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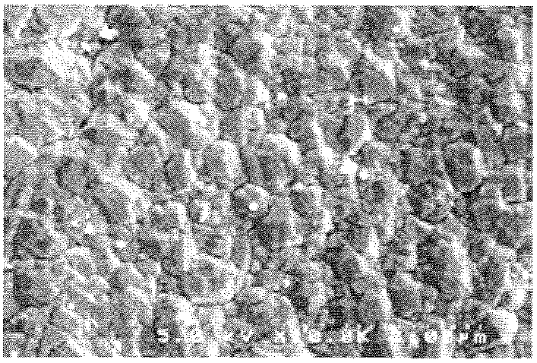
(54) STEEL SHEET FOR FUEL TANKS AND PROCESS FOR MANUFATURING THE SHEET

(57) A steel sheet for fuel tanks includes a Zn-Ni alloy electroplating layer disposed on at least one surface thereof and a chromate coating disposed on the alloy electroplating layer. The change in amount of chromium in the chromate coating immersed in boiling water for 30 minutes is 2% or less of the amount of chromium in the chromate coating not immersed in boiling water. An L-value indicating the color tone of the steel sheet is 55 or more. The difference between the maximum and minimum of the L-value is three or less. The chromating solution can be obtained in such a manner that a chromating solution is applied onto the alloy electroplating layer and then heated. The chromating solution contains chromic acid having a mass ratio (trivalent chromium) / (total chromium) of greater than 0.5, phosphoric acid having a mass ratio (phosphoric acid) / (total chromium) of 0.1 to 5.0, and an organic reducing agent. The steel sheet has a good appearance and excellent long-term corrosion resistance to fuels such as gasoline, alcohols, and alcohol-blended gasoline.

FIG. 1



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Description

Technical Field

[0001] The present invention generally relates to steel sheets for fuel tanks. The present invention particularly relates to a steel sheet for fuel tanks used in environments containing gasoline containing a small amount of water or environments, such as environments where formic acid is produced due to the degradation of gasoline, containing highly metal-corrosive organic acids and also relates to a method of producing the steel sheet.

Background Art

[0002] Conventional gasoline tanks for automobiles or motorcycles have been usually produced from steel sheets plated with a tin (Sn)-lead (Pb) alloy containing 20 mass percent or less lead (Pb) as disclosed in, for example, Japanese Examined Patent Application Publication No. 57-61833 or multilayer plated steel sheets including a nickel (Ni) electroplating layer and a Sn-Pb alloy layer formed thereon by hot dipping.

[0003] The Sn-Pb alloy-plated steel sheets have excellent workability and excellent resistance to chemicals such as gasoline. However, the plating layers are soft and vulnerable and have no galvanic action on iron (Fe) because the plating layers are electrochemically nobler than Fe. Therefore, in the case where gasoline tanks made from the Sn-Pb alloy-plated steel sheets are used in environments containing water, the presence of defects such as pinholes or cracks causes a problem in that gasoline leaks through holes pitted in the sheets and/or combustion filters are clogged with red rust caused by corrosion.

[0004] In consideration of the deterioration of petroleum situation, the following substances are used as automobile fuels in some cases: an alcohol such as methyl alcohol, ethyl alcohol, or methyl-t-butyl ether; derivatives (hereinafter also referred to as alcohols) thereof; and mixtures of the alcohols and gasoline. The Sn-Pb alloy-plated steel sheets are readily corroded with water contained in the alcohols; alcohol oxides, such as formaldehyde, acetaldehyde, formic acid, and acetic acid; and impurities and therefore are unsuitable for tanks for such fuels.

[0005] After the Sn-Pb alloy-plated steel sheets are pressed, the Sn-Pb alloy-plated steel sheets may be locally reduced in corrosion resistance because of plating stripping or galling even if the Sn-Pb alloy-plated steel sheets are painted, because the plating layers have no galvanic action on Fe. In the Sn-Pb alloy-plated steel sheets, the secondary adhesion between the plating layers and paint layers is small. Therefore, the paint layers may be stripped off by, for example, the impact caused by stones hitting fuel tanks of running motorcycles. This causes red rusts or paint blisters.

[0006] On the other hand, in view of environmental issues, the use of harmful substances such as Pb and hexavalent chromium (Cr) tends to be avoided. Japanese Unexamined Patent Application Publication No. 2005-290556 discloses a chromated steel sheet which is a Pb-free steel sheet for fuel tanks and in which the dissolution of hexavalent Cr is inhibited.

[0007] This steel sheet includes a Zn-Ni alloy electroplating layer disposed on at least one surface thereof and a chromate coating disposed on the electroplating layer. The electroplating layer contains five to 30 mass percent Ni and the amount of the electroplating layer per single surface is 1 to 40 g/m^2. The change in amount of chromium in the chromate coating immersed in boiling water for 30 minutes is 2% or less of the amount of chromium in the chromate coating not immersed in boiling water. The chromate coating is obtained in such a manner that a chromating solution is applied onto the electroplating layer and then heated. The chromating solution contains chromic acid having a mass ratio (trivalent chromium) / (total chromium) of greater than 0.5, phosphoric acid having a mass ratio (phosphoric acid) / (total chromium) of 0.1 to 5.0, and an organic reducing agent.

[0008] In this steel sheet, the chromate coating exhibits an interference color. This steel sheet has surface portions having different color tones and is inferior in appearance.

[0009] It is an object of the present invention to provide a steel sheet for fuel tanks and to provide a method of producing the steel sheet. The steel sheet is free from lead and has a good appearance and excellent long-term corrosion resistance to fuels such as gasoline, alcohols, and alcohol-blended gasoline.

