Be, Mg, and Ca may be added. Because, if these metals are added, below-mentioned reaction in the surface of the base material under the pre-drying process becomes more even, therefore, this makes it possible to stably manufacture the hot-dip galvanized steel sheet. Concentration of these alkali metal and alkali earth metal is 0.3 mol/L or less as a total of the above alkali metal and alkali earth metal. This is because, if more than 0.3 mol/L of the above alkali metal and alkali earth metal are added, these additives adhere to the surface of the base material and are brought into the post-process; stability of the treatment agent and the like in the post-process may possibly be deteriorated. These alkali metal and alkali earth metal may be added in forms of orthophosphate, metaphosphate, pyrophosphate, orthosilicate, metasilicate, carbonate, bicarbonate, borate, and etc. In addition, for pH control, ammonium salt or ammonium aqueous solution, and so on may be used. Further, if the concentration is a total of approximately 0.05 mol/L or less, metal or metal salt particles of such as Fe, Co, Ni, Cu, Mn, and Cr may be included. What is more, it is suitable to mix pH buffer and so on in the aqueous liquid. Examples of the buffer solution include one consisting of K_2HPO_4 and NaOH. As these buffer solutions inhibit pH change, stable manufacturing is sometimes carried out. As an aqueous liquid, commercially available surface conditioning agent, which is used for base treatment and the like for coating, may be used as long as it satisfies the above composition.

[0067] Hereinafter, pre-drying process (S2) will be described as follows. The pre-drying process (S2) is a process for drying a surface conditioning agent supplied to the surface of a base material without water rinsing. Drying temperature is not specifically limited to, in view of manufacturing cost and so on, the steel-sheet highest achieving temperature is preferably less than 200°C. More preferably, the temperature is less than 150°C, furthermore preferably 50 to 120°C.

Drying duration is not specifically limited to as well; from the viewpoint of surface appearance and productivity, it is preferably less than 30 seconds, more preferably less than 10 seconds. The drying method is not particularly limited to; it is suitably selected. Examples thereof include air knife, drier, and oven.

[0068] By this pre-drying process (S2), there is no fear that the surface conditioning agent is brought into the below-mentioned treatment agent supply process (S3). As contamination of the surface conditioning agent into the treatment agent cyclically used in this treatment agent supply process (S3) is inhibited, it is capable to minimize the change of composition balance of the treatment agent. Consequently, it becomes possible to inhibit refill and discharge of the treatment agent which was conventionally needed so as to control composition balance of the treatment agent.

[0069] This is because, by drying the surface conditioning agent after supply of the surface conditioning agent, it is possible to once inhibit activation of the galvanized steel sheet. Also, by this drying, without aggregating, zinc phosphate particles are absorbed to the galvanized surface while maintaining the particle size; by a protective-coating-like action, oxidation reaction of the steel sheet surface can be inhibited until the treatment agent supply process, and that allows reactions in the galvanized surface in the following dry process. On the other hand, in case of an aqueous liquid wherein Ti-colloid is dispersed in sodium pyrophosphate aqueous solution, crystal nucleating agent may possibly be dried and aggregated.

[0070] Next, treatment agent supply process (S3) will be described as follows. The treatment agent supply process (S3) is a process to supply a treatment agent for forming a zinc phosphate coating over a base material treated by the above pre-drying process (S2). Supplying method of the treatment agent to the base material is not particularly limited to; for example, there may be spray-wringer method and roll-coating method. Among them, by a combination with the above pre-drying process (S2), the equipment can be effectively simplified. So, in view of manufacturing the hot-dip galvanized steel sheet with lower cost, it is possible to suitably adopt a treatment by roll-coating method. In view of operatability of the treatment agent, treatment by roll-coating method is most preferable. Moreover, temperature of the fed steel sheet, which has come through the pre-drying process (S2), at a time of feeding into the treatment agent supply process (S3) is preferably less than 80˚C. Because, if temperature of the steel sheet is higher, activation of the steel sheet becomes more than a protective-coating-like effect of the surface conditioning agent, which may cause elution of galvanized coating into the treatment agent. The temperature is preferably less than 60˚C. The lower limit is preferably 30˚C or more. If the temperature is less than 30˚C, reaction by heating in the dry-process after the treatment process does not sufficiently occur; thereby coating may be uneven. Control of the above temperature of the fed steel sheet can be achieved by providing a cooling zone of the steel sheet, but also it can be achieved by using roll-cooling such as water-cooling roll.

[0071] The treatment agent supplied in the treatment agent supply process (S3) is a zinc phosphate solution. The zinc phosphate solution is an aqueous solution containing phosphate root and Zn ion. The wording "phosphate root" is a generic name of $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}; it is represented by $[PO_4^{3-}]$.

[0072] The zinc phosphate solution contains 0.001 to 0.7 mol/L of phosphate root $[PO_4^{3-}]$, and contains 0.7 or less of Zn ion in mole ratio to this phosphate root. The reason for specifying the concentration of phosphate root in the range of 0.001 to 0.7 mol/L is because, if the zinc phosphate solution contains more than 0.7 mol/L of phosphate root, stability of the treatment agent might be deteriorated. Meanwhile, if the concentration is in the range less than 0.001 mol/L, pH of the treatment agent becomes higher; reaction becomes inhibited thereby there is a possibility that the desired performance cannot be obtained. Further, the reason for containing 0.7 or less of Zn ion in mole ratio to this phosphate root is because, by making zinc phosphate solution contain the concentration of Zn ion, it is possible to form an even crystalline coating. This is also because there is a fear of occurrence of sludge that may deteriorate the surface quality. The content is preferably 0.5 or less. Here, the wording "sludge" means the one wherein $Zn_3(PO_4)_2$ is solidified in the aqueous solution.

[0073] More specifically, forming reaction of the crystalline zinc phosphate is a reaction shown by the following formula (A) or (B) ; 1.5 times of zinc atoms are required to the phosphate root in the treatment agent.

$$2H_3PO_4 + Zn \Leftrightarrow Zn(H_2PO_4)_2 + H_2 \qquad (A)$$

$$3Zn(H_2PO_4)_2 \Leftrightarrow Zn_3(PO_4)_2 \cdot 4H_2O \qquad (B)$$

Due to this, conventionally, further excessive amount of zinc must be contained in the treatment agent of the treatment agent supply process (S3). However, the excessive amount of zinc raises pH and solidifies the treatment agent.

[0074] pH of the treatment agent is preferably 4 or less. Because, if it becomes more than 4, stability of the treatment agent becomes lowered and sludge occurs, thereby these raise a possibility for damaging the surface quality; also, there is a fear that zinc phosphate coating cannot be formed since the reaction does not proceed smoothly. The pH is furthermore preferably 3 or less.

[0075] Other than Zn ion and phosphate root, adding one or more kinds of strong electrolyte anion selected from a group of strong electrolyte anion consisting of: 0.2 or less of nitrate root (NO^{3-}), 0.2 or less of nitrous root (NO^{2-}), 0.1 or less of hydrofluoric root (F^-), and 0.05 or less of sulfuric root (SO_4^{2-}) in mole ratio to the phosphate root is to have a stable reaction with the treatment agent for the purpose of improving the evenness of the coating. Specifically, by this reaction, it is capable to obtain etching effect and oxidation effect. If the strong electrolyte anion is added in an amount over the above upper limit, stability of the treatment agent is lowered and life of the treatment agent may be shortened.

[0076] Also, for pH control, ammonium salt, or ammonium aqueous solution, and so on may be added to the zinc phosphate solution. Concentration of ammonium ion is preferably 0.02 or less in mole ratio to phosphate root. Moreover, as long as satisfying the above configuration of the zinc phosphate solution, other metal ions apart from zinc may be mixed. In this case, a total mole ratio of the metal ion to the phosphate root is preferably 0.2 or less.

[0077] Adhesion quantity of the zinc phosphate solution in terms of adhesion quantity of coating eventually formed is calculated in phosphorus equivalent by a sum of supply in the above surface conditioning agent supply process (S1) and the treatment agent supply process (S3), it is preferably 30 to 500 mg/m^2. Because, if it is less than 30 mg/m^2, lubricity of the coating is not reflected to the formability of the steel sheet; meanwhile if it is over 500 mg/m^2, the effect becomes saturated. It is further preferably 30 to 400 mg/m^2.

[0078] Since the pre-drying process (S2) is provided as a pre-process of the treatment agent supply process (S3), the surface conditioning agent is not brought into the treatment agent supply process (S3); thereby it is possible to adequately keep balance of the treatment agent for a long time. Accordingly, treatment agent control and drain facility can be simplified.

[0079] The post-drying process (S4) will be described as follows. The post-drying process (S4) is a process to dry a treatment agent supplied to the surface of a base material without water rinsing. Drying temperature is not particularly limited to; in view of manufacturing cost, the steel-sheet highest achieving temperature is preferably less than 250˚C, more preferably less than 180˚C. Drying duration is not specifically limited to as well; from the viewpoint of surface appearance and productivity, it is preferably less than 100 seconds after the application, and more preferably less than 50 seconds. The drying method is not particularly limited to; it is suitably selected. Examples thereof include air knife, drier, and oven. By the post-drying process (S4), more even crystalline film of zinc phosphate coating can be formed.

[0080] Next, one embodiment of the galvanized steel sheet having a zinc phosphate coating of the present invention will be described. The galvanized steel sheet having a zinc phosphate coating comprises a base material, a galvanizing coating over a surface of the base material, and a zinc phosphate coating formed on outside of the galvanizing coating. These are respectively described as below.

(1) Base material

[0081] Kind of steel sheet to be the base material is not particularly limited to; any kind of cold-rolled steel sheet and hot-rolled steel sheet are applicable. Chemical composition of the base material is not specifically limited to, either; the applicable examples include dead soft steel and low-carbon steel both containing Ti, Nb, and so on depending on the necessity, or high-strength steel or high-tensile steel both adequately containing Si, Mn, P, Cr, Ni, Cu, V, and so on.

(2) Galvanizing

[0082] As the galvanizing of the galvanized steel sheet having a zinc phosphate coating of the invention, hot-dip galvanizing or electrogalvanizing may be adopted. By galvanizing the above base material, the galvanized steel sheet can be produced.

