



(11) **EP 2 806 051 A1**

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

(43) Date of publication:
26.11.2014 Bulletin 2014/48

(51) Int Cl.:
C23G 1/08 *(2006.01)* **C22C 38/00** *(2006.01)*
C22C 38/06 *(2006.01)*

(21) Application number: **13738039.0**

(86) International application number:
PCT/JP2013/050678

(22) Date of filing: **16.01.2013**

(87) International publication number:
WO 2013/108785 (25.07.2013 Gazette 2013/30)

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

(30) Priority: **18.01.2012 JP 2012007739**

(71) Applicant: **JFE Steel Corporation**
Tokyo 100-0011 (JP)

(72) Inventors:
• **MASUOKA, Hiroyuki**
Tokyo 100-0011 (JP)

- **ANDO, Satoru**
Tokyo 100-0011 (JP)
- **AIZAWA, Shigeyuki**
Tokyo 100-0011 (JP)
- **NAKAZATO, Kazuki**
Tokyo 100-0011 (JP)
- **TAIRA, Shoichiro**
Tokyo 100-0011 (JP)

(74) Representative: **Grünecker, Kinkeldey,
Stockmair & Schwanhäusser**
Leopoldstrasse 4
80802 München (DE)

(54) **METHOD FOR PREVENTING YELLOW DISCOLOURATION OF SURFACE OF ACID-CLEANED STEEL SHEET**

(57) In a method for prevention of yellowing on a surface of a steel sheet subjected to re-pickling, washing with water and drying after a surface of a continuously annealed steel sheet is pickled to remove Si-containing oxide layer from a surface layer of the steel sheet, the surface of the steel sheet is held at a wet state between the pickling and the re-pickling and between the re-pickling and the washing, and more preferably the washing

is carried out with water having an iron ion concentration decreased to not more than 20 g/L, whereby the yellowing on the surface of the steel sheet after the pickling is prevented. Thus, cold rolled steel sheets being excellent in not only the appearance quality but also the phosphatability and corrosion resistance after painting are manufactured stably.

EP 2 806 051 A1

Description

TECHNICAL FIELD

[0001] This invention relates to a technique for the prevention of yellowing on a pickled surface of a steel sheet.

BACKGROUND ART

[0002] Recently, it is strongly demanded to improve fuel consumption of an automobile from a viewpoint of protecting the global environment. Also, the improvement in the safety of the automobile is strongly demanded from a viewpoint of ensuring occupants' safety at the time of impact. In order to meet these demands, it is necessary to simultaneously attain weight saving and high strengthening of an automobile body. In this connection, thinning through the high strengthening is positively proceeding in cold rolled steel sheets as a raw material for members of the automobile. However, many members for the automobile are manufactured by shape forming of steel sheets, so that these steel sheets are required to have an excellent formability in addition to the high strength.

[0003] There are various methods for increasing the strength of the cold rolled steel sheet. As one of methods capable of attaining high strength without largely damaging the formability is mentioned a solid-solution strengthening method based on the addition of Si or Mn. However, when a greater amount of Si or Mn, particularly not less than 0.5 mass% of Si is added in the cold rolled steel sheet, it is known that Si-containing oxides such as SiO_2 , Si-Mn composite oxide and the like are formed on the surface of the steel sheet in the slab heating or in the annealing after hot rolling or cold rolling. Since the Si-containing oxide deteriorates the phosphatability remarkably, there is a problem that the high-strength cold rolled steel sheets containing a greater amount of Si are poor in not only the phosphatability but also the corrosion resistance after painting because they are liable to cause peeling of the coating as compared with ordinary steel sheets when they are exposed to severer corrosion environments such as an immersion test in hot salt water and a composite cycle corrosion test repeating wetting-drying after electrodeposition coating.

[0004] As a measure to this problem, Patent Document 1 proposes a high-strength cold rolled steel sheet wherein Si concentration is decreased on the surface of the steel sheet by heating a slab at a temperature of not lower than 1200°C in the hot rolling, descaling under a high pressure, grinding the surface of the hot rolled steel sheet with an abrasive-containing nylon brush before pickling and immersing in a 9% hydrochloric acid tank twice to conduct pickling. Also, Patent Document 2 proposes a high-strength cold rolled steel sheet having an improved corrosion resistance by making a line width of a linear Si-containing oxide, which is observed from the surface of the steel sheet to a depth of 1-10 μm thereof, to not more than 300 nm.

[0005] In the high-strength cold rolled steel sheet disclosed in Patent Document 1, however, the improvement of the corrosion resistance after painting is not obtained even if the Si concentration is decreased on the surface of the steel sheet before the cold rolling because the Si-containing oxide is formed on the surface of the steel sheet by annealing after the cold rolling. In the high-strength cold rolled steel sheet disclosed in Patent Document 2, the corrosion resistance does not come into question under corrosion environment such as salt water spraying test defined in JIS Z2371, but sufficient corrosion resistance after painting is not obtained under severer corrosion environment such as an immersion test in hot salt water or a composite cycle corrosion test. That is, high-strength cold rolled steel sheets having an excellent corrosion resistance after painting cannot be obtained only by decreasing Si concentration on the surface of the steel sheet after hot rolling or by decreasing the Si-containing linear oxide.

[0006] As a technique of solving the above problems, Patent Document 3 discloses a technique of improving the phosphatability wherein the Si-containing oxide enriched on the surface of the steel sheet at an annealing step or the like is removed by pickling and further a S-based compound is applied onto the surface to enhance reactivity with a phosphating solution. Patent Document 4 discloses a technique wherein a P-based compound is applied instead of the S-based compound in the aforementioned technique.