Disclosure of Invention

[0010] The scope of the present invention is as described below.

> [1] A steel sheet for fuel tanks includes a Zn-Ni alloy electroplating layer disposed on at least one surface of a steel sheet and a chromate coating disposed on the alloy electroplating layer. The change in amount of chromium in the chromate coating immersed in boiling water for 30 minutes is 2% or less of the amount of chromium in the chromate coating not immersed in boiling water. An L-value indicating the color tone of the steel sheet is 55 or more. The difference between the maximum and minimum of the L-value is four or less.

[2] In the steel sheet for fuel tanks specified in Item [1], the alloy electroplating layer includes a Zn oxide sub-layer which is located at the top thereof and which has a thickness of 20 nm or less and a P content of one atomic percent or less.

[3] In the steel sheet for fuel tanks specified in Item [1] or [2], the alloy electroplating layer has a surface with an average grain size of 0.8 μm or more.

[4] A method of producing a steel sheet for fuel tanks includes forming a Zn-Ni alloy electroplating layer on at least one surface of a steel sheet, applying a chromating solution onto the alloy electroplating layer, and then heating the chromating solution. The alloy electroplating layer includes a Zn oxide sub-layer which is located at the top thereof and which has a thickness of 20 nm or less and a P content of one atomic percent or less. The chromating solution contains chromic acid having a mass ratio (trivalent chromium) / (total chromium) of greater than 0.5, phosphoric acid having a mass ratio (phosphoric acid) / (total chromium) of 0.1 to 5.0, and an organic reducing agent.

[5] A method of producing a steel sheet for fuel tanks includes forming a Zn-Ni alloy electroplating layer on at least one surface of a steel sheet, applying a chromating solution onto the alloy electroplating layer, and then heating the chromating solution. The alloy electroplating layer has a surface with an average grain size of 0.8 μm or more. The chromating solution contains chromic acid having a mass ratio (trivalent chromium) / (total chromium) of greater than 0.5, phosphoric acid having a mass ratio (phosphoric acid) / (total chromium) of 0.1 to 5.0, and an organic reducing agent.

Brief Description of Drawings

[0011]

Fig. 1 is a photograph of a surface of a Zn-Ni alloy electroplating layer having a plating grain size of 1.0 μm (Example 1).

Fig. 2 is a photograph of a surface of a Zn-Ni alloy electroplating layer having a plating grain size of 0.3 μm (Example 1).

Best Modes for Carrying Out the Invention

[0012] In order to prevent Zn-plated steel sheets from rusting, a technique for forming a chromate coating on a plating layer by chromating has been widely used. The inventors have studied that Zn-plated steel sheets including chromate coatings formed as described above are used for fuel tanks. As a result, the inventors have obtained findings below.

(A) Among Zn-plated steel sheets, a Zn-Ni alloy-electroplated steel sheet has excellent corrosion resistance to fuels such as gasoline, alcohols, and alcohol blended gasoline.

(B) A chromate coating is capable of securely preventing the dissolution of Cr even if the chromate coating is used in environments containing gasoline containing a small amount of water or environments, such as environments where formic acid is produced due to the degradation of gasoline, containing highly metal-corrosive organic acids. The change in amount of chromium in the chromate coating immersed in boiling water for 30 minutes is 2% or less of the amount of chromium in the chromate coating not immersed in boiling water.

(C) A steel sheet can be prevented from being deteriorated in appearance by defining an L-value indicating a color tone and the difference between the maximum and minimum of the L-value, the L-value being an index used to evaluate the degree of the surface unevenness of steel sheets.

(D) In order to adjust the L-value of a steel sheet to a predetermined value or less and in order to adjust the difference between the maximum and minimum of the L-value thereof to a predetermined value or less, it is preferred that a Zn-Ni alloy plating layer includes a Zn oxide sub-layer which is located at the top thereof and which has a thickness of 20 nm or less and a P content of one atomic percent or less.

(E) In order to adjust the L-value of a steel sheet to a predetermined value or less and in order to adjust the difference between the maximum and minimum of the L-value thereof to a predetermined value or less, it is preferred that after a Zn-Ni alloy electroplating layer is formed such that the average grain size of a Zn-Ni alloy is 0.8 μm or more, a predetermined chromate coating is formed.

[0013] The present invention has been made on the basis of the above findings. The present invention will now be described in detail.

1) Zn-Ni alloy electroplating layer

[0014] A Zn-Ni alloy electroplating layer is effectively prevented from being corroded due to water, alcohol oxides such as formaldehyde, acetaldehyde, formic acid, and/or acetic acid, and impurities contained in fuels, such as alcohols and alcohol-blended gasoline, different from conventional gasoline. Therefore, at least one surface of a steel sheet that contacts a fuel needs to include the Zn-Ni alloy electroplating layer.

[0015] The Zn-Ni alloy electroplating layer is not particularly limited and preferably contains five to 30 mass percent Ni and the amount of the Zn-Ni alloy electroplating layer per single surface is 1 to 40 g/m^2.

[0016] When the content of Ni in the plating layer is less than five mass percent, the corrosion of coating defects cannot be prevented and therefore sufficient corrosion resistance cannot be achieved in some cases. Meanwhile, when the Ni content is greater than 30 mass percent, the plating layer has high hardness and therefore cracks are formed in the plating layer during pressing to cause corrosion. Therefore, the Ni content of the plating layer is preferably five to 30 mass percent. When the amount of the plating layer per single surface is less than 1 g/m^2, sufficient corrosion resistance cannot be achieved in some cases. Meanwhile, when the amount thereof is greater than 40 g/m^2, press workability may be reduced. Therefore, the amount of the plating layer per single surface is preferably 1 to 40 g/m^2.