[0083] As a hot-dip galvanized steel sheet, for example, there may be GI steel sheet which does not have thermal alloying treatment and thermal alloyed GA steel sheet. "GI steel sheet" means a steel sheet where alloying treatment is not given after hot-dip galvanizing and that contains 2 mass % or less of Fe. If Fe content becomes more than 2 mass %, Fe-Zn alloy layer appears at a part of the surface, which is not preferable with regard to the appearance. Meanwhile, "GA steel sheet" means a steel sheet where alloying treatment is given after hot-dip galvanizing and that contains 7 to 15 mass % of Fe to that of the galvanized layer. If Fe content is less than 7 mass %, eta-phase remains in the vicinity of surface of the alloyed hot-dip galvanized layer, which is not preferable with regard to the appearance. It is preferably 8 mass % or more. If Fe content becomes over 15 mass %, powder tends to be generated at a time of press forming. It is preferably 13 mass % or less.

[0084] The hot-dip galvanized layer of the above GI steel sheet and GA steel sheet may contain 0.05 to 0.5 mass % of Al. As a result, it is capable to enhance the adhesiveness between the hot-dip galvanized coating and the base material. Other than Al, metals of Cu, Ni, Cr, Si, Mn, Pb, Sb, Sn, misch metal, and so on may be slightly contained or added to the hot-dip galvanized layer. Further, alloy phase is not specifically limited to; eta-phase, zeta-phase, delta-phase may be mixed in the GI steel sheet; meanwhile zeta-phase, delta 1-phase, gamma 1-phase, gamma-phase may be mixed in the GA steel sheet.

[0085] Moreover, adhesion quantity of the hot-dip galvanized coating is not particularly limited to. However, from the viewpoint of workability, weldability, and productivity, the adhesion quantity of the hot-dip galvanized coating is preferably

150 g/m^2 or less.

[0086] So far, GI steel sheet and GA steel sheet have been described; other than these, 5 mass % Al-Zn plated steel sheet (GF steel sheet), 55 mass % Al-Zn plated steel sheet (GL), and 3 mass % Mg-Al-Zn plated steel sheet (MZ steel sheet) may be available.

[0087] Examples of the electrogalvanized steel sheet include EG steel sheet consisting of eta-phase, 10 mass % Fe-Zn electrogalvanized steel sheet (FZ steel sheet), and 13 mass % Ni-Zn (ZnNi steel sheet). Among these, applying the zinc phosphate coating of the invention to the EG steel sheet is preferable.

[0088] Manufacturing of the galvanized steel sheet to be used for the present invention can apply any kinds of galvanizing methods. For instance, GI steel sheet is dipped into the plating bath and also cooled in the bath. On the other hand, GA steel sheet is dipped into the plating bath, later alloying treatment is given. If necessary, temper rolling (skin-pass rolling), planarization (leveler), and so on may be imparted. By temper rolling, surface condition and surface roughness of the GI steel sheet and GA steel sheet are varied, these changes may be permitted. These changes do not affect adhesiveness and the like.

(3) Zinc phosphate coating

[0089] The zinc phosphate coating is a coating of a crystalline zinc phosphate formed on the outer layer of the above galvanized steel sheet. The zinc phosphate coating of the galvanized steel sheet having zinc phosphate coating of the present invention has any one of configurations as follows:

> (i) a spectrum obtained by absorption spectrum measurement method measuring a surface reflected light of infrared light incoming from a direction at an angle of 60° to a normal line of the galvanized steel sheet having zinc phosphate coating has a plurality of absorption bands within a wavelength range of 8 to 12 μm; further, ratio of integrated absorption strength (P/S) of a p-polarized light to a s-polarized light within the wavelength range is 1.2 or more.
>
> (ii) a spectrum obtained by absorption spectrum measurement method measuring the surface reflected light of infrared light incoming from a direction at an angle of 60° to a normal line of the galvanized steel sheet having zinc phosphate coating has a plurality of absorption bands within a wavelength range of 8 to 12 μm; further, ratio (Pa/Sa) of an absorbance (Pa) of p-polarized light to an absorbance (Sa) of s-polarized light in case of an absorption (absorption A) within a wavelength of 8.4 to 9.2 μm and ratio (Pb/Sb) of an absorbance (Pb) of p-polarized light to an absorbance (Sb) of s-polarized light in case of an absorption (absorption B) within a wavelength of 10.2 to 11.0 μm are respectively two or more.

[0090] In both of the above (i) and (ii), the zinc phosphate coating of the galvanized steel sheet having zinc phosphate coating of the invention has a plurality of absorption bands within a wavelength range of 8 to 12 μm in a spectrum obtained by absorption spectrum measurement method measuring a surface reflected light of infrared light incoming from a direction at an angle of 60° to a normal line of the galvanized steel sheet having zinc phosphate coating. This is attributed to P-O bonds of zinc phosphate forming the zinc phosphate coating, the coating usually has about five absorption bands.

[0091] The reason for making the infrared light income from a direction at an angle of 60° to a normal line of the galvanized steel sheet having zinc phosphate coating is to inhibit the influence of reflected light coming from the galvanized steel sheet to the absorption spectrum. As a result, it is capable to obtain a desirable SN ratio. The reflected light is detected from a direction at an angle of 60° corresponding to the incident light. Reflected light may be diffused depending on the roughness of the steel sheet surface, which sometimes decreases intensity of reflected light coming into the detector. In such a case, a light-concentrating device may be provided in front of the detector.

[0092] The zinc phosphate coating described in the above (i) has a configuration such that a ratio of integrated strength (P/S) obtained by an absorption spectrum of the p-polarized light (P) to an absorption spectrum of the s-polarized light (S) is 1.2 or more. This shows a degree of orientation of P-O bond constituting the zinc phosphate coating. In other words, "P/S is 1.2 or more" means that p-polarized light is stronger than s-polarized light. Accordingly, the zinc phosphate coating of the galvanized steel sheet having zinc phosphate coating of the invention has a configuration such that almost vertical orientation to the steel sheet is stronger. P/S is further preferably 2 or more.

Furthermore preferable orientation of P-O band is a zinc phosphate coating having a configuration in the range described in (ii). The orientation described in (ii) shows a configuration of absorbance of the zinc phosphate coating used for the galvanized steel sheet having zinc phosphate coating of the invention by paying attention to two wavelength ranges of 8.4 to 9.2 μm and 10.2 to 11.0 μm within the wavelength range of 8 to 12 μm of the above P-O bond. The reason for specifying these two wavelength ranges is because these two generate characteristic absorption of spectrums.

[0093] Specifically, it is composed such that ratio (Pa/Sa) of (absorption A): absorbance (Pa) of p-polarized light to absorbance (Sa) of s-polarized light is 2 or more in an absorption spectrum within the wavelength range of 8.4 to 9.2 μm, and ratio (Pb/Sb) of (absorption B): absorbance (Pb) of p-polarized light to absorbance (Sb) s-polarized light is 2 or more in an absorption spectrum within the wavelength range of 10.2 to 11.0 μm. Both ratios are further preferably 3 or more.

[0094] As described above, in either configuration of (i) or (ii), by making a zinc phosphate coating having a configuration of which orientation of the P-O bond is mainly vertical to the steel sheet (p-polarized light is stronger) in the steel sheet surface, it is capable to provide a galvanized steel sheet having zinc phosphate coating which exhibits excellent adhesiveness while maintaining excellent lubricity. This is assumed that interactions between a P-O bond and a C-O bond of submaterial (mainly resin) increase by this orientation. This interaction makes it possible to provide a galvanized steel sheet having zinc phosphate coating which exhibits excellent compatibility with submaterial for automotive manufacturing, especially vinyl-chloride-series adhesive used for structural bonding and Mastic-type adhesive having sealing function.

[0095] Adhesion quantity of the zinc phosphate coating may be 30 mg/m^2 or more. It is more preferably 50 mg/m^2 or more. This is because adhesion quantity thereof affects lubricity; so if it is less than 30 mg/m^2, preferable lubricity may not be obtained. In addition, adhesion quantity of the zinc phosphate coating is preferably 250 mg/m^2 or less, furthermore preferably 200 mg/m^2 or less, and most preferably 150 mg/m^2 or less. If adhesion quantity of the zinc phosphate coating is larger, the adhesiveness may be deteriorated.

[0096] With the galvanized steel sheet having zinc phosphate coating satisfying the above configuration, it is possible to provide a steel sheet which exhibits excellent lubricity and adhesiveness.

[0097] Hereinafter, the invention will be more specifically described with reference to the following examples.

Examples

(Example 1)

[0098] As Example 1, operatability and lubricity evaluations were carried out about two hot-dip galvanized steel sheets: one was a dead soft GI steel sheet (plating adhesion quantity: 90 g/m^2, Al concentration of the coating: 0.4 mass %, Fe concentration: 1.5 mass %) having a size of 0.8 mm in thickness and 200 mm x 250 mm; and another one was a same size of GA steel sheet (plating adhesion quantity: 60 g/m^2, Al concentration of the coating: 0.30 mass %, Fe concentration: 9.5 mass %). In this Example, the evaluation is based on whether or not the above pre-drying process is included in the manufacturing process in case of changing the components of surface conditioning agent and treatment agent. The component of surface conditioning agent is shown in Table 1 and the content of treatment agent is also shown in Table 2.

[0099] (Table 1)

(Table 1)

Components contained in the surface conditioning agent											
No.	Content									Average particle diameter	pH
	Zn mol/L	zinc phosphate mol/L	Li mol/L	Be mol/L	Na mol/L	Mg mol/L	K mol/L	Ca mol/L	Total alkali metal mol/L	μm	
1	0.0005	0.0002	0.0001	0	0.002	0	0.006	0	0.0081	5	9.1
2	0.013	0.0043	0	0	0.003	0	0.292	0	0.295	1	7.3
3	0.09	0.0300	0.0001	0	0.01	0.003	0	0.0002	0.0133	3	8.2
4	0.12	0.0400	0	0	0.004	0	0.0033	0	0.0073	0.5	8.1
5	0.2	0.0667	0.02	0.09	0	0.005	0.1	0.04	0.255	5	8.3
6	0.38	0.1267	0	0	0.013	0	0.01	0	0.023	8	7.2
7	0.8	0.2667	0.001	0.2	0.2	0	0	0	0.401	7	7.4
8	0.98	0.3267	0	0	0.235	0.05	0.009	0	0.294	5	7.2
9	1.29	0.4300	0	0	0.03	0	0.043	0	0.073	3	6
10	1.1	0.3667	0.005	0	0.003	0	0	0.0002	0.0082	11	6
11	1.5	0.5000	0.001	0	0	0.06	0.02	0	0.081	6	4.5
12	1.9	0.6333	0.02	0	0.004	0	0	0.004	0.028	5	7
13	7 mass % NaOH										
14	2 mass % H_2SO_4										
15	Aqueous liquid where Ti-colloid is dispersed in a sodium pyrophosphate solution (commodity name: "PALENE Z" (PL-Z) manufactured by Nihon Parkerizing Co., LTD., 0.005mol/L)										8