[0007] On the other hand, the lowering of the temperature in the phosphating solution is recently proceeding for the purpose of decreasing industrial waste (suppressing formation of sludge) and reducing the running cost, and hence the reactivity of the phosphating solution to the steel sheet largely decreases as compared with the conventional phosphate coating condition. The lowering of the temperature in the phosphating solution does not become problematic by improvement of surface adjustment technique prior to phosphating or the like in the plain steel sheets with a less alloy addition used from the past. In the high-strength cold rolled steel sheets containing a greater amount of Si, however, the reactivity with the phosphating solution is considerably deteriorated by an influence of the Si-containing oxide formed on the surface layer of the steel sheet at the annealing step, so that it is necessary to enhance the reactivity from the side of the steel sheet in some way. However, the techniques disclosed in Patent Documents 3 and 4 are effective for the conventional plain steel sheets, but have a problem that sufficient improving effects capable of coping with the lowering of the temperature in the phosphating solution cannot be expected in the high-strength cold rolled steel sheets containing a greater amount of Si.

[0008] Now, the inventors have developed a production technique of cold rolled steel sheets being excellent in not only the phosphatability but also the corrosion resistance after painting by pickling the surface of the steel sheet continuously annealed after cold rolling with a strong acid to remove the Si-containing oxide layer formed on the surface layer of the steel sheet during annealing together with iron matrix and also by removing iron-based oxide produced on the surface of the steel sheet after the above pickling through re-pickling, which was filed as Japanese Patent Application No. 2011-177861.

[0009] In the cold rolled steel sheet obtained by subjecting the continuously annealed steel sheet to pickling, re-pickling, washing with water (rinsing) and drying, however, the color in the surface of the steel sheet may be sometimes changed into yellow to considerably damage the appearance quality.

[0010] As a technique of preventing the above yellowing are made some proposals. For example, Patent Document 5 proposes a technique of preventing tarnish of a steel band by blowing a mixture of a rinsing solution containing a yellowing-control agent and a nitrogen gas to the steel band at a rinsing step for pickling treatment of pickling the steel band, and Patent Document 6 proposes a technique of preventing tarnish of a steel band by starting spray of a tarnish-preventing agent just before the stop of a line in a cleaning step of spraying the tarnish-preventing agent to the pickled steel sheet and then stopping spray of washing water and thereafter passing the sheet over a given distance and sequentially conducting stop of sheet passing and stop of spraying the tarnish-preventing agent. Furthermore, Patent Documents 7 and 8 propose a technique of preventing tarnish by conducting spray of hydrochloric acid between pickling and rinsing steps to hold pH of a liquid film on the steel sheet at a low state.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0011]

Patent Document 1: JP-A-2004-204350
 Patent Document 2: JP-A-2004-244698
 Patent Document 3: JP-A-2007-217743
 Patent Document 4: JP-A-2007-246951
 Patent Document 5: JP-A-2000-178775
 Patent Document 6: JP-A-2006-131924
 Patent Document 7: JP-A-2003-193275
 Patent Document 8: JP-A-H02-270977

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0012] However, when a strong oxidative acid such as nitric acid is used as a pickling solution even in the application of the techniques disclosed in Patent Documents 5-8, it is difficult to prevent the tarnish on the surface of the steel sheet completely. Also, in case of spraying the yellowing-preventive agent of a high concentration or hydrochloric acid, the yellowing-preventive agent or hydrochloric acid flows into subsequent rinsing step, and hence there are problems that the phosphatability is rather deteriorated and the sufficient corrosion resistance cannot be obtained under severer corrosion test after painting such as immersion test in hot salt water or composite cycle corrosion test.

[0013] The present invention is made in view of the aforementioned problems of the conventional techniques and is to propose a method wherein yellowing is prevented on the surface of the steel sheet after pickling and hence cold rolled steel sheets being excellent in not only the appearance quality but also the phosphatability and corrosion resistance after painting are manufactured stably.

MEANS FOR SOLVING PROBLEM

[0014] The inventors have made various studies on the method for preventing the yellowing on the surface of the steel sheet in order to solve the above problems. As a result, it has been found out that when cold rolled steel sheets are manufactured by pickling the surface of the steel sheet and further re-pickling it, and thereafter washing with water and drying, the surface of the steel sheet is always held at a wet state over the above whole process and more preferably concentrations of various contamination components introduced into the water used for the above washing, particularly concentration of iron ion are controlled, which are very effective for preventing the yellowing on the surface of the steel sheet, and the invention has been accomplished.

[0015] The invention proposes a method for prevention of yellowing on a surface of a steel sheet subjected to re-pickling, washing with water and drying after a surface of a continuously annealed steel sheet is pickled to remove Si-containing oxide layer from a surface layer of the steel sheet, characterized in that the surface of the steel sheet is held at a wet state between the pickling and the re-pickling and between the re-pickling and the washing.

[0016] The method for prevention of yellowing on the surface of the steel sheet according to the invention is characterized in that the washing is carried out with water having an iron ion concentration decreased to not more than 20 g/L.

[0017] In the method for prevention of yellowing on the surface of the steel sheet according to the invention, the washing water is further characterized by decreasing a concentration of nitric acid ion to not more than 10 g/L, a concentration of chloride ion to not more than 5 g/L, a concentration of fluoride ion to not more than 5 g/L and a concentration of sulfuric acid ion to not more than 5 g/L.

[0018] The method for prevention of yellowing on the surface of the steel sheet according to the invention is characterized in that the washing is conducted by immersing into water at a temperature of not lower than 20°C for not less than 3 seconds.

[0019] Also, the method for prevention of yellowing on the surface of the steel sheet according to the invention is characterized in that the re-pickling is conducted with a re-pickling solution having an iron ion concentration decreased to not more than 40 g/L.

[0020] Further, the re-pickling solution according to the invention is characterized by decreasing a concentration of nitric acid ion to not more than 20 g/L.

[0021] The method for prevention of yellowing on the surface of the steel sheet according to the invention is characterized in that the re-pickling is conducted with a non-oxidizing acid.

[0022] The non-oxidizing acid according to the invention is characterized to be any one of hydrochloric acid, sulfuric acid, phosphoric acid, pyrophosphoric acid, formic acid, acetic acid, citric acid, hydrofluoric acid, oxalic acid and a mixture of these two or more acids.