[0017] The Zn-Ni alloy electroplating layer preferably includes a Zn oxide sub-layer which is located at the top thereof and which has a thickness of 20 nm or less and a P content of one atomic percent or less. This allows the appearance of the Zn-Ni alloy electroplating layer subjected to chromating to be maintained stable.

[0018] In the present invention, an L-value indicating the color tone of the steel sheet is 55 or more and the difference between the maximum and minimum of the L-value is four or less. In order to meet these requirements, the Zn-Ni alloy electroplating layer preferably has such surface conditions that the thickness of the Zn oxide sub-layer is 20 nm or less and the P content of the Zn oxide sub-layer is one atomic percent or less. When the thickness of the oxide sub-layer is greater than 20 nm and the P content of the oxide sub-layer is greater than one atomic percent, the interference of light is likely to occur because the plating layer has a blackish tone and extremely fine irregularities are formed on plating crystals, so that the scattering of light is prevented. The oxide layer preferably has a thickness less than 20 nm.

[0019] In order to adjust the thickness of the Zn oxide sub-layer of the Zn-Ni alloy electroplating layer to 20 nm or less, the time from Zn-Ni electroplating to chromating is preferably 120 hours or less. This is because when the time therefrom is greater than 120 hours, the thickness of the oxide layer exceeds 20 nm and therefore the plating layer has a blackish tone, resulting in an increase in difference between color tones.

[0020] The thickness of a layer of an oxide or a hydroxide can be determined by a combination of Auger electron spectroscopy (AES) and Ar ion sputtering. After the layer is sputtered to a predetermined depth, the composition of a region located at the depth can be determined in such a manner that the peak intensity of each target element is corrected with a relative sensitivity factor. The content of 0 originating from the oxide or the hydroxide peaks at a certain depth (the content thereof may peak at the top of the layer) and then decreases to a constant value. The thickness of the oxide layer can be determined in such a manner that the following time is converted on the basis of the sputtering rate of a SiO_2 layer having a known thickness: the time taken to sputter the oxide layer to a portion which has an O content equal to half of the sum of the maximum O content and such a constant value and which is located under a position at which the O content peaks.

[0021] The content of P can be determined by a combination of X-ray photoelectron spectroscopy (XPS) and Ar ion sputtering. Measurement is performed in the same manner as above, whereby the concentration profile of P is determined in the depth direction. The value of the concentration of P that peaks at a depth corresponding to the thickness of the oxide layer is determined to be the P content of the oxide layer.

[0022] The Zn-Ni alloy electroplating layer preferably has a surface with an average grain size of 0.8 μm or more. This allows the appearance of the Zn-Ni alloy electroplating layer subjected to chromating to be maintained stable.

[0023] In the present invention, the L-value, which indicates the color tone of the steel sheet, is 55 or more and the difference between the maximum and minimum of the L-value is four or less. In order to meet these requirements, the Zn-Ni alloy electroplating layer preferably has such surface conditions that the thickness of the Zn oxide sub-layer is 20 nm or less and the P content of the Zn oxide sub-layer is one atomic percent or less or the Zn-Ni alloy electroplating layer surface to be coated with a chromate coating preferably has a surface with a grain size of 0.8 μm or more. When the grain size thereof is less than 0.8 μm, the interference of light is likely to occur because the plating layer has a blackish tone and the scattering of light is prevented. Meanwhile, when the grain size thereof is 0.8 μm or more, the interference of light is prevented because the plating layer has a whitish tone and the scattering of light is likely to occur.

[0024] Although the upper limit of the grain size thereof is not limited, it is probably difficult to form Zn-Ni alloy grains having a size of 2 μm or more by an electroplating process. In the electroplating process, in order to achieve a large grain size, the number of sites generating nuclei of precipitates needs to be reduced such that grains are largely grown. In order to secure this, the current density used for electroplating needs to be low. However, a reduction in current density leads to a reduction in speed of a plating line or a reduction in producibility and therefore is not preferred.

[0025] The average grain size can be determined in such a manner that a 3000-20000x magnification scanning electron micrograph of grains is observed, the number of the grains per unit area is counted, and the equivalent circle diameter of the grains is then determined.

2) Chromate coating

[0026] The change in amount of Cr in the chromate coating immersed in boiling water for 30 minutes is 2% or less of the amount of Cr in the chromate coating not immersed in boiling water as described above. The chromate coating is capable of securely preventing the dissolution of Cr even if the chromate coating is used in environments containing highly metal-corrosive organic acids; hence, the chromate coating has excellent resistance to fuels such as gasoline.

[0027] The change in amount of Cr in the chromate coating immersed in boiling water for 30 minutes can be determined by a boiling water resistance test specified in JIS K 5400-1990 8.20 in such a manner that the amount of Cr in the chromate coating not immersed in boiling water and the amount of Cr in the chromate coating immersed in boiling water for 30 minutes are measured by X-ray fluorescence spectrometry. In X-ray fluorescence spectrometry, the amount of Cr is determined from a calibration curve between the amount of Cr and the number of Cr counts determined using standard samples in which the amount of Cr is known.

[0028] The dissolution of hexavalent Cr is evaluated by a method in which the type of a liquid for dissolution, the temperature of dissolution, and the time of dissolution are defined and the concentration of Cr dissolved in the liquid is used for evaluation as specified in a Volvo Leach test (Volvo Standard News 1990.10) or a method in which the amount of Cr dissolved by alkali degreasing is used for evaluation as specified in Japanese Unexamined Patent Application Publication No. 10-46353. In the present invention, the dissolution of hexavalent Cr is evaluated from the change in amount of Cr in the chromate coating immersed in boiling water for 30 minutes. This is because the amount of dissolved Cr reaches a constant value after the chromate coating is immersed in boiling water for 30 minutes and there is a good correlation between the amount thereof and the amount of the remaining chromate coating.