[0100] (Table 2)

(Table 2)

Components contained in the treatment agent								
No.	[Zn] mol/L	$[PO_4^{3-}]$ mol/L	$[Zn] / [PO_4^{3-}]$	$[NO_3^-] / [PO_4^{3-}]$	$[NO_2^-] / [PO_4^{3-}]$	$[F^-] / [PO_4^{3-}]$	$[SO_4^{2-}] / [PO_4^{3-}]$	pH
a	0.007	0.02	0.35	0.09	0	0.04	0	3.2
b	0.001	0.002	0.50	0	0.15	0	0.05	3.1
c	0.1	0.50	0.20	0	0.07	0.01	0.02	2.7
d	0.2	0.60	0.33	0.05	0	0.07	0	2.5
e	0.25	0.60	0.42	0.09	0	0.05	0	2.9
f	0.4	0.60	0.67	0.1	0	0.02	0	2.2
g	0.5	0.70	0.71	0.02	0.02	0.03	0.01	2.5
h	0.5	0.60	0.83	0.01	0.02	0.05	0.01	3.2
i	0.5	0.60	0.83	0.01	0.02	0.05	0.01	4.1
j	0.2	0.60	0.33	0.22	0	0	0	2.5
k	0.2	0.60	0.33	0	0.25	0	0	2.5
l	0.2	0.60	0.33	0	0	0.13	0	2.6
m	0.2	0.60	0.33	0	0	0	0.07	3.1

[0101] Also, conditions of each process are as follows.

(Surface conditioning agent supply process)

[0102]

Method for supplying surface conditioning agent: spray or roll coater
Adhesion quantity: 3 mg/m^2 in phosphorus equivalent

(Pre-drying process)

[0103]

Drying equipment: drier
Drying temperature: steel-sheet highest achieving temperature: 60˚C
Drying duration: 10 seconds

(Treatment agent supply process)

[0104]

Supplying method: roll coater (temperature of the fed steel sheet: 50˚C)
Total adhesion quantity: 80 mg/m^2 in phosphorus equivalent

(Post-drying process)

[0105]

Drying equipment: oven
Drying temperature: steel-sheet highest achieving temperature: 70˚C

Drying duration: 30 seconds

[0106] In addition to this, conventional examples wherein cleaning with alkali and acid were done are shown. In these cases, specifically, base materials rinsed by water after cleaned with alkali and acid were fed into the treatment agent supply process. In these Examples, existence of drying process after water rinsing and before the treatment agent supply process is also shown. The test conditions are shown below.

Pre-cleaning condition: 7 mass % NaOH and 2 mass % H_2SO_4 (Nos. 13 and 14 of Table 1)
Dipping condition: dipping in 7% NaOH aqueous solution (70˚C) for 5 seconds;

: dipping in 2% H_2SO_4 aqueous solution (50˚C) for 5 seconds

(1) Evaluation items

[0107] In accordance with the above conditions, the below-described evaluations were carried out.

(1-1) Operatability evaluation

[0108] So as to evaluate operatability, concentration, to 10L of treatment agent, of carry-in portion (alkali metal of the surface conditioning agent) from the surface conditioning agent to this treatment agent at a time of treatment agent supply to a $10m^2$ base material (a total area of the above cut-plate was $10m^2$) and concentration, to the same, of mainly Zn contained in the treatment agent were measured, and change of concentration of the treatment agent between before and after the supply was evaluated. Evaluation criteria of the operatability are as follows. "No need to adjust concentration" in the following evaluation criteria means that there were no need for water-rinsing equipment and supplement, waste-liquid facilities.
○ (good): increased portion of concentration of alkali metal and zinc in the treatment agent is 2 mass % or less to the original concentration (No need to adjust concentration);
△ (not bad) : increased portion of concentration of alkali metal and zinc in the treatment agent is more than 2 mass % and 4 mass % or less to the original concentration (Almost no need to adjust concentration); and
× (bad) : increased portion of concentration of alkali metal and zinc in the treatment agent is more than 4 mass % to the original concentration (Need to adjust concentration).

(1-2) Lubricity evaluation

[0109] Rust preventive oil was applied onto the obtained hot-dip galvanized steel sheet having zinc phosphate coating, and friction coefficient measurement was carried out under the following condition using Pin-On-Disk type friction and wear tester. The lubricity was evaluated based on the friction coefficient. Evaluation criteria of the friction coefficient are shown as below.

Test condition

[0110]

Load: 30 kN
Material of slider: SKD steel
Shape of slider: a 5 mm diameter of steel ball
Test temperature: 60˚C
Radius gyration: 10 mm
Sliding speed: 1 rpm
Number of Test revolution: 20 revolutions
Number of Measurement point: Coefficient measured at 12 points per revolution was averaged. The maximum value in 20 revolutions adopted as the representing coefficient.

Evaluation criteria

[0111]

◎ (very good): friction coefficient: less than 0.12 (extremely preferable as a lubricating treatment);

○ (good): friction coefficient: 0.12 or more and less than 0.15 (preferable as a lubricating treatment); and
× (bad): friction coefficient: 0.15 or more (inadequate as a lubricating treatment)

(1-3) Stability of the surface conditioning agent and the treatment agent

[0112] Stability of each surface conditioning agent and treatment agent was measured by "40˚C by 7 days Test". This is a test wherein each conditioning agent and treatment agent is kept at 40˚C for 7 days. Evaluation criteria of stability of surface conditioning agent and treatment agent are as follows.

Surface conditioning agent

[0113]

○ (good): dispersed condition was maintained; and
× (bad): precipitation occurred.

Treatment agent

[0114]

○ (good): no occurrence of sludge; and
× (bad): sludge occurs.

(2) Evaluation results

[0115] Results about Example 1 evaluated based on the above condition are described as follows.

(2-1) Operatability and lubricity

[0116] The results are shown in Table 3.
[0117] (Table 3)

(Table 3)

Code	Kinds of steel sheet	Process					Operatability		Performance	Notes
		Surface conditioning agent supplying process		Pre-drying process	Treatment agent supplying process		Surface conditioning agent	Treatment agent	Lubricity	
		Surface conditioning agent No.	Supplying method		Treatment agent No.	Supplying method				
R1	GI	1	Spraying	included	a	Roll coater	○	○	◎	Example
R2	GA	1	Roll coater	included	c	Roll coater	○	○	◎	Example
R3	GI	1	Spraying	included	d	Roll coater	○	○	◎	Example
R4	GA	1	Spraying	none	d	Roll coater	○	×	◎	Comparative example
R5	GA	1	Spraying	included	e	Roll coater	○	○	◎	Example
R6	GA	1	Roll coater	included	f	Roll coater	○	○	◎	Example
R7	GA	2	Roll coater	included	a	Roll coater	○	○	◎	Example
R8	GA	2	Roll coater	included	b	Roll coater	○	○	◎	Example
R9	GA	2	Roll coater	none	b	Roll coater	○	×	◎	comparative example
R10	GA	2	Spraying	included	e	Roll coater	○	○	◎	Example
R11	GI	2	Roll coater	included	f	Roll coater	○	○	◎	Example
R12	GA	3	Spraying	none	a	Roll coater	○	×	◎	Comparative example
R13	GA	3	Roll coater	included	b	Roll coater	○	○	◎	Example
R14	GI	4	Spraying	included	b	Roll coater	○	○	◎	Example
R15	GA	4	Roll coater	none	c	Roll coater	○	×	◎	Comparative example
R16	GA	4	Spraying	included	d	Roll coater	○	○	◎	Example
R17	GI	4	Roll coater	included	e	Roll coater	○	○	◎	Example

(continued)

Code	Kinds of steel sheet	Process					Operatability		Performance	Notes
		Surface conditioning agent supplying process		Pre-drying process	Treatment agent supplying process		Surface conditioning agent	Treatment agent	Lubricity	
		Surface conditioning agent No.	Supplying method		Treatment agent No.	Supplying method				
R18	GA	4	Spraying	none	f	Roll coater	○	×	◎	Comparative example
R19	GA	4	Roll coater	included	f	Roll coater	○	○	◎	Example
R16	GA	5	Spraying	included	a	Roll coater	○	○	◎	Example
R17	GA	5	Roll coater	included	d	Roll coater	○	○	◎	Example
R18	GI	6	Spraying	none	f	Roll coater	○	×	◎	Comparative example
R19	GI	6	Spraying	included	d	Roll coater	○	○	◎	Example
R20	GA	8	Roll coater	included	b	Roll coater	○	○	◎	Example
R21	GA	8	Spraying	included	d	Roll coater	○	○	◎	Example
R22	GA	9	Spraying	included	d	Roll coater	○	○	◎	Example
R23	GA	9	Roll coater	included	f	Roll coater	○	○	◎	Example
R24	GA	11	Spraying	included	a	Roll coater	×	○	◎	Example
R25	GI	11	Roll coater	included	f	Roll coater	×	○	◎	Example
R26	GI	13	Spraying	included	b	Roll coater	×	○	×	Conventional example
R27	GA	13	Spraying	none	b	Roll coater	×	×	×	Conventional example
R28	GI	14	Roll coater	included	d	Roll coater	×	○	×	Conventional example
R29	GA	14	Roll coater	none	d	Roll coater	×	×	×	Conventional example
R30	GA	15	Roll coater	included	a	Roll coater	○	Δ	○	Example

(continued)

Code	Kinds of steel sheet	Process					Operatability		Performance	Notes
		Surface conditioning agent supplying process		Pre-drying process	Treatment agent supplying process		Surface conditioning agent	Treatment agent	Lubricity	
		Surface conditioning agent No.	Supplying method		Treatment agent No.	Supplying method				
R31	GA	1	Roll coater	included	a	Spraying	○	×	○	Comparative example

※ note: "Example" means an example of the present invention.

[0118] As seen from the table, when surface conditioning agent was supplied and the agent was later dried in the pre-drying process, all of the treatment agents showed high operatability, and lubricity of the obtained hot-dip galvanized steel sheet was also desirable; these remarkably represented effects of the present invention. In addition, it is understood that the operatability and lubricity do not depend on the supply process of the surface conditioning agent.

[0119] Meanwhile, in cases of applying conventional cleaning agent indicated in the codes R26 to R29 as conventional examples, as these cases also had pre-drying process, operatability only of the treatment agent is preferable. This means that the pre-drying process largely affect the enhancement of operatability of the treatment agent. However, under the condition of codes R26 to R29, a desired lubricity was not imparted to the hot-dip galvanized steel sheet, it is also understood that supply of surface conditioning agent is required.