[0023] Also, the non-oxidizing acid according to the invention is characterized to be hydrochloric acid having a concentration of 0.1-50 g/L, sulfuric acid having a concentration of 0.1-150 g/L or a mixture of hydrochloric acid having a concentration of 0.1-20 g/L and sulfuric acid having a concentration of 0.1-60 g/L.

[0024] Furthermore, the method for prevention of yellowing on the surface of the steel sheet according to the invention is characterized in that the pickling is conducted with nitric acid, hydrochloric acid, hydrofluoric acid, sulfuric acid or a mixture of these two or more acids as a pickling solution.

[0025] Also, the method for prevention of yellowing on the surface of the steel sheet according to the invention is characterized in that the pickling is conducted with a mixture of nitric acid and hydrochloric acid or a mixture of nitric acid and hydrofluoric acid as a pickling solution.

[0026] The steel sheet in the method for prevention of yellowing on the surface of the steel sheet according to the invention is characterized to be a cold rolled steel sheet containing Si: 1.0-2.0 mass%.

[0027] Also, the steel sheet in the method for prevention of yellowing on the surface of the steel sheet according to the invention is further characterized to contain C: 0.01-0.20 mass%, Mn: 1.0-3.0 mass%, P: not more than 0.05 mass%, S: not more than 0.005 mass% and Al: not more than 0.06 mass% in addition to Si: 1.0-2.0 mass%.

[0028] Moreover, the steel sheet in the method for prevention of yellowing on the surface of the steel sheet according to the invention is characterized in that a content ratio (Si/Mn) of Si to Mn exceeds 0.4.

EFFECT OF THE INVENTION

[0029] According to the invention, the yellowing on the surface of the steel sheet after the pickling can be prevented, so that it is possible to stably manufacture cold rolled steel sheets being excellent in not only the appearance quality but also the phosphatability and corrosion resistance after painting.

EMBODIMENT FOR CARRYING OUT THE INVENTION

[0030] At first, a basic technical idea of the invention will be described.

[0031] Recently, high-strength cold rolled steel sheets are frequently manufactured by recrystallizing the steel sheet after cold rolling and simultaneously subjecting to finish annealing in a continuous annealing furnace for providing desirable strength and workability. In the continuous annealing furnace, a non-oxidizing or reducing gas is usually used as an atmosphere gas, so that a dew point is severely controlled. Even if the component or dew point of the atmosphere gas in the annealing is severely controlled, however, elements such as Si, Mn and the like, which are easy-oxidizable as compared with Fe, form a Si-containing oxide layer such as Si oxide (SiO_2), Si-Mn composite oxide or the like on the surface of the steel sheet. Among them, the Si-Mn composite oxide is easily dissolved in an acid, but SiO_2 is formed not only on the surface of the steel sheet but also in the inside of iron matrix because it is hardly soluble in an acid. Therefore, it is known that the latter obstructs the etching property of the steel sheet surface in the phosphating subjected

as an underground treatment for electrodeposition (phosphate treatment) and badly affects the formation of sound phosphate coating.

[0032] Now, the inventors have examined a method of improving the phosphatability of the aforementioned steel sheet and found out that it is effective to remove Si-containing oxide layer formed on the surface of the steel sheet through continuous annealing or the like together with iron matrix by pickling the surface of the cold rolled steel sheet after the continuous annealing with a strong acid such as nitric acid or the like. The term "Si-containing oxide" means SiO_2 or Si-Mn composite oxide formed on the surface of the steel sheet or along crystal grain boundaries inside the steel sheet in the annealing after slab heating or hot rolling or cold rolling. The range existing these Si-containing oxides varies depending upon the components of the steel sheet, annealing conditions (temperature, time, and atmosphere) or the like, but is said to be usually about 1 μm from the surface of the steel sheet.

[0033] Since nitric acid is strong oxidizable, however, when the pickling is carried out with nitric acid, the Si-containing oxide in the surface layer of the steel sheet can be removed, but an iron-based oxide is newly formed and deposited on the surface of the steel sheet after the pickling. As the surface coating ratio of such an iron-based oxide becomes higher, the phosphatability and the corrosion resistance after painting are rather deteriorated. The inventors developed a technique of dissolving and removing such an iron-based oxide by re-pickling with a non-oxidizing acid and filed as aforementioned Japanese Patent Application No. 2011-177861.

[0034] The phosphatability is largely improved by applying the above technique wherein the surface of the steel sheet after continuous annealing is strongly pickled with nitric acid to remove the Si-containing oxide layer existing on the surface layer and further the iron-based oxide produced by the strong pickling is removed with the non-oxidizing acid.

[0035] In the case of conducting the strong pickling as mentioned above, however, the surface of the steel sheet may be changed into yellow at moments (also referred to as "yellowing" hereinafter). Also, when the phosphatability and the corrosion resistance after painting are examined on such a yellowed steel sheet, they become clear to be largely poor as compared with the steel sheet not tarnished.

[0036] The inventors have ascertained causes of the yellowing and found that the yellowing is caused when the steel sheet taken out from a pickling tank is dried prior to the entering into a next re-pickling tank or further when the steel sheet taken out from the re-pickling tank is dried prior to the entering into a next washing tank and that once the yellowing is caused, it retains without easily removed even by the re-pickling or washing with water and badly affects the subsequent phosphatability and the corrosion resistance after painting.

[0037] Now, the inventors have made further examination on the method for prevention of yellowing on the surface of the steel sheet, and found that it is necessary to always hold the surface of the steel sheet at a wet state (water wetting state) and more preferably it is important to limit the concentration of contaminant ingredient, particularly iron ion contained in water used in the washing or a re-pickling solution used in the re-pickling.