[0029] In the chromate coating according to the present invention, the L-value, which indicates the color tone of the steel sheet, is 55 or more and the difference between the maximum and minimum of the L-value is four or less and preferably three or less. Chromated steel sheets, particularly steel sheets chromated with trivalent chromium, commonly exhibit an interference color. The interference color ideally depends on the thickness of an oxide coating and the equation "reflected light + transmitted light = white light (complementary)" holds. The variation of an oxide coating on a steel sheet may cause unevenness in interference color. This leads to deterioration in appearance. In the steel sheet according to the present invention, the amount of the chromate coating is preferably within a range from 10 to 50 mg/m^2 on the basis of metallic Cr and the oxide coating has a thickness sufficient to cause unevenness in interference color. Therefore, in the present invention, the L-value, which indicates the color tone of the steel sheet, is 55 or more and the difference between the maximum and minimum of the L-value is four or less and preferably three or less. An increase in L-value increases whiteness and a reduction in L-value increases blackness. Since the difference between the maximum and minimum of the L-value is four or less, the difference between color tones can be minimized and the deterioration of appearance can be prevented. The reason why the lower limit of the L-value is limited to 55 or more is that an increase in blackness increases the difference between color tones. When the L-value is less than 55, the difference between color tones is conspicuous even if the difference between the maximum and minimum of the L-value is four or less. This leads to deterioration in appearance. The L-value can be measured by a method (for example, a multi-light source spectrocolorimeter, MSC-1S-2B, manufactured by Suga Test Instruments Co. or the like) specified in JIS Z 8722.

[0030] The chromate coating is not particularly limited except that the treated chromate coating has a predetermined color tone and the amount of dissolved chromium in the treated chromate coating is within a predetermined range. The chromate coating can be formed in such a manner that, for example, a chromating solution described below is applied onto the Zn-Ni alloy electroplating layer and then heated. The amount of the chromate coating is preferably 10 to 50 mg/m^2 on the basis of metallic Cr. This is because sufficient corrosion resistance cannot be achieved when the amount thereof is less than 10 mg/m^2 and high cost is incurred when the amount thereof is greater than 50 mg/m^2.

3) Production method

[0031] A method of producing the steel sheet according to the present invention includes a step of forming the Zn-Ni alloy electroplating layer on at least one surface of the steel sheet and a step of forming the chromate coating on the alloy electroplating layer.

[0032] The producing method is not particularly limited except that the change in amount of chromium in the chromate coating immersed in boiling water for 30 minutes is 2% or less of the amount of chromium in the chromate coating not immersed in boiling water, the L-value, which indicates the color tone of the steel sheet, is 55 or more, and the difference between the maximum and minimum of the L-value is four or less.

[0033] For example, chromating for allowing the amount of dissolved chromium to be within a predetermined range can be performed in such a manner that the chromating solution is applied onto the layer and then heated. The chromating solution contains chromic acid having a mass ratio ((trivalent chromium) / (total chromium)) of trivalent chromium to total chromium of greater than 0.5, phosphoric acid having a mass ratio ((phosphoric acid) / (total chromium)) of phosphoric acid to total chromium of 0.1 to 5.0, and an organic reducing agent.

[0034] A chromate coating produced as described above has a problem in that unlike a hexavalent chromate coating, this chromate coating is unlikely to have a good appearance. In particular, a Zn-Ni plating and chromate coating treated in different lines usually have defective appearances. The inventors have made intensive investigations and have then found that a good appearance can be obtained in such a manner that a surface having no chromate coating is maintained in an appropriate condition. One way is as follows: a Zn-Ni alloy electroplating layer is formed so as to include a Zn oxide sub-layer which is located at the top thereof and which has a thickness of 20 nm or less and a P content of one atomic percent or less in advance of forming a chromate coating. It has been confirmed that such a surface condition is effective in achieving a good appearance.

[0035] Furthermore, it has been found that a good appearance can be achieved in such a manner that a Zn-Ni alloy electroplating layer is formed so as to have a surface having an average grain size of 0.8 μm and a chromate coating is then formed.

[0036] The amount of the Zn oxide sub-layer, which is located at the top of the Zn-Ni alloy electroplating layer, and the content of P in the Zn oxide sub-layer may be adjusted and/or the average grain size of the Zn-Ni alloy electroplating layer may be adjusted.

[0037] Conditions for forming the Zn-Ni alloy electroplating layer are not particularly limited. The plating layer preferably contains five to 30 mass percent and the amount of the plating layer is preferably 1 to 40 g/m^2.

[0038] It is an effective way to implement the present invention that a coater is placed in the final section of an electroplating line and chroming is performed immediately after the chromate coating is formed.

[0039] The presence of a large amount of P in the oxide layer is disadvantageous in appearance. Therefore, if degreasing and/or surface conditioning is performed in advance of chromating, it is effective that a thin degreasing or surface-conditioning solution is used or powerful cleaning is performed such that no P remains.

[0040] A technique for suppressing the content of P is not particularly limited and an ordinary technique may be used. For example, powerful cleaning is performed after degreasing or surface-conditioning or the concentration of a treating solution used is reduced.