[0120] Moreover, under the condition indicated in codes R24 and R25 as reference examples, there is no influence to operatability of the treatment agent, on the other hand, operatability of the surface conditioning agent is not preferable. The reason for this is assumed that surface treatment agent shown in No. 11 of Table 1 used for codes R24 and R25 marks pH 4.5, which is relatively low. Therefore, by enlarging pH up to at least over 4.5, it is capable to enhance the operatability of the surface conditioning agent.

(2-2) Stability of the surface conditioning agent and the treatment agent

[0121] Results of stability of each surface conditioning agent and treatment agent shown in Tables 1 and 2 are described as below. Stability evaluation result of the surface conditioning agent is shown in Table 4, and stability evaluation result of the treatment agent is also shown in Table 5.

[0122] (Table 4)

(Table 4)

Stability of the surface conditioning agent		
No.	Stability	Notes
1	○	Example
2	○	Example
3	○	Example
4	○	Example
5	○	Example
6	○	Example
7	×	Reference example
8	○	Example
9	○	Example
10	×	Reference example
11	○	Reference example
12	×	Reference example
13	-	Conventional example
14	-	Conventional example
15	○	Example
※ note: "Example" means an example of the present invention.		

[0123] (Table 5)

(Table 5)

Stability of the treatment agent		
No.	Stability	Notes
a	○	Example
b	○	Example
c	○	Example
d	○	Example
e	○	Example
f	○	Example
g	×	Comparative example
h	×	Comparative example
i	×	Comparative example
j	×	Comparative example
k	×	Comparative example
l	×	Comparative example
m	×	Comparative example
※ note: "Example" means an example of the present invention.		

[0124] The surface conditioning agent in terms of Nos. 7, 10, and 12 shown in Table 4 did not show excellent stability. In terms of No. 7, according to Table 1, this is thought that a total of alkali metal and alkali earth metal reaches 0. 401 mol/L. Also, in terms of Nos. 10 and 12, it is thought that particle diameter and content of zinc phosphate are respectively large in both cases. These elements do not necessarily affect the operatability of treatment agent; nevertheless, higher stability is preferable.

[0125] In terms of g to m of the treatment agents shown in Table 5, the stability was not good. This is thought that with regard to g to i, Zn ion ratio to phosphate root is large. Moreover, i marks pH 4.1, which is high. In terms of j to m, it is though that anion ratio of the added strong electrolyte being large is the cause. These do not necessarily affect operatability of the treatment agent; nevertheless higher stability is preferable.

(Example 2)

[0126] As Example 2, in a manufacturing line of continuous hot-dip galvanized steel sheet, a 0.8 mm thick GA steel sheet (dead soft steel sheet, plating adhesion quantity: 45 g/m^2, Al concentration of the coating: 0.25 mass %, Fe concentration: 9.0 mass %) was treated with skin-pass mill (rolling reduction ratio: 1.0 %); in the surface conditioning agent supply process, surface conditioning agents of Nos. 1, 4, and 6 shown in Table 1 were supplied; in the treatment agent supply process, zinc phosphate coating treatment was carried out using treatment agent of a, d, e, and i shown in Table 2. Conditions of each process are as follows.

(Surface conditioning agent supply process)

[0127]

Supplying method: spray or roll coater
Drying equipment: drier
Adhesion quantity: 3 mg/m^2 in phosphorus equivalent

(Pre-drying process)

[0128]

Drying temperature: steel-sheet highest achieving temperature: 70˚C
Drying duration: 5 seconds

(Treatment agent supply process)

[0129]

Supplying method : roll coater (temperature of the fed steel sheet: 50˚C)

(Post-drying process)

[0130]

Drying equipment: oven
Drying temperature: steel-sheet highest achieving temperature: 80˚C
Drying duration: 30 seconds

[0131] As comparative examples, test without having pre-drying process was also carried out.

(3) Evaluation items

[0132] In accordance with the above conditions, the below-described evaluation was carried out.

(3-1) Operatability evaluation

[0133] Concentration, to 100L of treatment agent, of carry-in portion (alkali metal of the surface conditioning agent) from the surface conditioning agent to the treatment agent and of mainly Zn contained in the treatment agent when a 0.8 mm thick and 1 m wide steel sheet was taken for 100 m through the treatment agent were measured, and change of concentration of the treatment agent between before and after the supply was evaluated. Evaluation criteria of the operatability are as follows. "No need to adjust concentration" in the following evaluation criteria means that there were no need for water-rinsing equipment and supplement, waste-liquid facilities.
○ (good): increased portion of concentration of alkali metal and zinc in the treatment agent is 2 mass % or less to the original concentration (No need to adjust concentration);
△ (not bad): increased portion of concentration of alkali metal and zinc in the treatment agent is more than 2 mass % and 4 mass % or less to the original concentration (Almost no need to adjust concentration); and
× (bad): increased portion of concentration of alkali metal and zinc in the treatment agent is more than 4 mass % to the original concentration (Need to adjust concentration).

(3-2) Lubricity evaluation

[0134] Rust preventive oil was applied onto the obtained hot-dip galvanized steel sheet having zinc phosphate coating and friction coefficient measurement was carried out under the following condition by using Pin-On-Disk type friction and wear tester. The lubricity was evaluated based on the friction coefficient. Evaluation criteria of the friction coefficient are shown as below.

Test condition

[0135]

Load: 30 kN
Material of slider: SKD steel
Shape of slider: a 5 mm diameter of steel ball
Test temperature: 60˚C
Radius gyration: 10 mm
Sliding speed: 1 rpm
Number of Test revolution: 20 revolutions
Number of Measurement point: Coefficient measured at 12 points per revolution was averaged. The maximum value in 20 revolutions adopted as the representing coefficient.

Evaluation criteria

[0136]

◎ (very good): friction coefficient: less than 0.12 (extremely preferable as a lubricating treatment);
○ (good) : friction coefficient: 0.12 or more and less than 0.15 (preferable as a lubricating treatment); and
× (bad): friction coefficient: 0.15 or more (inadequate as a lubricating treatment).

(3-3) Spot weldability evaluation

[0137] Spot welding was carried out to the obtained hot-dip galvanized steel sheet having zinc phosphate coating by using spot welding machine in accordance with the following conditions; and number of points of welding in which nugget diameter (mm) is up to 4t and 1/2 (t: steel sheet thickness (mm)) or less was evaluated.

Evaluation criteria

[0138]

Electrode diameter: 6 mm
Electrode tip diameter: 40R dome-type
Material of electrode: 1 mass % Cr-Cu
Welding pressure: 2 kN
Up-slope: 3 cycles
Energizing duration: 10 cycles (frequency: 50 Hz)
Flow of coolant: 3 L/min
Welding current: 10.5 kA

Evaluation criteria

[0139]

○ (good): 2000 points or more (adequate)
× (bad): less than 2000 points (inadequate)

(3-4) anticorrosion evaluation

[0140] Anticorrosion evaluation was carried out by a method generally used as a performance evaluation of steel sheet for automotive manufacturing and so on. Specifically, a steel sheet was coated by electrodeposition after chemical conversion treatment and then it was provided with a single cut; finally evaluated with maximum swelling width after 500 hours of 5 mass % salt-spray test. Conditions of the chemical conversion treatment and electrodeposition coating are shown as follows.

[0141] Chemical conversion treatment (zinc phosphate treatment) was carried out after a series of process in order of alkaline degreasing, water rinsing, and surface treatment. Conditions and the like in each process are shown as below.
Alkaline degreasing: dipping in 200 g/L of "fine cleaner E2001" (manufactured by Nihon Parkerizing Co., Ltd.) (50˚C) for 2 minutes;
Water rinsing: 30 seconds
Surface conditioning: dipping in 1 g/L of "PALENE Z" (manufactured by Nihon Parkerizing Co., Ltd.) (at room temperature) for 10 seconds;
Chemical conversion treatment: spraying "PB-L3080" (manufactured by Nihon Parkerizing Co., Ltd., liquid temperature: 43˚C) for 2 minutes.

[0142] Followed by the above chemical conversion treatment, GT-10 (cation electrodeposition coating: 20 μ) electrodeposition coating was carried out. The evaluation criteria are as below. Evaluation criteria: one-side maximum swelling width
○ (good): less than 3 mm (adequate);
× (bad): 3 mm or more (inadequate)

(4) Evaluation results

[0143] Results based on the above conditions and evaluation items are described as follows. The results are shown in Table 6.

[0144] (Table 6)

(Table 6)

Code	Process				Operatability	P adhesion quantity	Performance			Notes
	Surface conditioning agent supplying process		Pre-drying process	Treatment agent	Treatment agent supplying process	mg/m^2	Lubricity	Spot weldability	Corrosion resistance	
	Surface conditioning agent	Supplying method								
Z1	1	Spraying	included	a	○	31	○	○	○	Example
Z2	1	Spraying	included	d	○	83	◎	○	○	Example
Z3	1	Spraying	included	e	○	250	◎	○	○	Example
Z4	1	Spraying	none	a	×	32	○	○	○	Comparative example
Z5	1	Spraying	none	d	×	85	◎	○	○	Comparative example
Z6	1	Roll coater	included	a	○	64	◎	○	○	Example
Z7	1	Roll coater	included	d	○	160	◎	○	○	Example
Z8	1	Roll coater	included	e	○	490	◎	○	○	Example
Z9	1	Roll coater	none	d	×	223	◎	○	○	Comparative example
Z10	4	Roll coater	none	e	×	415	◎	○	○	Comparative example
Z11	4	Spraying	included	a	○	18	×	○	○	Reference example
Z12	4	Spraying	included	d	○	77	◎	○	○	Example
Z13	4	Spraying	included	e	○	119	◎	○	○	Example
Z14	4	Spraying	none	a	×	23	×	○	○	Comparative example
Z15	4	Spraying	none	d	×	81	◎	○	○	Comparative example

(continued)

Code	Process				Operatability	P adhesion quantity	Performance			Notes
	Surface conditioning agent supplying process		Pre-drying process	Treatment agent	Treatment agent supplying process	mg/m^2	Lubricity	Spot weldability	Corrosion resistance	
	Surface conditioning agent	Supplying method								
Z16	4	Roll coater	included	a	○	25	×	○	○	Reference example
Z17	4	Roll coater	included	d	○	87	◎	○	○	Example
Z18	4	Roll coater	included	e	○	201	◎	○	○	Example
Z19	4	Roll coater	none	a	×	35	○	○	○	Comparative example
Z20	6	Roll coater	none	e	×	91	◎	○	○	Comparative example
Z21	6	Spraying	included	a	○	36	○	○	○	Example
Z22	6	Spraying	included	d	○	72	◎	○	○	Example
Z23	6	Spraying	included	e	○	153	◎	○	○	Example
Z24	6	Spraying	none	d	×	38	○	○	○	Comparative example
Z25	6	Spraying	none	e	×	62	◎	○	○	Comparative example
Z26	6	Roll coater	included	a	○	35	○	○	○	Example
Z27	6	Roll coater	included	d	○	79	◎	○	○	Example
Z28	6	Roll coater	included	e	○	147	◎	○	○	Example
Z29	6	Roll coater	none	a	×	36	○	○	○	Comparative example
Z30	6	Roll coater	none	e	×	88	◎	○	○	Comparative example

(continued)

Code	Process				Operatability	P adhesion quantity	Performance			Notes
	Surface conditioning agent supplying process		Pre-drying process	Treatment agent	Treatment agent supplying process		Lubricity	Spot weldability	Corrosion resistance	
	Surface conditioning agent	Supplying method				mg/m^2				
Z31	6	Roll coater	included	i	○	88	○	○	○	Example

※ note: "Example" means an example of the present invention.