[0038] Although the causes of the yellowing become not clear sufficiently, the inventors think as follows:

In the case of the strong pickling with nitric acid, the Si-containing oxide layer is removed from the surface layer of the steel sheet, but a film of the pickling solution containing nitric acid ingredient with a strong oxidation force retains on the surface of the steel sheet until washing with water. As a result, the film of the pickling solution is dried on the surface of the steel sheet during the drying process to concentrate the pickling solution, and iron dissolving reaction is continuously proceeding in the film of the pickling solution to simultaneously generate iron ion (Fe^{2+} , Fe^{3+} or the like) and hydrogen to thereby raise pH, and hence the iron ion is deposited on the surface of the steel sheet as an iron-based hydroxide. Also, since a greater amount of the iron ion produced in the pickling solution through pickling is introduced at a state of attaching to the steel sheet into the washing water or the re-pickling solution and present therein, it is also deposited on the surface of the steel sheet as an iron-based hydroxide. Further, nitric acid ion, fluoride ion and the like introduced by the same pickling solution are included in the washing water or the re-pickling solution. If the concentration of these ions is high, iron dissolving reaction is proceeding on the surface of the steel sheet to produce iron ion, which further increases the iron-based hydroxide. The iron-based hydroxide is removed by subsequent washing with water as it is at a water wetting state. However, if the iron-based hydroxide is adhered to the surface of the steel sheet as an iron-based oxide by taking out water molecule from the hydroxide once the surface of the steel sheet is dried, such an oxide cannot be easily removed by subsequent washing or re-pickling and is thought to cause the yellowing on the surface of the steel sheet.

[0039] The steel sheet prior to the pickling according to the invention is a steel sheet continuously annealed after cold rolling, which is preferable to have the following chemical composition.

Si: 1.0-2.0 mass%

[0040] Si is an element effective for attaining the increase of the strength in steel because it is large in the solid-solution strengthening capacity and increases the strength of the steel without largely damaging the workability. When it is added

as a way for attaining high strength, the addition of not less than 1.0 mass% is preferable. Si is also an element badly exerting on the phosphatability and the corrosion resistance after painting, but when it is less than 1.0 mass%, the influence due to the deterioration of phosphating conditions is small. Also, when the addition amount of Si is not more than 2.0 mass%, the bad influence upon the productivity due to the deterioration of the hot rolling or cold rolling property is small, and there is no deterioration of the ductility in a steel sheet product. Therefore, the addition of Si is preferably within a range of 1.0-2.0 mass%, more preferably within a range of 1.0-1.6 mass%.

[0041] Also, the steel sheet of the invention is preferable to have the following chemical composition in addition to Si when it is applied to a high-strength cold rolled steel sheet used in an automobile body and having a tensile strength TS of not less than 590 MPa.

C: 0.01-0.20 mass%

[0042] C is an element effective for increasing the strength of steel and is further effective for producing residual austenite having a TRIP (Transformation induced plasticity) effect, or bainite and martensite. When C is not less than 0.01 mass%, the above effect is obtained. Also, when C is not more than 0.20 mass%, there is caused no deterioration of the weldability. Therefore, C is added preferably within a range of 0.01-0.20 mass%, more preferably within a range of 0.10-0.20 mass%.

Mn: 1.0-3.0 mass%

[0043] Mn is an element for solid-solution strengthening the steel to increase the strength and enhance the hardenability and having an action promoting the formation of residual austenite or bainite and martensite. Such effects are developed by the addition of not less than 1.0 mass%. On the other hand, when Mn is not more than 3.0 mass%, the effects can be obtained without increasing the cost. Therefore, Mn is added preferably within a range of 1.0-3.0 mass%, more preferably within a range of 1.0-2.8 mass%.

P: not more than 0.05 mass%

[0044] P is an element not damaging the drawability though the solid-solution strengthening capacity is large, and is also an element effective for attaining the high strength. Therefore, it is preferable to be included in an amount of not less than 0.005 mass%. Although P is an element damaging the spot weldability, there is caused no problem when it is not more than 0.05 mass%. Therefore, P is preferably not more than 0.05 mass%, more preferably not more than 0.03 mass%.

S: not more than 0.005 mass%

[0045] Si is an impurity element inevitably incorporated into steel, and is a harmful ingredient precipitating as MnS to deteriorate the elongation and flange formability of the steel sheet. In order not to deteriorate the elongation and flange formability, S is preferable to be limited to not more than 0.005 mass%. More preferably, it is not more than 0.003 mass%.

Al: not more than 0.06 mass%

[0046] Al is an element added as a deoxidizer at a steel-making step, and is also an element effective for separating a non-metal inclusion, which degrades the elongation and flange formability, as a slug. Therefore, it is preferable to be included in an amount of not less than 0.01 mass%. On the other hand, when the addition amount of Al is not more than 0.06 mass%, the above effect can be obtained without bringing about the increase of the raw material cost, so that the upper limit is preferable to be 0.06 mass%. More preferably, it is a range of 0.02-0.04 mass%.

Si/Mn: more than 0.4

[0047] In the steel sheet of the invention, it is preferable that a content ratio of Si to Mn (Si/Mn) is more than 0.4. When (Si/Mn) exceeds 0.4, the high strength of not less than 590 MPa and the excellent workability can be easily established simultaneously. More preferably, it is more than 0.6.

[0048] The remainder other than the above components in the steel sheet of the invention is Fe and inevitable impurities. However, the other components may be added when they are included in the chemical composition of the usual cold rolled steel sheet and within a range not damaging the action and effect of the invention.

[0049] The production method of the cold rolled steel sheet according to the invention will be described below.

[0050] The production method of the cold rolled steel sheet according to the invention comprises the steps of heating

a steel raw material (slab) containing components such as Si, Mn and the like, which are easily oxidizable as compared with Fe, hot rolling, hot band annealing after hot rolling, if necessary, pickling, cold rolling, continuously annealing to provide desired strength and workability, pickling with a strongly oxidizable acid such as nitric acid or the like as a pickling solution to remove Si-containing oxide layer on a surface layer of a steel sheet together with iron matrix, re-pickling with a non-oxidizing acid to remove an iron-based oxide formed on the surface of the steel sheet through the above pickling, washing with water to remove the pickling solution or re-pickling solution adhered to the surface of the steel sheet and reaction products produced by the pickling or re-pickling, and then drying.