[0041] After the Zn-Ni alloy electroplating layer is formed, the chromating solution is applied onto the Zn-Ni alloy electroplating layer. In the present invention, the chromate coating needs to be formed on the Zn-Ni alloy electroplating layer such that the change in amount of Cr in the chromate coating immersed in boiling water for 30 minutes is 2% or less. Therefore, the chromating solution, which contains chromic acid having a mass ratio ((trivalent chromium) / (total chromium))) of trivalent chromium to total chromium of greater than 0.5, phosphoric acid having a mass ratio (phosphoric acid) / (total chromium)) of phosphoric acid to total chromium of 0.1 to 5.0, and the organic reducing agent, may be applied onto the Zn-Ni alloy electroplating layer and then heated.

[0042] Hexavalent Cr contained in the chromating solution react with the organic reducing agent during heating and therefore is reduced into trivalent Cr. When the mass ratio of trivalent Cr to total Cr is 0.5 or less, the amount of hexavalent Cr is excessive and therefore hexavalent Cr remains in the chromate coating after heating. Therefore, if the chromate coating is immersed in boiling water, hexavalent Cr is dissolved; hence, the change in amount of Cr in the chromate coating immersed in boiling water for 30 minutes exceeds 2% and high corrosion resistance to fuels such as gasoline cannot be achieved. When the mass ratio of phosphoric acid to total Cr is less than 0.1, trivalent Cr is polymerized into a gel precipitate and the chromate coating cannot keep its properties. Meanwhile, when this ratio is greater than 5.0, phosphoric acid remains in the chromate coating; hence, phosphoric acid is dissolved to cause pitting and/or blackening.

[0043] The organic reducing agent, which is contained in the chromating solution, is preferably at least one selected from the group consisting of diols and sugars. Among the diols, particularly preferred is ethylene glycol, propylene glycol, trimethylene glycol, or 1,4-butan diol. Among the sugars, advantageously suitable is glycerin, polyethylene glycol, saccharose, lactose, sucrose, glucose, or fructose.

[0044] The organic reducing agent is preferably contained in the chromating solution such that the mass ratio of the organic reducing agent to total Cr is 0.1 to 0.4. This is because the chromating solution does not have a sufficient reducing effect when the mass ratio thereof is less than 0.1 and the stability of the chromating solution cannot be maintained when the mass ratio thereof is greater than 0.4. In order to enhance the stability of the chromating solution, the organic reducing agent is preferably added to the chromating solution immediately before the use of the chromating solution.

[0045] For the purpose of corrosion resistance enhancement, the chromating solution may contain an inorganic inhibitor as required. Examples of the inorganic inhibitor include inorganic colloids such as silica, ZrO_2, TiO_2, zirconium sulfate, and aluminum biphosphate and heteropoly acids such as phosphomolybdic acid, silicotungstic acid, and phosphovanadomolybdic acid. The presence of the inorganic inhibitor in the chromating solution inhibits the reaction of the organic reducing agent with hexavalent Cr and therefore promotes the dissolution of hexavalent Cr when the chromate coating is immersed in boiling water; hence, the content of the inorganic inhibitor is preferably adjusted such that the mass ratio of the inorganic inhibitor to hexavalent Cr is less than 0.05. The reason why the inorganic inhibitor decreases the rate of the reaction of the organic reducing agent with hexavalent Cr is not clear but is probably that the inorganic inhibitor is ionized in the chromating solution or interacts with hexavalent Cr after the inorganic inhibitor is dispersed in the chromating solution.

[0046] For the purpose of enhancing the reactivity of the chromating solution with the Zn-Ni alloy electroplating layer, the chromating solution may contain an acid such as fluoric acid, sulfuric acid, or hydrochloric acid.

[0047] In order to inhibit the dissolution of Cr from the chromate coating, the chromating solution may further contain a water-soluble or water-dispersible polymeric compound. Examples of the water-soluble or water-dispersible polymeric compound include polyvinyl alcohol, polyacrylic acids, polyacrylic amides, epoxy ester polymers, melamine-alkyd resins, natural polymeric compounds such as starch and casein, partial hydrolysates of alkyl silicates, partial hydrolysates of alkyl phosphates, and silanes such as silane coupling agents and epoxy silanes. The water-soluble or water-dispersible polymeric compound has a function as a protective layer which inhibits the dissolution of Cr from the chromate coating and which protects the chromate coating from external mechanical shock. The water-soluble or water-dispersible polymeric compound has terminal functional groups acting as reductants for hexavalent Cr ions. Therefore, in order to secure the stability of the chromating solution, the content of the compound is preferably adjusted such that the mass ratio of the compound to hexavalent Cr is less than 0.05.

[0048] The chromating solution is applied onto the layer and then heated. The chromating solution is preferably heated such that the temperature of the steel sheet is 120°C or higher. When the temperature thereof is lower than 120°C, the reduction of Cr does not proceed sufficiently and therefore an increased amount of Cr may be dissolved from the chromate coating when the chromate coating is immersed in boiling water.

[0049] Before the chromating solution is applied onto the layer, an aqueous solution containing a Ti colloid is applied onto the layer and then dried, whereby the dissolution of Cr from the chromate coating can be inhibited. This is probably because the Ti colloid adsorbed on the Zn-Ni alloy electroplating layer acts as a site reactive with the chromating solution, which is acidic, and therefore the reduction of hexavalent Cr into trivalent Cr is promoted during heating.

[0050] The Ti colloid-containing aqueous solution preferably has a Ti colloid concentration of 1 to 10 ppm by volume and a pH of 7.5 to 10 and is preferably applied onto the layer at a temperature of 40°C to 60°C for one to 30 seconds.