[0145] As seen from Table 6, the examples having pre-drying process and noted to be the Examples of the present invention are individually favorable in operatability of the treatment agent. Whereas, all of the other examples without having pre-drying (noted to be Comparative examples) are not favorable in operatability of the treatment agent. Accordingly, these remarkably represented effects of the present invention.

[0146] When having pre-drying process, each performance was favorable. In terms of codes Z11 and Z16, the reason for the unfavorable lubricity is because phosphorous adhesion quantity is small. This is not caused by the influence of existence of pre-drying process included in the present invention.

(Example 3)

[0147] Steel sheets provided with various galvanized layer on both side of 0.8 mm thick dead soft steel sheets were treated by 30-second spray degreasing with "FCL4480" (20 g/L, 45˚C) manufactured by Nihon Parkerizing Co., Ltd., then these were water-rinsed and dried to become test pieces. Thereafter, a series from the surface conditioning agent supply process (S1) to the post-drying process (S4) were treated thereto to produce galvanized steel sheets having zinc phosphate coating. Later, various evaluations were carried out about galvanized steel sheets having zinc phosphate coating. The conditions, evaluation items, evaluation results, and so on are described as follows. Further, as a comparison, a sample where only the surface conditioning agent supply process (S1) and the pre-drying process (S2) were carried out, and some other samples where only the treatment agent supply process (S3) and the post-drying process (S4) were carried out were respectively produced. Furthermore, as a conventional example, an electrogalvanized layer (adhesion quantity: 2 g/m^2 to each side) having a composition of 80 mass % Fe-20 mass % Zn over the galvanized upper layer was produced. Various galvanized steel sheets used for these Examples are shown in Table 7. Moreover, surface conditioning agents used for the Examples are shown in Table 8, and treatment agents of the same are shown in Table 9.

[0148] (Table 7)

(Table 7)

Abbrev.	Galvanizing method	Galvanizing adhesion quantity (per side) (mg/m^2)	Galvanizing component (excluding Zn, mass %)		
			Fe	Al	Mg
GA	Hot-dip galvanizing ⇒ Alloyed in a hot furnace	50	9.5	0.3	0
GI	Hot-dip galvanizing	70	0.2	0.4	0
EG	Electrogalvanizing	50	0	0	0
MZ	Hot-dip galvanizing	60	0	3.4	3

[0149] (Table 8)

(Table 8)

Code	Type	Concentration (mol/L)	Average particle diameter (μm)	pH	Additive materials
1A	Ti + Sodium pyrophosphate solution	0.005	0.4	8	
1B	Zinc phosphate particle-dispersed solution	0.4	0.1	7.5	K_2HPO_4+NaOH buffer solution
1C	Zinc phosphate particle-dispersed solution	0.4	0.6	7.5	K_2HPO_4+NaOH buffer solution
1D	Zinc phosphate particle-dispersed solution	0.4	1.2	7.5	K_2HPO_4+NaOH buffer solution
1E	Zinc phosphate particle-dispersed solution	0.4	3	7.5	K_2HPO_4+NaOH buffer solution

(continued)

Code	Type	Concentration (mol/L)	Average particle diameter (μm)	pH	Additive materials
1F	Zinc phosphate particle-dispersed solution	0.4	5	7.5	K_2HPO_4+NaOH buffer solution
1G	Zinc phosphate particle-dispersed solution	0.4	0.6	5.2	
1H	Zinc phosphate particle-dispersed solution	0.4	0.6	4	H_3PO_4 addition
1J	Zinc phosphate particle-dispersed solution	0.4	0.6	10	Na_2HPO_4 addition
1K	Zinc phosphate particle-dispersed solution	0.4	0.6	11	Na_2HPO_4 addition
1L	Zinc phosphate particle-dispersed solution	0.05	0.6	7.5	K_2HPO_4+NaOH buffer solution
1M	Zinc phosphate particle-dispersed solution	0.1	0.6	7.5	K_2HPO_4+NaOH buffer solution
1P	Zinc phosphate particle-dispersed solution	1.0	0.6	7.5	K_2HPO_4+NaOH buffer solution
1Q	Zinc phosphate particle-dispersed solution	2.0	0.6	7.5	K_2HPO_4+NaOH buffer solution
1R	Zinc phosphate particle-dispersed solution	5.0	0.6	7.5	K_2HPO_4+NaOH buffer solution
Note: Concentration value of Code 1A shows Ti-concentration, concentration value of rest of the codes show Zinc phosphate-concentration.					

[0150] (Table 9)

(Table 9)

No.	[Zn] mol/L	[PO_4^{3-}] mol/L	[Zn]/ [PO_4] mol ratio	[NO_3^-]/ [PO_4^{3-}] mol ratio	[NO_2^-]/ [PO_4^{3-}] mol ratio	[F^-]/ [PO_4^{3-}] mol ratio	[SO_4^{2-}]/ [PO_4^{3-}] mol ratio	pH
2A	0.2	0.60	0.33	0	0	0	0	3.2
2B	0.2	0.60	0.33	0.07	0	0	0	3.1
2C	0.2	0.60	0.33	0	0	0.05	0	2.7
2D	0.2	0.60	0.33	0.05	0	0.07	0	2.5
2E	0.2	0.60	0.33	0	0	0	0.02	2.8
2F	0.12	0.60	0.20	0.05	0	0.07	0	2.7
2G	0.06	0.60	0.10	0.05	0	0.07	0	2.8
2H	0.01	0.60	0.02	0.05	0	0.07	0	3.1
2I	0	0.60	0.00	0.05	0	0.07	0	3.3
2J	0.3	0.60	0.50	0.1	0	0	0	2.2
2K	0.5	0.60	0.83	0.01	0	0.01	0	4.1
2L	0.6	0.60	1.00	0.01	0	0.04	0	4.1

(1) Manufacturing condition

[0151] The manufacturing conditions are described as below.

(1-1) Surface conditioning agent supply process (S1)

[0152] A surface conditioning agent shown in Table 8 was supplied to a galvanized steel sheet. Supplying method was any one of spray (S in Table 10), post-spraying squeezing roll (SR in Table 10), post-spraying air knife (AK in Table 10), and roll coating (RC in Table 10). The adhesion quantity was obtained by fluorescent X-ray.

(1-2) Pre-drying process (S2)

[0153] Drying in pre-drying process (S2) was done by hot-air drier. The drying temperature was set with reference to the steel-sheet temperature; it was carried out within the range of no drying to drying at 150˚C. Drying duration for all examples having pre-drying process was standardized to 10 seconds.

(1-3) Treatment agent supply process (S3)

[0154] A treatment agent shown in Table 9 was supplied to a galvanized steel sheet. Supply process was done by either of post-spray squeezing roll or roll coating.

(1-4) Post-drying process (S4)

[0155] Drying in post-drying process (S4) was carried out by hot-air oven. The drying temperature was set with reference to the steel-sheet temperature; it was standardized at 80˚C when carrying out the post-drying. Drying duration for all examples having post-drying process was standardized to 10 seconds.

(2) Evaluation items and evaluation methods thereof (2-1) P/S calculation by infrared absorption spectroscopy

[0156] The obtained galvanized steel sheet having a coating was cut into a size of 25mm x 100 mm, and measured in accordance with the following method. For the measurement, "S-300" manufactured by Bio-Rad Laboratories was used.

[0157] Measurement was carried out by making the infrared light income from a direction at an angle of 60˚ to a normal line of the galvanized steel sheet as the object to be measured to detect infrared lights reflected to a direction corresponding to the angle of 60˚. At this moment, incoming infrared light was polarized into a vertical direction (p-polarized light) and a horizontal direction (s-polarized light) against the surface by KRS-5 polarized photon; the reflected infrared light were all detected. Specifically, this was done in accordance with the following procedure.

[0158] First of all, as a standard sample of Au evaporated film, infrared reflectance spectrum of respective p-polarized light and s-polarized light were measured. Then, about p-polarized light, p-polarized light relative reflectance spectrum of steel sheet surface to p-polarized light reflectance of evaporated film was measured; meanwhile about s-polarized light, relative reflectance spectrum of steel sheet surface to s-polarized light reflectance of Au evaporated film was also measured. Finally, by using the following formulas (C) and (D) :

$$\text{p-polarized light absorbance} = -\log(\text{p-polarized light relative reflectance}) \quad (C)$$

$$\text{s-polarized light absorbance} = -\log(\text{s-polarized light relative reflectance}) \quad (D),$$

infrared absorption (absorbance) spectrums of respective p-polarized light and s-polarized light were obtained. FIGs. 2 (a) and 2 (b) show an example of relation between the obtained wavelength and absorbance in a form of graph. FIG. 2 (a) is a graph about p-polarized light, and FIG. 2 (b) is a graph about s-polarized light. In these graphs, Pa and Sa respectively means absorbance of p-polarized light and s-polarized light within the wavelength range of 8.4 to 9.2 μm;

Pb and Sb respectively means absorbance of p-polarized light and s-polarized light within the wavelength range of 10.2 to 11.0 μm.