[0051] In the above production method, the procedure up to the continuous annealing step may be conducted according to the conventionally known usual manner and is not particularly limited. However, the subsequent pickling and later steps are preferable to be carried out under conditions mentioned below. In the invention, it is particularly important that the surface of the steel sheet is always kept at a wet state (water wetting state) without drying over a period from the pickling to the re-pickling and a period from the re-pickling to the washing with water and more preferably that the concentration of iron ion in water used for the washing and the re-pickling solution used for the re-pickling is reduced to not more than a given value.

[0052] Next, the conditions of the pickling and subsequent steps will be described concretely.

<Pickling>

[0053] On the surface layer of the steel sheet after the continuous annealing containing more than 0.5 mass% of easy-oxidizing components such as Si, Mn and the like are formed a greater amount of Si-containing oxides such as SiO_2 , Si-Mn based composite oxide and the like, so that the phosphatability and the corrosion resistance after painting are considerably deteriorated. Therefore, it is necessary that the Si-containing oxides in the surface layer of the steel sheet after the continuous annealing are removed by pickling with any acid such as nitric acid, hydrochloric acid, hydrofluoric acid, sulfuric acid or a mixture of these acids.

[0054] Since SiO_2 is hardly soluble in the acid, in order to remove it through pickling, it is desirable to remove together with iron matrix of the steel sheet with a strong acid such as nitric acid or hydrofluoric acid. However, since nitric acid is strong-oxidizable, Fe eluted by pickling is oxidized to produce iron-based oxide covering the surface of the steel sheet, which adversely exerts on the subsequent phosphatability and the corrosion resistance after painting. In case of using nitric acid, therefore, the concentration of nitric acid is preferable to be a range of 100-200 g/L for suppressing the above adverse effect. When it is not less than 100 g/L, the pickling force is sufficient. While when it is not more than 200 g/L, the amount of the iron-based oxide formed does not increase. More preferably, it is a range of 110-150 g/L.

[0055] However, when the concentration of nitric acid is merely limited to the above range, it is difficult to suppress the formation of the iron-based oxide produced on the surface of the steel sheet. In order to more surely suppress the formation of the iron-based oxide on the surface of the steel sheet after the pickling, it is preferable to conduct the pickling with such a mixed acid that a concentration ratio R of hydrochloric acid having an effect of breaking an oxide film to nitric acid (HCl/HNO_3) is within a range of 0.01-0.25 in addition to the limitation of nitric acid concentration to the aforementioned range. When the ratio R is not less than 0.01, the effect of suppressing the formation of the iron-based oxide is obtained sufficiently. While, when it is not more than 0.25, the dissolving amount of the steel sheet does not decrease and the Si-containing oxide layer can be removed easily.

[0056] Alternatively, when hydrofluoric acid is used instead of the mixed acid of nitric acid and hydrochloric acid, the concentration is preferable to be a range of 30-70 g/L. Further, in case of using a mixed acid of nitric acid and hydrofluoric acid, it is preferable to conduct the pickling with such a mixed acid that the concentration ratio R (HF/HNO_3) to nitric acid is within a range of 0.01-0.25. When the ratio R is not less than 0.01, the effect of suppressing the formation of the iron-based oxide is obtained sufficiently. While, when it is not more than 0.25, the dissolving amount of the steel sheet does not decrease and the Si-containing oxide layer can be removed easily.

[0057] Moreover, the pickling is preferably conducted under conditions that a temperature of the pickling solution is 20-70°C and a pickling time is 3-30 seconds even in the use of any pickling solutions. Particularly, it is preferable to use a mixed acid of nitric acid and hydrochloric acid or a mixed acid of nitric acid and hydrofluoric acid because the excellent effect of suppressing the formation of the iron-based oxide and the effect of removing the Si-containing oxide layer are obtained. It is more preferable to use a mixed acid of nitric acid and hydrochloric acid.

<Re-pickling>

[0058] In the steel sheet after the pickling, it is necessary to conduct re-pickling for subsequently dissolving and removing the iron-based oxide produced on the surface of the steel sheet through the pickling. As an acid used in the re-pickling, it is preferable to use a non-oxidizing acid, particularly any one of hydrochloric acid, sulfuric acid, phosphoric acid, pyrophosphoric acid, formic acid, acetic acid, citric acid, hydrofluoric acid, oxalic acid and a mixed acid of two or more. For example, when hydrochloric acid is used as an acid for re-pickling, the concentration of hydrochloric acid is

preferably 0.1-50 g/L. Also, when sulfuric acid is used, the concentration of sulfuric acid is preferably 0.1-150 g/L, while when the mixed acid of hydrochloric acid and sulfuric acid is used in the re-pickling, it is preferable that the concentration of hydrochloric acid in the mixed acid is 0.1-20 g/L and the concentration of sulfuric acid is 0.1-60 g/L. Further, in case of using phosphoric acid, pyrophosphoric acid, formic acid, acetic acid, citric acid, hydrofluoric acid or oxalic acid, it is preferable that the concentration is 0.1-130 g/L in phosphoric acid, 0.1-240 g/L in pyrophosphoric acid, 0.1-60 g/L in formic acid, 0.1-80 g/L in acetic acid, 0.1-260 g/L in citric acid, 0.1-30 g/L in hydrofluoric acid and 0.1-120 g/L in oxalic acid, respectively.

[0059] Moreover, the re-pickling is preferable to be conducted under conditions that the temperature of the re-pickling solution is 20-70°C and the treating time is 1-30 seconds even in the use of any re-pickling solutions.