[0051] The steel sheet, according to the present invention, for fuel tanks preferably contains, for example, 0.0007% to 0.0050% C, 0.5% or less Si, 2.0% or less Mn, 0.1% or less P, 0.015% or less S, 0.01% to 0.20% Al, 0.01% or less N, 0.005% to 0.08% Ti, and 0.001% to 0.01% B on a mass basis, the remainder being Fe and unavoidable impurities. The steel sheet has excellent deep drawability.

[0052] The reason for limiting each component is described below.

C: 0.0007% to 0.0050%

[0053] C adversely affects deep drawability and therefore the content thereof is preferably 0.0050% or less. When the content thereof is less than 0.0007%, an improvement in deep drawability is not achieved and an increase in decarburization cost is caused. Therefore, the content of C is preferably 0.0007% to 0.0050%.

Si: 0.5% or less

[0054] Si has a function of enhancing the strength of steel; hence, the steel sheet may contain Si depending on desired strength. However, a Si content exceeding 0.5% causes a reduction in deep drawability; hence, the content of Si is preferably 0.5% or less.

Mn: 2.0% or less

[0055] Mn, as well as Si, has a function of enhancing the strength of steel; hence, the steel sheet may contain Mn depending on desired strength. However, when the content thereof is greater than 2.0%, a reduction in deep drawability is caused; hence, the content of Mn is preferably 2.0% or less.

P: 0.1% or less

[0056] P precipitates at grain boundaries to strengthen the grain boundaries, prevents welded portions from cracking, and has a function of enhancing the strength of steel. However, when the content thereof is greater than 0.1%, a reduction in deep drawability is caused; hence, the content of P is preferably 0.1% or less. In order to securely prevent the welded portions from cracking, the P content is more preferably 0.01% to 0.05%.

S: 0.015% or less

[0057] S adversely affects deep drawability and therefore the content thereof is preferably 0.015% or less.

Al: 0.01% to 0.20%

[0058] Al is used to deoxidize steel or to increase the yield of a carbonitride-forming element such as Ti. When the content thereof is less than 0.01%, its effect is insufficient. Meanwhile, when the content thereof is greater than 0.20%, its effect is saturated. Therefore, the content of Al is preferably 0.01% to 0.20%.

N: 0.01% or less

[0059] N adversely affects deep drawability and therefore the content thereof is preferably 0.01% or less.

Ti: 0.005% to 0.08%

[0060] Ti forms a precipitate with C or N in steel to reduce the amount of solute C or N and therefore has an effect of enhancing deep drawability. When the content thereof is less than 0.005%, its effect is small. Meanwhile, when the content thereof is greater than 0.08%, its effect is saturated. Therefore, the content of Ti is preferably 0.005% to 0.08%.

B: 0.001% to 0.01%

[0061] B, as well as P, has a function of preventing welded portions from cracking. When the content thereof is less than 0.001%, its effect is small. Meanwhile, when the content thereof is greater than 0.01%, a reduction in deep drawability is caused. Therefore, the content of B is preferably 0.001% to 0.01% and more preferably 0.001% to 0.004%.

[0062] The reason why B and P prevent the welded portions from cracking is probably as described below. The cracking of the welded portions is probably due to liquid-metal embrittlement that is caused in such a manner that Cu which is a principal component of an electrode and/or Zn which is a plating component is liquefied during welding and enters grain boundaries in steel to embrittle the grain boundaries. B and P precipitate at the grain boundaries to strengthen the grain boundaries and therefore prevent the welded portions from cracking.

[0063] The remainder is Fe and unavoidable impurities. The content of each unavoidable impurity may be within a usual range. For example, the content of O is 0.010% or less.

[0064] The steel sheet preferably further contains 0.0005% to 0.0050% Nb in addition to the above components because of the enhancement of deep drawability.

Example 1

[0065] Zn-Ni alloy electroplated steel sheets (a Ni content of 12 mass percent and an amount per single surface of 20 g/m^2) were prepared by a usual method using a hot-rolled steel sheet containing 0.0015% C, 0.01% Si, 0.08% Mn, 0.011% P, 0.008% S, 0.05% Al, 0.0019% N, 0.035% Ti, 0.003% Nb, and 0.004% B on a mass basis, the remainder being Fe and unavoidable impurities.

[0066] In this operation, a Zn-Ni alloy electroplating layer was formed on each sheet in such a manner that the density of a current used was varied and the speed of an electroplating line was varied in two levels: 90 mpm and 160 mpm. Surfaces of the Zn-Ni alloy electroplating layers had an average grain size of 1.0 or 0.3 μm. Figs. 1 and 2 show one of the electroplating layer surfaces having an average grain size of 1.0 μm and one of the electroplating layer surfaces having an average grain size of 0.3 μm, respectively. The average grain size was determined in such a manner that a 3000-20000x magnification scanning electron micrograph of grains was observed, the number of the grains per unit area was counted, and the equivalent circle diameter of the grains was then determined.

[0067] Some of the sheets were surface-conditioned in such a manner that these sheets were immersed in a hydrogen disodium phosphate solution with a pH of 10 at 50°C, whereby an acidic electroplating solution was neutralized. The resulting sheets were water-washed, whereby a surface portion of each layer was formed into a Zn oxide sub-layer containing P. The other sheets were not surface-conditioned.

[0068] The thickness of a layer of an oxide or a hydroxide can be determined by a combination of Auger electron spectroscopy (AES) and Ar ion sputtering. After the content of each element in a surface portion of the layer was measured by AES and the layer was then sputtered to a predetermined depth, the content of the element in a surface portion of the resulting layer was measured by AES. This operation was repeated, whereby the distribution of the element was measured in the depth direction of the layer.