[0159] Further, integral intensities P and S were calculated by carrying out background correction by deducting absorbance at a wavelength of 12 μm from each absorbance of each wavelength within the range of 8 μm to 12 μm about infrared absorption spectrum of the obtained p-polarized light and s-polarized light, and adding absorbance of each wavelength. Specifically, these are represented by the following formulas (E) and (F).

$$P = (P8\ \mu m - P12\ \mu m) + \ldots + (P12\ \mu m - P12\ \mu m) \quad (E)$$

$$S = (S8\ \mu m - S12\ \mu m) + \ldots + (S12\ \mu m - S12\ \mu m) \quad (F)$$

Using the obtained P and S, P/S could be calculated.

(2-2) Evaluation in adhesion quantity of zinc phosphate coating and crystallization characteristics

[0160] Adhesion quantity of zinc phosphate coating could be obtained by phosphorus adhesion quantity using fluorescent X-ray measurement method about the obtained steel sheet. Crystallization characteristics of zinc phosphate were evaluated using "RINT2500" measuring device manufactured by Rigaku Industrial Corp. in accordance with the following method.

X-ray diffraction measurement with 2θ (CoKα) in a direction at an angle of 5 to 60° was carried out, identifying two kinds of diffraction lines A, B attributed to zinc phosphate·4 hydrate; then, coating having both of diffraction lines A and B were determined as a crystalline material. The A and B are respectively:

A: (020) face of zinc phosphate·4 hydrate 2θ = 10.8°;
B: (311 + 241 + 151) face of zinc phosphate·4 hydrate 2θ = 36.7°.

(2-3) Adhesiveness

(2-3-1) Evaluation using vinyl-chloride type adhesive

[0161] The obtained steel sheet was cut into a size of 25 mm x 200 mm; rust preventive oil was applied thereto at an amount of 2 g/m^2 per side; then adhesive "PV5308" manufactured by Cemedine Henkel Co., Ltd. was applied to the surface at an area of 25 mm x 150 mm and thickness of 0.15 mm; later, the sheet was baked. Baking was done at 170°C for 20 minutes, 30 minutes, 40 minutes, and 50 minutes. After baking, T-Peeling test was carried out. FIG. 3 shows a schematic view of method of T-Peeling test. As shown in FIG. 3, the test was carried out by clutching respective ends, where adhesive 2 was not adhered, of steel sheets 1, 1 a part of which were adhered to each other, and pulling the respective ends in directions shown by arrows T, T which were vertical to the adhered face and opposite each other. The evaluation was done based on a baking duration as a standard such that cohesive-failure area ratio became 90% or more; the specific criteria were as follows.
◎ (very good): 20 minutes or less;
○ (good): over 20 minutes and 30 minutes or less;
△ (not bad): 30 minutes and 40 minutes or less;
× (bad): over 40 minutes.

(2-3-2) Evaluation using Mastic-type adhesive

[0162] The obtained steel sheet was cut into a size of 25 mm x 100 mm; rust preventive oil was applied thereto at an amount of 2 g/m^2 per side; then adhesive "OROTEX 580" manufactured by Iida Industry Co., Ltd. was applied to the surface at an area of 25 mm x 25 mm and thickness of 0.1 mm; later, the sheet was baked. Baking was done at 170°C for 20 minutes, 30 minutes, and 40 minutes; after baking, Shear-tensile test was carried out. The method for shear-tensile test is schimatically shown in FIG. 4. As shown in FIG. 4, the test was carried out by clutching respective ends, where adhesive 4 was not adhered, of steel sheets 3, 3 a part of which were adhered to each other, and pulling the respective ends in directions shown by arrows S, S which were parallel to the adhered face and opposite each other. The evaluation was done based on a baking duration as a standard such that cohesive-failure area ratio became 90%

or more; the specific criteria were as follows.
◎ (very good): 20 minutes or less;
○ (good): over 20 minutes and 30 minutes or less;
△ (not bad): over 30 minutes and 40 minutes or less;
× (bad): over 40 minutes.

(2-4) Lubricity

[0163] Measurement of lubricity with regard to a galvanized steel sheet having the obtained coating was carried out by measuring the friction coefficient. Specifically, by using Pin-On-Disk type friction and wear tester, rust preventive oil "NOX-RUST 550S" manufactured by Parker Industries, Inc. was applied to the steel sheet at an amount of 2 g/m^2 per side; then friction coefficient was measured. The test duration and evaluation criteria are shown as follows.

Test condition

[0164]

Load: 30 kN
Material of slider: SUJ2 (bearing steel)
Shape of slider: φ5 mm
Test temperature: 60°C
Radius gyration: 10 mm
Sliding speed: 1 rpm
Number of Test revolution: 20 revolutions
Number of Measurement point: Coefficient measured at 12 points per revolution was averaged. The maximum value in 20 revolutions was adopted as the representing coefficient. to make it an average of 20 revolutions.

Evaluation criteria

[0165]

◎ (very good): friction coefficient is 0.12 or less (extremely preferable as lubricating treatment (equivalent to Fe-Zn outer plating));
○ (good): friction coefficient is over 0.12 and 0.15 or less (preferable as lubricating treatment);
× (bad) : friction coefficient is over 0.15 (inadequate as lubricating treatment (equivalent to normal plated steel sheet)).

(2-5) Operatability

(2-5-1) Change of concentration of zinc and alkali metal in the treatment agent

[0166] As one of the evaluations of operatability, there is component maintenance in the treatment agent. This was carried out by measuring the concentration of zinc and alkali metal in the treatment agent. Specifically, when a total of 10 m^2 size of a cut galvanized steel sheet was treated with 10 L of a treatment agent in the treatment agent supply process, concentration of zinc and alkali metal in the treatment agent was measured; after that change of concentration was compared with that before the treatment. Evaluation criteria are as follows.
○ (good): concentration of alkali metal and zinc in the treatment agent increased by 2 mass % or less to initial concentration (no need for concentration adjustment);
× (bad): concentration of alkali metal and zinc in the treatment agent increased by over 2 mass % to initial concentration (concentration adjustment is necessary).

(2-5-2) Coatability

[0167] In the surface conditioning agent supply process and the pre-drying process, if condition of the surface conditioning agent is unstable, or drying is insufficient, the surface condition of the galvanized steel sheet after the post-drying process may be negatively affected. This was regarded as unevenness and it was evaluated by visual observation. Evaluation criteria are as follows.
○ (good): unevenness was observed by visual observation;

× (bad) : no unevenness was observed by visual observation.

(3) Results

[0168] Evaluation results based on the above conditions and Evaluation items are shown in Tables 10 to 12. Table 10 shows conditions of each Example, Comparative example, and Reference example. In Table 10, distinction of process is expressed by S1 process, S2 process, S3 process, and S4 process. S1 process means a surface conditioning agent supply process; S2 process means a pre-drying process; S3 process means a treatment agent supply process; and S4 process means a post-drying process. Moreover, kinds of plating are identified by abbreviated names described in Table 7; kinds of surface conditioning agent are identified by codes shown in Table 8; kinds of treatment agent are identified by Nos. shown in Table 9. Further, as Supplying method of surface conditioning agent and treatment agent, spray is identified as S, squeezing roll after spraying is identified as SR, air knife after spraying is identified as AK, and roll coater is identified as RC. Tables 11 and 12 show results of examples tested under various conditions shown in Table 10.

[0169] (Table 10)

(Table 10)

Test No.	Plating type	S1 process			S2 process	S3 process		S4 process	Notes
		Type of Surface conditioning agent	Supply		Temperature of steel sheet (˚C)	Type of Treatment agent	Supplying method	Drying	
			Method	Quantity					
1	GA	1A	S	0.1	60	-			Comparative example
2	GA	-				2D	RC	included	Comparative example
3	GA	-				2D	SR	included	Comparative example
4	GA	1A	S	0.1	-	2D	SR	included	Comparative example
5	GA	1A	RC	0.1	60	2D	RC	included	Example
6	GA	1B	RC	1	60	2D	RC	included	Example
7	GA	1C	RC	1	60	2D	RC	included	Example
8	GA	1D	RC	1	60	2D	RC	included	Example
9	GA	1E	RC	1	60	2D	RC	included	Example
10	GA	1F	RC	1	60	2D	RC	included	Example
11	GA	1G	RC	1	60	2D	RC	included	Example
12	GA	1H	RC	1	60	2D	RC	included	Reference example
13	GA	1J	RC	1	60	2D	RC	included	Example
14	GA	1K	RC	1	60	2D	RC	included	Reference example
15	GA	1L	RC	0.05	60	2D	RC	included	Example
16	GA	1M	RC	0.3	60	2D	RC	included	Example
17	GA	1P	RC	2.4	60	2D	RC	included	Example
18	GA	1Q	RC	4.7	60	2D	RC	included	Example
19	GA	1R	RC	19.3	60	2D	RC	included	Example

(continued)

Test No.	Plating type	S1 process			S2 process	S3 process		S4 process	Notes
		Type of Surface conditioning agent	Supply		Temperature of steel sheet (˚C)	Type of Treatment agent	Supplying method	Drying	
			Method	Quantity					
20	GA	1C	RC	1	60	2D	RC	included	Example
21	GA	1C	RC	1	60	2D	RC	included	Example
22	GA	1C	RC	1	60	2D	RC	included	Example
23	GA	1C	RC	1	60	2D	RC	included	Example
24	GA	1C	RC	1	60	2D	RC	included	Example
25	GA	1C	RC	1	60	2D	RC	included	Example
26	GA	1C	RC	1	60	2D	RC	included	Example
27	GA	1C	S	1	60	2D	RC	included	Example
28	GA	1C	SR	1	60	2D	RC	included	Example
29	GA	1C	AK	1	60	2D	RC	included	Example
30	GA	1C	RC	1	60	2A	RC	included	Example
31	GA	1C	RC	1	60	2B	RC	included	Example
32	GA	1C	RC	1	60	2C	RC	included	Example
33	GA	1C	RC	1	60	2E	RC	included	Example
34	GA	1C	RC	1	60	2F	RC	included	Example
35	GA	1C	RC	1	60	2G	RC	included	Example
36	GA	1C	RC	1	60	2H	RC	included	Example
37	GA	1C	RC	1	60	2J	RC	included	Example
38	GA	1C	RC	1	30	2D	RC	included	Example
39	GA	1C	RC	1	50	2D	RC	included	Example
40	GA	1C	RC	1	110	2D	RC	included	Example
41	GA	1C	RC	1	150	2D	RC	included	Example
42	GA	1C	RC	1	60	2K	RC	included	Reference example

(continued)

Test No.	Plating type	S1 process			S2 process	S3 process		S4 process	Notes
		Type of Surface conditioning agent	Supply		Temperature of steel sheet (˚C)	Type of Treatment agent	Supplying method	Drying	
			Method	Quantity					
43	GA	1C	RC	1	60	2L	RC	included	Reference example
44	GA	2 g/m^2 of 80 mass % Fe - 20 mass % Zn electroplated layer per side							Comparative example
45	GA	Remained as GA steel sheet							Comparative example
46		Remained as Cold-rolled steel sheet							Comparative example
47	GI	1D	RC	1	60	2D	RC	included	Example
48	EG	1D	RC	1	60	2D	RC	included	Reference example
49	MZ	1D	RC	1	60	2D	RC	included	Example

※ note: "Example" means an example of the present invention.