<Washing with water, Drying>

[0060] The steel sheet after the re-pickling is subsequently subjected to a step of washing with water by immersing in the washing water or by spraying or brushing the washing water to remove the pickling solution or re-pickling solution adhered to the surface of the steel sheet and the reaction product produced on the surface of the steel sheet through the pickling or re-pickling, and then rapidly dried so as not to cause drying unevenness to thereby provide a product sheet.

<Keep wet>

[0061] In the production procedure of the invention comprising the above pickling, re-pickling, washing and drying steps, it is important that the surface of the steel sheet is necessary to be always kept at a wet state (water wetting state) without drying the surface of the steel sheet over a period from the completion of the pickling to the start of the subsequent re-pickling step and over a period from the completion of the re-pickling to the start of the subsequent washing step for preventing yellowing of the steel sheet. On the surface of the steel sheet after the pickling and the re-pickling is existent the iron-based oxide produced by pickling, while greater amounts of iron ion included in the pickling solution or the re-pickling solution or iron ion generated by dissolution reaction of nitric acid ion or the like adhered to the surface of the steel sheet is adhered as an iron-based hydroxide. These iron-based oxide and iron-based hydroxide are modified upon drying to cause yellowing.

[0062] Moreover, the method of keeping the surface of the steel sheet at the wet state is not particularly limited. For example, a method of spraying or mist-spraying water onto the surface of the steel sheet, a method of increasing humidity to suppress drying, or the like can be carried out between the pickling and the re-pickling and between the re-pickling and the washing with water. Moreover, water to be sprayed onto the surface of the steel sheet is preferable to be fresh water. Especially, fresh water with pH ≥ 6 is preferable between the re-pickling and the washing with water, and fresh water with pH: 6-7 is further preferable. However, the re-pickling solution may be used between the pickling and the re-pickling.

<Washing water, re-pickling solution>

[0063] By always keeping the surface of the steel sheet at the wet state as mentioned above can be prevented the yellowing caused due to the modification of the iron-based oxide or iron-based hydroxide adhered to the surface of the steel sheet to a certain extent. However, the iron-based hydroxide causing the yellowing is not reduced, so that the sufficient effect may not be obtained. In the invention, therefore, it is preferable that the concentration of iron ion included in water used in the washing is limited to not more than 20 g/L in order to prevent the adhesion of iron ion causing the iron-based hydroxide onto the surface of the steel sheet. More preferably, it is not more than 10 g/L.

[0064] In addition to the iron ion, the washing water contains a greater amount of nitric acid ion, chloride ion, hydrofluoric acid ion, sulfuric acid ion and the like, which are introduced from the pickling solution or re-pickling solution into the steel sheet. There is a fear that when these ions adhere to the surface of the steel sheet, they dissolve iron matrix to increase the concentration of iron ion on the surface of the steel sheet and hence the iron-based hydroxide is produced and deposited onto the surface of the steel sheet. Therefore, it is desirable to reduce the concentration of these ions. Concretely, it is preferable to limit the concentration to nitric acid ion: not more than 10 g/L, chloride ion: not more than 5 g/L, fluoride ion: not more than 5 g/L and sulfuric acid ion: not more than 5 g/L, respectively. More preferably, it is nitric acid ion: not more than 5 g/L, chloride ion: 2.5 g/L, fluoride ion: not more than 2.5 g/L and sulfuric acid ion: not more than 2.5 g/L.

[0065] Moreover, the aforementioned iron ion, nitric acid ion and the like in the washing water are mainly introduced due to adhesion of contaminant components in the re-pickling solution at the re-pickling step to the surface of the steel sheet. In order to reduce the iron ion or nitric acid ion in the washing water, therefore, it is also desirable to set an upper limit on that the concentration of iron ion or nitric acid ion in the re-pickling solution. In the invention, it is preferable to limit the concentrations of iron ion and nitric acid ion in the re-pickling solution to not more than 40 g/L and not more

than 20 g/L, respectively. More preferably, iron ion is not more than 20 g/L and nitric acid ion is not more than 10 g/L.

[0066] Moreover, it is preferable that the washing with water is conducted by immersing in water at a temperature of not lower than 20°C for 3 seconds or more. When the temperature of the washing water is not lower than 20°C and the washing time is not less than 3 seconds, the surface of the steel sheet can be washed sufficiently. On the other hand, when the temperature of the washing water is not higher than 70°C, there is no increase of energy cost. Also, when the washing time is not more than 30 seconds, it is not required to make equipment length long or slow down the sheet passing rate. More preferably, the temperature of the washing water is 30-50°C, and the immersion time is 4-20 seconds.

EXAMPLES

[0067] Steel raw materials A-F containing greater amounts of Si and Mn as shown in Table 1 are subjected to hot rolling, pickling, cold rolling and continuous annealing, and thereafter pickled, re-pickled, washed with water and dried under various conditions shown in Table 2 to provide high-strength cold rolled steel sheets having various strengths. Then, a sample is taken out from each of the above high-strength cold rolled steel sheets to evaluate the degree of yellowing on the surface of the steel sheet by the following method, while the sample is subjected to phosphating and painting treatments under the following conditions and then subjected to three corrosion tests of immersion test in hot salt water, salt water spraying test and composite cycle corrosion test to evaluate the corrosion resistance after painting.

(1) Evaluation of yellowing

[0068] A test piece of 70 mm x 150 mm is cut out from the sample of the high-strength cold rolled steel sheet and an area ratio of a yellowed portion are visually measured.

(2) Evaluation of corrosion resistance after painting

a. Phosphating conditions

[0069] Each of the test pieces used for the evaluation of the yellowing is subjected to phosphating with a degreasing agent: FC-E2011, a surface adjusting agent: PL-X and a phosphating agent: Palbond PB-L3065 made by Japan Perkalizing Co., Ltd. so that an amount of a phosphated film adhered is 1.7-3.0 g/m² under the following standard condition and comparative condition of lowering a temperature of a phosphating solution.