[0069] The content of O originating from the oxide or the hydroxide peaks at a certain depth and then decreases to a constant value. The thickness of the oxide layer was determined to be the depth of a portion which had an O content equal to half of the sum of the maximum O content and the constant value and which was located under a position at which the O content peaks. For pretreatment, Ar sputtering was performed for 30 seconds, whereby a contamination layer was removed from a surface of a test specimen.

[0070] Measurement was performed by X-ray photoelectron spectroscopy (XPS) in the same manner as above, whereby the concentration profile of P was determined in the depth direction. The value of the concentration of P that peaked at a depth corresponding to the thickness of the oxide layer was determined to be the P content of the oxide layer.

[0071] The sheets were chromated immediately after plating (a lapse of ten seconds), after a lapse of 100 hours from plating, or after a lapse of 200 hours from plating in such a manner that chromating solutions shown in Table 2 were applied onto the Zn-Ni alloy electroplating layers with roll coaters. The resulting sheets were heated a temperature shown in Table 2, whereby Sample Nos. 1 to 9 having chromate coatings with a Cr amount shown in Table 2 were prepared. The term "heating temperature" herein means the maximum temperature that each steel sheet reaches. The chromated steel sheets obtained as described above were investigated for L-value, corrosion resistance to gasoline, resistance to Cr dissolution, and appearance. Measurement methods and evaluation standards are as described below. Table summarizes the obtained results.

L-value

[0072] The L-value of each sheet was measured by a method (for example, a multi-light source spectrocolorimeter, MSC-1S-2B, manufactured by Suga Test Instruments Co. or the like) specified in JIS Z 8722.

[0073] A surface of the steel sheet was measured for maximum L-value and minimum L-value and the difference therebetween was calculated.

Corrosion resistance to gasoline

[0074] A unworked sample with a size of 20 mm x 100 mm and a blanked sample with a 60-mm diameter hole were immersed in a fuel, prepared by mixing unlead gasoline and an aqueous solution with a concentration of 500 ppm by volume of formic acid together at a mass ratio of 1 : 1, for one month at room temperature and then measured for red rust area percentage. The obtained measurements were averaged. Each sheet was evaluated for corrosion resistance to gasoline on the basis of the following standards:

A: a red rust area percentage of less than 50% (a target of the present invention) and
B: a red rust area percentage of 50% or more.

Resistance to Cr dissolution

[0075] The change in amount of Cr was determined by a boiling water resistance test specified in JIS K 5400-1990 8.20 in such a manner that the amount of Cr in each chromate coating not immersed in boiling water and that of the chromate coating immersed in boiling water for 30 minutes were measured by X-ray fluorescence spectrometry. In X-ray fluorescence spectrometry, the amount of Cr is determined from a calibration curve between the amount of Cr and the number of Cr counts determined using standard samples in which the amount of Cr was known.

A: a reduction in amount of Cr of 2% or less
B: a reduction in amount of Cr of greater than 2%

Appearance

[0076] The chromated steel sheets were visually evaluated for appearance.

A: good
B: slightly uneven
C: uneven

Table 1

Coating No.	Average grain size of Zn-Ni alloy plating (µm)	Conditions of oxide layer located at top of Zn-Ni alloy plating just formed		Time from plating to chromating	Zn-Ni alloy directly before chromating	Chromating	Resistance to Cr dissolution	Gasoline resistance	L-value	Difference between maximum and minimum of L-value	Appearance	Remarks
		Thickness of oxide layer (nm)	Content of P in oxide layer (atomic percent)		Thickness of oxide layer of plating (nm)							
1	1	18	0.2	10s s	18	b	B	B	60	1.5	A	Comparative Example
2	1	18	0.2	10s s	18	a	A	A	59	2.0	A	Example
3	1	16	0.2	100 h	24	a	A	A	57	2.7	A	Example
4	1	17	0.2	200 h	30	a	A	A	56	3.5	B	Example
5	0.3	17	0.2	10s	18	a	A	A	57	2.5	A	Example
6	0.3	18	0.2	100 h	25	a	A	A	56	3.6	B	Example
7	0.3	19	0.2	200 h	32	a	A	A	49	5.5	C	Comparative Example
8	0.3	12	1.2	100 h	18	a	A	A	57	3.9	B	Example
9	0.3	12	1.2	200 h	24	a	A	A	50	5.3	C	Comparative Example

Table 2

No.	Chromating solution				Heating temperature	Target Cr amount (mg/m^2)	Resistance to Cr dissolution
	Mass ratio of trivalent Cr to total Cr	Mass ratio of phosphoric acid to total Cr	Organic reducing agent	Mass ratio of organic reducing agent to total Cr			
a	0.55	1.2	Glucose	0.4	150°C	35	A
b	0.4	0	Glucose	0.4	150°C	35	B

[0077] As is clear from above, the examples of the present invention have excellent gasoline resistance and good appearances. In contrast, the comparative examples have corrosion resistance to gasoline or an L-value outside the scope of the present invention and therefore are inferior in gasoline resistance or appearance.

[0078] That is, the examples of the present invention include chromate coatings having good appearances. The chromate coatings exhibit excellent long-term corrosion resistance to fuels such as gasoline, alcohols, and alcohol-blended gasoline and inhibit the dissolution of Cr due to boiling water immersion.

Industrial Applicability

[0079] A steel sheet according to the present invention has excellent corrosion resistance to fuels such as gasoline, alcohols, and alcohol-blended gasoline and a good appearance and therefore is suitable for, for example, fuel tanks such as gasoline tanks for automobiles or motorcycles.