[0170] (Table 11)

(Table 11)

Test No.	Infrared absorption			P adhesion quantity	Crystalline characteristics	Lubricity	Submaterial compatibility		Notes
	P/S Integrated strength	Pa/Sa	Pb/Sb				Vinyl chloride	Mastic	
1	-	-	-	0	×	×	Δ	×	Comparative example
2	0.3	0.5	0.5	80	×	○	×	×	Comparative example
3	0.2	0.3	0.3	80	×	○	×	×	Comparative example
4	0.7	1.3	1.2	80	○	○	Δ	Δ	Comparative example
5	1.2	2.2	2.0	80	○	○	○	○	Example
6	2.1	3.8	3.2	80	○	◎	○	○	Example
7	2.7	4.9	4.1	80	○	◎	◎	◎	Example
8	3.0	5.4	4.5	80	○	◎	◎	◎	Example
9	1.7	3.0	2.5	80	○	◎	◎	◎	Example
10	1.3	2.4	2.0	80	○	○	○	○	Example
11	1.7	3.0	2.5	80	○	○	○	○	Example
12	0.1	0.2	0.2	80	○	○	×	×	Reference example
13	1.3	2.3	1.9	80	○	○	○	○	Example
14	0.3	0.5	0.5	80	○	○	×	×	Reference example
15	1.2	1.9	1.6	80	○	○	○	△	Example
16	2.0	3.6	3.0	80	○	◎	◎	◎	Example
17	3.1	5.6	4.7	80	○	◎	◎	◎	Example
18	2.6	4.6	3.9	100	○	◎	◎	◎	Example
19	1.4	2.5	2.1	120	○	○	○	○	Example
20	1.3	2.4	2.0	20	○	△	◎	◎	Example
21	1.3	2.4	2.0	40	○	△	◎	◎	Example
22	1.9	3.5	2.9	50	○	○	◎	◎	Example
23	3.9	7.0	5.9	110	○	◎	◎	◎	Example

(continued)

Test No.	Infrared absorption			P adhesion quantity	Crystalline characteristics	Lubricity	Submaterial compatibility		Notes
	P/S Integrated strength	Pa/Sa	Pb/Sb				Vinyl chloride	Mastic	
24	4.5	8.1	6.8	150	○	◎	◎	○	Example
25	5.1	9.2	7.7	200	○	◎	○	○	Example
26	3.7	6.7	5.6	250	○	○	○	○	Example
27	1.3	2.4	2.0	80	○	◎	◎	○	Example
28	3.1	5.6	4.7	80	○	◎	◎	○	Example
29	2.3	4.1	3.4	80	○	◎	◎	○	Example
30	1.5	2.7	2.3	60	○	○	○	○	Example
31	1.7	3.0	2.5	60	○	◎	◎	○	Example
32	1.9	3.5	2.9	60	○	◎	◎	○	Example
33	1.6	2.8	2.3	60	○	◎	◎	○	Example
34	2.3	4.1	3.4	70	○	◎	◎	◎	Example
35	1.7	3.0	2.5	70	○	◎	◎	○	Example
36	1.4	2.5	2.1	70	○	◎	◎	○	Example
37	1.3	2.3	2.0	70	○	◎	○	○	Example
38	2.7	4.9	4.1	80	○	◎	◎	○	Example
39	2.5	4.5	3.8	80	○	◎	◎	◎	Example
40	2.9	5.2	4.3	80	○	◎	◎	◎	Example
41	2.5	4.5	3.8	80	○	◎	◎	◎	Example
42	0.7	1.3	1.1	80	○	Δ	Δ	×	Reference example
43	0.8	1.4	1.2	80	○	Δ	Δ	×	Reference example
44	-	-	-	-	-	◎	◎	◎	Comparative example
45	-	-	-	-	-	×	◎	◎	Comparative example
46	-	-	-	-	-	○	◎	◎	Comparative example

(continued)

Test No.	Infrared absorption			P adhesion quantity	Crystalline characteristics	Lubricity	Submaterial compatibility		Notes
	P/S Integrated strength	Pa/Sa	Pb/Sb				Vinyl chloride	Mastic	
47	2.8	4.2	4.5	80	○	◎	◎	◎	Example
48	2.6	5.5	3.6	80	○	◎	◎	◎	Reference example
49	2.4	4.8	4.2	80	○	◎	◎	◎	Example
※ note: "Example" means an example of the present invention.									

[0171] (Table 12)

(Table 12)

Test No.	Operatability		Notes
	Zn, Na Concentration increase	Coating unevenness	
1	-	○	Comparative example
2	○	○	Comparative example
3	×	○	Comparative example
4	×	×	Comparative example
5	○	○	Example
6	○	×	Example
7	○	○	Example
8	○	○	Example
9	○	○	Example
10	○	×	Example
11	○	○	Example
12	×	×	Reference example
13	○	○	Example
14	×	○	Reference example
15	○	○	Example
16	○	○	Example
17	○	○	Example
18	○	○	Example
19	○	×	Example
20	○	○	Example
21	○	○	Example
22	○	○	Example
23	○	○	Example
24	○	○	Example
25	○	○	Example
26	○	×	Example
27	×	×	Example
28	○	○	Example
29	×	○	Example
30	○	○	Example
31	○	○	Example
32	○	○	Example
33	○	○	Example
34	○	○	Example
35	○	○	Example
36	○	○	Example

(continued)

Test No.	Operatability		Notes
	Zn, Na Concentration increase	Coating unevenness	
37	○	○	Example
38	○	×	Example
39	○	○	Example
40	○	○	Example
41	○	○	Example
42	○	×	Reference example
43	○	×	Reference example
44	-	-	Comparative example
45	-	-	Comparative example
46	-	-	Comparative example
47	○	○	Example
48	○	○	Reference example
49	○	○	Example
※ note: "Example" means an example of the present invention.			

[0172] As seen from Tables 10 and 11, all the examples identified as "Example" in the column of "Notes" showed 1.2 or more of P/S, the adhesiveness at the time was preferable in both cases of vinyl chloride and Mastic-type adhesive. In test No. 15, compatibility of Mastic-type adhesive is Δ (not bad). However, among the tests wherein drying was carried out in S2 process, other Comparative examples and Reference examples, of which P/S is less than 1. 2, were evaluated as × (bad) ; therefore, it can be said that it is preferable. Also, compared with Comparative examples: test Nos. 45 to 47 which have been thought to have better adhesiveness than zinc phosphate coating, many of the galvanized steel sheets having zinc phosphate coating of the present invention show adhesiveness equivalent to the above Comparative examples. Thus, it remarkably expresses the effect of the present invention which makes it possible to obtain adhesiveness and lubricity having equivalent performance to those of conventional one with lower cost.

[0173] Comparing adhesiveness of among Examples of which P/S is 1.2 or more, the above P/S, Pa/Sa, and Pb/Sb these of which having larger value tend to show higher adhesiveness. Thus, in P-O bond, stronger vertical orientation to the surface is thought to be excellent in adhesiveness.

[0174] Test Nos. 1 to 4 are the results of examples in cases that any one of processes S1 to S4 for manufacturing the galvanized steel sheet having zinc phosphate coating are skipped. According to these, if any one of processes are skipped, adequate value of P/S cannot be obtained, adhesiveness is also unfavorable. Consequently, by having manufacturing process from the above S1 process to S4 process, it is capable to manufacture the galvanized steel sheet having zinc phosphate coating which exhibits high repeatability, as well as excellent adhesiveness and lubricity. Meanwhile, test No. 12 in which no process was skipped has only 0.1 of P/S. As pH of the surface conditioning agent is 5 or less, so as to obtain more favorable P/S, it is preferable not to skip process and preferable to control pH of the surface conditioning agent.

[0175] Table 12 shows a result of operatability. According to the table, the operatability was varied depending on surface conditioning agent applied to each process, kinds of treatment agent, and pre-and-post drying condition. So, by having manufacturing process under adequate conditions, a galvanized steel sheet having zinc phosphate coating which exhibits excellent performance in view of cost and environment can be manufactured.

[0176] The above has described the present invention associated with the most practical and preferred embodiments thereof. However, the invention is not limited to the embodiments disclosed in the specification. Thus, the invention can be appropriately varied as long as the variation is not contrary to the subject substance and conception of the invention which can be read out from the claims and the whole contents of the specification. It should be understood that a method for manufacturing hot-dip galvanized steel sheet and steel sheet with such an alternation are included in the technical scope of the invention.

Claims

1. A method for continuously manufacturing hot-dip galvanized steel sheet having zinc phosphate coating comprising the steps of:

   a surface conditioning agent supply process for supplying a surface conditioning agent to a surface of hot-dip galvanized steel sheet;
   a pre-drying process for drying said surface conditioning agent in a post-process of said surface conditioning agent supply process; and
   a treatment agent supply process for supplying a treatment agent containing zinc phosphate solution to the surface of said hot-dip galvanized steel sheet in a post-process of said pre-drying process.

2. The method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to claim 1, wherein the surface conditioning agent used in said surface conditioning agent supply process is an aqueous liquid containing zinc phosphate particles.

3. The method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to claim 2, wherein average diameter of the zinc phosphate particles contained in the surface conditioning agent of said surface conditioning agent supply process is 10 μm or less.

4. The method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to claim 2, wherein average diameter of the zinc phosphate particles contained in the surface conditioning agent of said surface conditioning agent supply process is 10 μm or less, and pH of said surface conditioning agent is 5 or more.

5. The method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to any one of claims 1 to 4, wherein the surface conditioning agent used in said surface conditioning agent supply process contains more than 0 mol/L and 0.5 mol/L or less of zinc phosphate particles, and contains a total of 0.3 mol/L or less of one element selected from a group consisting of Li, Na, K, Be, Mg, and Ca.

6. The method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to any one of claims 1 to 5, wherein the treatment agent used in said treatment agent supply process contains 0.001 to 0.7 mol/L of phosphate root and contains 0.7 or less of Zn ion in mole ratio to said phosphate root.