<Standard condition>

[0070]

- Degreasing step; treating temperature: 40°C, treating time: 120 seconds
- Spray degreasing, surface adjusting step; pH: 9.5, treating temperature: room temperature, treating time: 20 seconds
- Phosphating step; temperature of phosphating solution: 35°C, treating time: 120 seconds

<Condition of lowering temperature>

[0071] Condition of lowering the temperature of the phosphating solution in the above standard condition to 33°C

b. Corrosion test

[0072] The surface of the test piece subjected to the phosphating is subjected to electrodeposition with an electrodeposition paint V-50 made by Nippon Paint Co., Ltd. so as to provide a film thickness of 25 μm and then subjected to the following three corrosion tests.

<Immersion test in hot salt water>

[0073] After a cross cut flaw of 45 mm in length is formed on the surface of the test piece subjected to the phosphating and electrodeposition by means of a cutter, the test piece is immersed in a solution of 5 mass% NaCl (60°C) for 240 hours, washed with water and then dried and thereafter a tape peeling test of adhering an adhesive tape onto a cut flaw portion and peeling off therefrom is conducted to measure a maximum peeling full width ranging from right to left of the cut flaw portion. When the maximum peeling full width is not more than 5.0 mm, the corrosion resistance in the immersion test in hot salt water can be evaluated to be good.

<Salt water spraying test (SST)>

[0074] After a cross cut flaw of 45 mm in length is provided on the surface of the test piece subjected to the phosphating and electrodeposition by means of a cutter, the test piece is subjected to a salt water spraying test with an aqueous solution of 5 mass% NaCl for 1000 hours according to a neutral salt water spraying test defined in JIS Z2371:2000, and then a tape peeling test is conducted on the cross cut flaw portion to measure a maximum peeling full width ranging from right to left of the cut flaw portion. When the maximum peeling full width is not more than 4.0 mm, the corrosion resistance in the salt water spraying test can be evaluated to be good.

<Composite cycle corrosion test (CCT)>

[0075] After a cross cut flaw of 45 mm in length is provided on the surface of the test piece subjected to the phosphating and electrodeposition by means of a cutter, the test piece is subjected to a corrosion test of 90 cycles repeating a cycle of salt water spraying (aqueous solution of 5 mass% NaCl: 35°C, relative humidity: 98%) x 2 hours → drying (60°C, relative humidity: 30%) x 2 hours → wetting (50°C, relative humidity: 95%) x 2 hours and then washed with water and dried, and thereafter a tape peeling test is conducted on the cross cut flaw portion to measure a maximum peeling full width ranging from right to left of the cut flaw portion. When the maximum peeling full width is not more than 6.0 mm, the corrosion resistance in the composite cycle corrosion test can be evaluated to be good.

[0076] The results of the above tests are also shown in Table 2. As seen from these results, the steel sheets of the invention, which are obtained by pickling, re-pickling and washing with water under conditions adaptable for the invention after the continuous annealing, are small in not only the degree of yellowing but also the maximum peeling full width in the all of the hot salt water immersion test, salt water spraying test and composite cycle corrosion test, and indicate good corrosion resistance after painting. On the contrary, the steel sheets of the comparative examples not satisfying the pickling conditions of the invention cause yellowing or are poor in the corrosion resistance after painting.

Table 1

Steel symbol	Chemical composition (mass%)							Remarks
	C	Si	Mn	P	S	Al	Si/Mn	
A	0.04	1.4	2.2	0.025	0.003	0.04	0.64	590 grade high tensile strength
B	0.12	1.1	1.4	0.030	0.002	0.03	0.79	590 grade high tensile strength
C	0.12	1.6	1.3	0.028	0.003	0.03	1.23	590 grade high tensile strength
D	0.17	1.2	2.0	0.015	0.002	0.04	0.60	780 grade high tensile strength
E	0.18	1.5	2.6	0.010	0.003	0.03	0.58	1180 grade high tensile strength
F	0.13	1.5	2.8	0.020	0.003	0.03	0.54	1180 grade high tensile strength