Claims

1. A steel sheet for fuel tanks, comprising a Zn-Ni alloy electroplating layer disposed on at least one surface of a steel sheet and a chromate coating disposed on the alloy electroplating layer, wherein the change in amount of chromium in the chromate coating immersed in boiling water for 30 minutes is 2% or less of the amount of chromium in the chromate coating not immersed in boiling water, an L-value indicating the color tone of the steel sheet is 55 or more, and the difference between the maximum and minimum of the L-value is four or less.

2. The steel sheet for fuel tanks according to Claim 1, wherein the alloy electroplating layer includes a Zn oxide sub-layer which is located at the top thereof and which has a thickness of 20 nm or less and a P content of one atomic percent or less.

3. The steel sheet for fuel tanks according to Claim 1 or 2, wherein the alloy electroplating layer has a surface with an average grain size of 0.8 μm or more.

4. A method of producing a steel sheet for fuel tanks, comprising forming a Zn-Ni alloy electroplating layer on at least one surface of a steel sheet, applying a chromating solution onto the alloy electroplating layer, and then heating the chromating solution, wherein the alloy electroplating layer includes a Zn oxide sub-layer which is located at the top thereof and which has a thickness of 20 nm or less and a P content of one atomic percent or less and the chromating solution contains chromic acid having a mass ratio (trivalent chromium) / (total chromium) of greater than 0.5, phosphoric acid having a mass ratio (phosphoric acid) / (total chromium) of 0.1 to 5.0, and an organic reducing agent.

5. A method of producing a steel sheet for fuel tanks, comprising forming a Zn-Ni alloy electroplating layer on at least one surface of a steel sheet, applying a chromating solution onto the alloy electroplating layer, and then heating the chromating solution, wherein the alloy electroplating layer has a surface with an average grain size of 0.8 μm or more and the chromating solution contains chromic acid having a mass ratio (trivalent chromium) / (total chromium) of greater than 0.5, phosphoric acid having a mass ratio (phosphoric acid) / (total chromium) of 0.1 to 5.0, and an organic reducing agent.

FIG.1

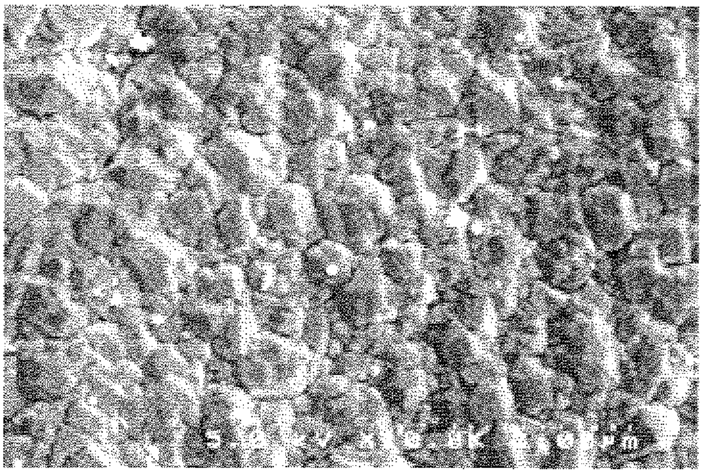
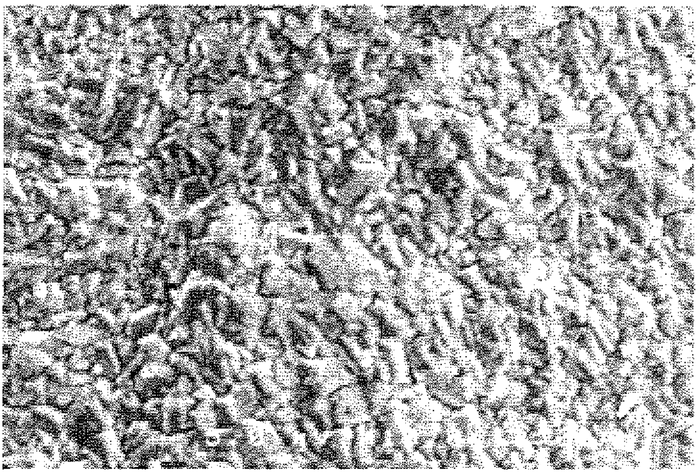


FIG.2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2008/072107

A. CLASSIFICATION OF SUBJECT MATTER
C23C28/00(2006.01)i, *C23C22/30*(2006.01)i, *C23C22/33*(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)
C23C28/00, C23C22/30, C23C22/33, C25D5/00-7/12, B32B1/00-35/00

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	1996-2008
Kokai Jitsuyo Shinan Koho	1971-2008	Toroku Jitsuyo Shinan Koho	1994-2008

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.
A	JP 2005-290556 A (JFE Steel Corp.), 20 October, 2005 (20.10.05), Full text & WO 2005/087981 A1	1-5
A	JP 07-166366 A (Kawasaki Steel Corp.), 27 June, 1995 (27.06.95), Full text (Family: none)	1-5
A	JP 05-106058 A (Kawasaki Steel Corp.), 27 April, 1993 (27.04.93), Full text (Family: none)	1-5

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"&" document member of the same patent family

Date of the actual completion of the international search 24 December, 2008 (24.12.08)	Date of mailing of the international search report 13 January, 2009 (13.01.09)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2007)

INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 09-263954 A (Kawasaki Steel Corp.), 07 October, 1997 (07.10.97), Full text (Family: none)	1-5

Form PCT/ISA/210 (continuation of second sheet) (April 2007)

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- JP 2005290556 A **[0006]**
- JP 10046353 A **[0028]**