7. The method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to any one of claims 1 to 6, wherein zinc phosphate solution of the treatment agent used in said treatment agent supply process contains Zn ion and phosphate root, has a pH of 4 or less, and contains one element, other than said Zn ion and said phosphate root, selected from a group of strong electrolyte anion consisting of 0.2 or less of nitrate root, 0.2 or less of nitrous root, 0.1 or less of hydrofluoric root, and 0. 05 or less of sulfuric root in mole ratio to 1 mole of said phosphate root.

8. The method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to any one of claims 1 to 7, wherein phosphorus adhered to a hot-dip galvanized surface by said surface conditioning agent supply process and said treatment agent supply process is prepared to be 30 to 500 mg/m^2 in phosphorus equivalent.

9. The method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to claim 2, wherein pH of said surface conditioning agent used in said surface conditioning agent supply process is 5 or more, and average diameter of said zinc phosphate particles is 0.1 to 3 μm.

10. The method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to claim 2 or 9, wherein 0.01 to 5 mg/m^2 of said zinc phosphate particles in phosphorus equivalent is adhered to a surface of galvanized steel sheet which has come through said surface conditioning agent supply process and said pre-drying process.

11. The method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to any one of claims 2, 9, and 10, wherein the treatment agent used in said treatment agent supply process contains Zn and phosphate root, has a pH of 4 or less, and contains one element, other than said zinc and phosphate root, selected from a group of strong electrolyte anion consisting of 0.2 or less of nitrate root, 0.2 or less of nitrous root, 0.1 or less of hydrofluoric root, 0. 05 or less of sulfuric root in mole ratio to 1 mole of phosphate root.

12. The method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to any one of claims 2, and 9 to 11, wherein the method further comprising a post-drying process for drying said treatment agent after the treatment agent supply process, and
said zinc phosphate coating is adhered at an amount of 30 to 250 mg/m^2 in phosphorus equivalent after said post-drying process.

13. The method for manufacturing hot-dip galvanized steel sheet having zinc phosphate coating according to any one of claims 1 to 12, wherein either one of or both of supplying methods for said surface conditioning agent in said surface conditioning agent supply process and for said treatment agent in said treatment agent supply process is roll coating method.

14. A hot-dip galvanized steel sheet having crystalline zinc phosphate coating formed on the surface thereof manufactured in accordance with the methods described in any one of claims 9 to 13, said hot-dip galvanized steel sheet is **characterizing in that**
an absorption spectrum obtained by a reflected light of infrared light incoming from a direction at an angle of 60° to a normal line of said zinc phosphate coating surface has a plurality of absorption bands within a wavelength range of 8 to 12 μm,
further, ratio of integrated absorption strength of a p-polarized light to a s-polarized light (P/S) within said wavelength range is 1.2 or more.

15. A hot-dip galvanized steel sheet having crystalline zinc phosphate coating formed on the surface thereof manufactured in accordance with the methods described in any one of claims 9 to 13, said hot-dip galvanized steel sheet is **characterizing in that**
an absorption spectrum obtained from the reflected light of infrared light incoming from a direction at an angle of 60° to a normal line of said phosphate coating has a plurality of absorption bands within a wavelength range of 8 to 12 μm,
a p-polarized light absorbance within a wavelength of 8.4 to 9.2 μm of said absorption spectrum is twice as much as a s-polarized light absorbance, and
the p-polarized light absorbance within wavelength range of 10.2 to 11.0 μm is twice as much as the s-polarized light absorbance.

FIG. 1

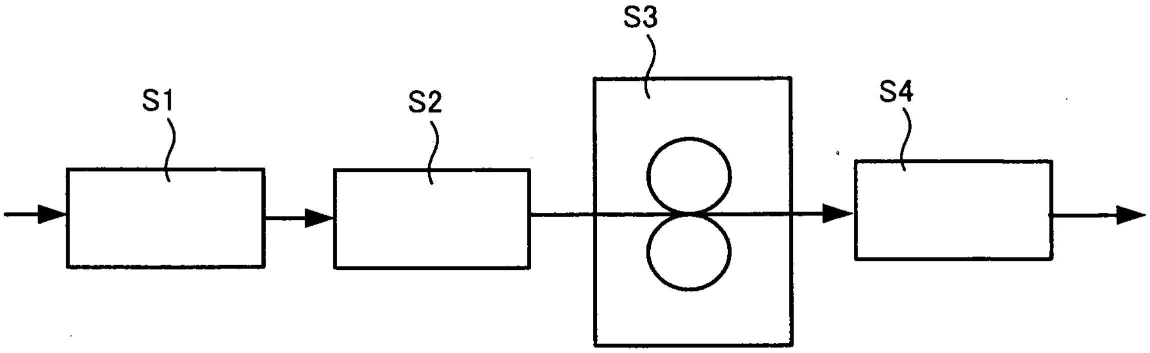


FIG. 2(a)

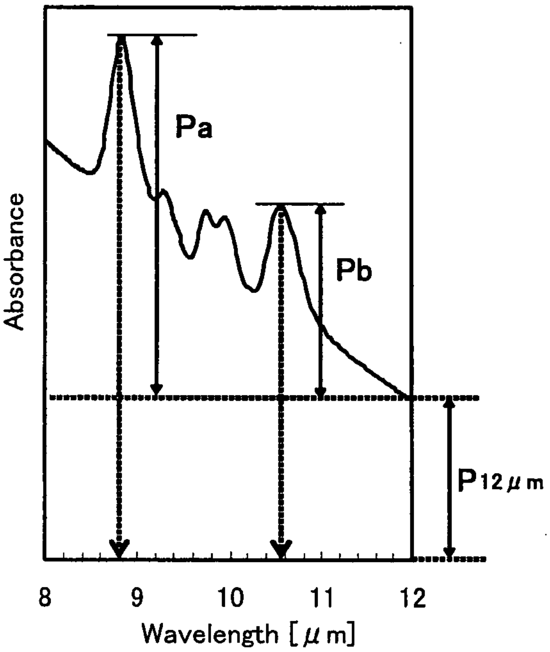

Pa
Pb
P12μm
Absorbance
8
9
10
11
12
Wavelength [μm]

FIG. 2(b)

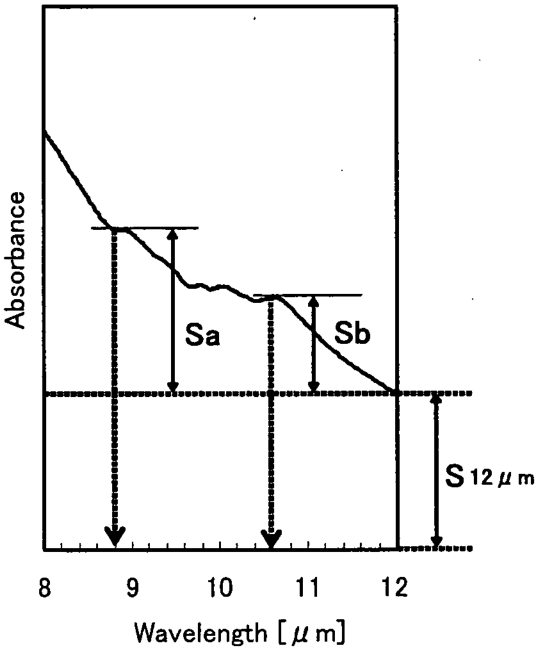

Sa
Sb
S12μm
Absorbance
8
9
10
11
12
Wavelength [μm]

FIG. 3

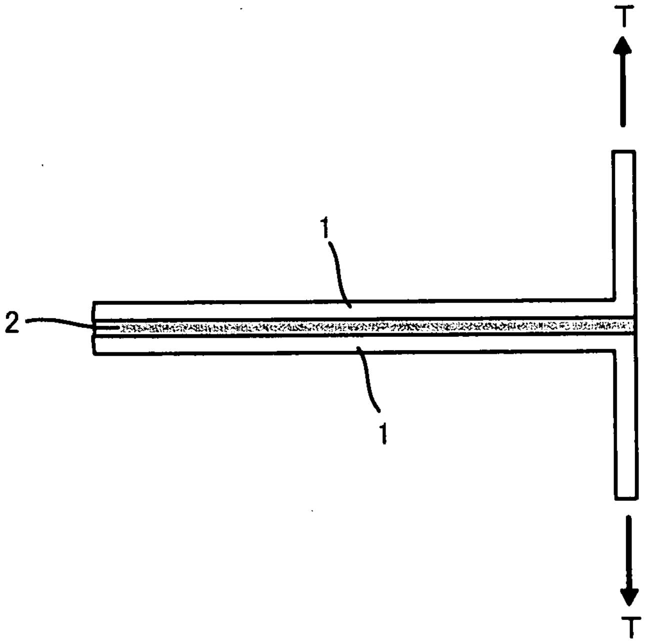
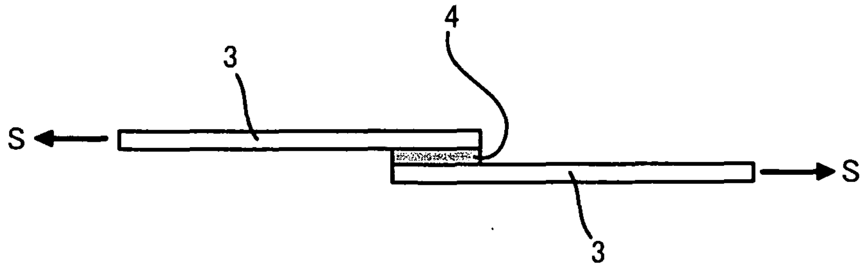


FIG. 4



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/050650

A. CLASSIFICATION OF SUBJECT MATTER
C23C22/12(2006.01)i, *C23C22/78*(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)
C23C22/12, C23C22/78

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	1996-2007
Kokai Jitsuyo Shinan Koho	1971-2007	Toroku Jitsuyo Shinan Koho	1994-2007

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.
X A	JP 2004-68149 A (Nippon Paint Co., Ltd.), 04 March, 2004 (04.03.04), Claims 1 to 4; Par. Nos. [0012] to [0017], [0043] to [0044], [0056] to [0057] & EP 1378586 A1 & US 2004011429 A1 & CN 1470672 A & KR 2003096065 A	1-13 14,15
A	JP 2003-171779 A (Nisshin Steel Co., Ltd.), 20 June, 2003 (20.06.03), Par. No. [0012] (Family: none)	1-15
A	JP 2001-64781 A (Kansai Paint Co., Ltd.), 13 March, 2001 (13.03.01), Claim 1 (Family: none)	1-15

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search 12 March, 2007 (12.03.07)	Date of mailing of the international search report 20 March, 2007 (20.03.07)
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/050650

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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