Test No.	Steel symbol	Pickling conditions				Keep wet conditions				Re-pickling conditions				Keep wet conditions				Remarks		
		composition of pickling solution (g/L)	tem- per- ature (°C)	time (s)	presence or absence of keep wet	Wet solution			spray or mist	presence or absence of keep wet	composition of pickling solution (g/L)	tem- per- ature (°C)	time (s)	ion concentration (g/L)		wet solution				
						kind	tem- per- ature (°C)	pH						iron ion	nitric acid ion	kind	tem- per- ature (°C)		pH	
1	A	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.6	spray	presence	hydrochloric acid:10	45	4	5.3	3.8	spray	fresh water	25	6.9	invention Example
2	B	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.7	spray	presence	hydrochloric acid:10	45	4	4.9	3.9	spray	fresh water	25	6.8	invention Example
3	C	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.7	spray	presence	hydrochloric acid:10	45	4	5.2	4.2	spray	fresh water	25	6.9	invention Example
4	D	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.7	spray	presence	hydrochloric acid:10	45	4	5.1	4.4	spray	fresh water	25	6.9	invention Example
5	E	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	7	spray	presence	hydrochloric acid:10	45	4	4.8	4.1	spray	fresh water	25	7.1	invention Example
6	F	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.9	spray	presence	hydrochloric acid:10	45	4	5.2	3.6	spray	fresh water	25	6.8	invention Example
7	A	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.7	spray	presence	hydrochloric acid:10	45	4	4.9	25.4	spray	fresh water	25	6.7	invention Example
8	A	nitric acid:100+ hydrochloric acid:25	45	10	presence	fresh water	25	6.8	spray	presence	hydrochloric acid:10	45	4	5.1	9.5	spray	fresh water	25	6.7	invention Example
9	A	nitric acid:100+ hydrochloric acid:15	45	10	presence	fresh water	25	6.8	spray	presence	hydrochloric acid:10	45	4	5.2	8.2	spray	fresh water	25	6.8	invention Example
10	A	nitric acid:100	45	10	presence	fresh water	25	6.5	spray	presence	hydrochloric acid:10	45	10	5.3	7.8	spray	fresh water	25	6.6	invention Example
11	A	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.2	mist	presence	hydrochloric acid:10	45	4	7.8	4.9	spray	fresh water	25	6.1	invention Example
12	A	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.5	spray	presence	hydrochloric acid:10 + sulfuric acid:30	45	4	6.3	6.3	spray	fresh water	25	6.8	invention Example
13	A	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.7	spray	presence	hydrochloric acid:60	45	4	2.9	5.5	spray	fresh water	25	6.7	invention Example
14	A	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.7	spray	presence	sulfuric acid:200	45	4	10.1	9.1	spray	fresh water	25	6.5	invention Example
15	A	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.7	spray	presence	hydrochloric acid:30 + sulfuric acid:70	45	4	5.3	8.2	spray	fresh water	25	6.7	invention Example
16	A	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.8	spray	presence	hydrochloric acid:10	45	4	7.2	4.3	spray	fresh water	25	6.6	invention Example
17	A	nitric acid:100+ hydrofluoric acid:10	45	10	presence	fresh water	25	6.1	spray	presence	hydrochloric acid:10	45	4	6.1	5.1	spray	fresh water	25	6.7	invention Example
18	A	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.9	mist	presence	hydrochloric acid:10	45	4	41.2	2.1	spray	fresh water	25	6.3	invention Example
19	A	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.8	spray	presence	hydrochloric acid:10	45	4	5.8	3.3	spray	fresh water	25	6.5	invention Example
20	A	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.8	spray	presence	hydrochloric acid:10	45	4	3.3	2.8	spray	fresh water	25	6.4	invention Example
21	A	nitric acid:100+ hydrofluoric acid:10	45	10	presence	fresh water	25	6.8	spray	presence	hydrochloric acid:10	45	4	7.6	3.4	spray	fresh water	25	6.8	invention Example
22	A	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.7	spray	presence	hydrochloric acid:10 + sulfuric acid:30	45	4	7.7	11.5	spray	fresh water	25	6.8	invention Example
23	A	nitric acid:100+ hydrochloric acid:10	45	10	presence	fresh water	25	6.3	spray	presence	hydrochloric acid:10	45	4	5.3	3.9	spray	fresh water	25	6.7	invention Example
24	A	nitric acid:100+ hydrochloric acid:10	45	10	absence	-	-	-	-	absence	hydrochloric acid:10	45	4	4.9	12.8	-	-	-	-	Comparative Example
25	A	nitric acid:100+ hydrochloric acid:10	45	10	absence	-	-	-	-	absence	hydrochloric acid:10	45	4	4.5	10.1	spray	fresh water	25	6.7	Comparative Example
26	A	nitric acid:100+ hydrochloric acid:10	45	10	absence	-	-	-	-	absence	hydrochloric acid:10	45	4	5.3	10.9	spray	fresh water	25	6.7	Comparative Example

Table 2-2

Test No.	Steel No.	Water washing condition						Ratio of yellowing after pickling (%)	Maximum peeling full width after corrosion test (mm)				Remarks	
		immersion or spray	temperature (°C)	time (s)	ion concentration in washing water (g/L)				temperature of phosphating solution : 35°C		33°C			
					iron ion	nitric acid ion	chloride ion		fluoride ion	sulfuric acid ion		hot salt water immersion test		salt water spray test
1	A	immersion	60	4	3.2	1.1	2.3	-	-	4.0	2.9	5.1	5.2	Invention Example
2	B	immersion	60	4	3.1	1.5	3.3	-	-	4.1	3.1	5.0	5.3	Invention Example
3	C	immersion	60	4	3.5	1.5	3.2	-	-	4.0	3.0	5.2	5.0	Invention Example
4	D	immersion	60	4	3.9	2.1	2.9	-	-	4.0	3.1	5.1	5.2	Invention Example
5	E	immersion	60	4	3.4	1.6	2.4	-	-	4.1	3.2	5.2	5.3	Invention Example
6	F	immersion	60	4	3.2	2.3	1.8	-	-	4.1	3.1	5.1	5.4	Invention Example
7	A	immersion	60	4	2.9	5.3	1.5	-	-	4.4	3.4	5.4	5.6	Invention Example
8	A	immersion	60	4	3.1	3.8	1.8	-	-	4.3	3.5	5.3	5.5	Invention Example
9	A	immersion	60	4	3.0	4.2	1.5	-	-	4.4	3.4	5.4	5.7	Invention Example
10	A	immersion	60	4	2.9	4.5	2.1	-	-	4.9	4.0	5.7	6.1	Invention Example
11	A	immersion	60	4	4.3	3.9	1.4	-	-	4.5	3.5	5.3	5.9	Invention Example
12	A	immersion	60	4	11.5	4.2	3.2	-	1.5	4.6	3.7	5.3	5.8	Invention Example

(continued)

Test No.	Steel No.	Water washing condition						Ratio of yellowing after pickling (%)	Maximum peeling full width after corrosion test (mm)				Remarks	
		immersion or spray	temperature (°C)	time (s)	ion concentration in washing water (g/L)				temperature of phosphating solution : 35°C		33°C			
					iron ion	nitric acid ion	chloride ion		fluoride ion	sulfuric acid ion	hot salt water immersion test	salt water spray test		composite cycle corrosion test
13	A	immersion	60	4	8.2	5.1	2.9	-	-	4.3	3.6	5.5	5.7	Invention Example
14	A	immersion	60	4	2.1	2.9	4.5	-	4.8	4.5	3.7	5.5	5.7	Invention Example
15	A	immersion	60	4	1.6	5.8	4.8	-	1.5	4.5	3.5	5.4	5.8	Invention Example
16	A	immersion	60	4	3.6	6.2	3.2	-	-	4.6	3.6	5.5	5.8	Invention Example
17	A	immersion	60	4	7.1	6.9	4.9	1.2	-	4.3	3.7	5.4	5.8	Invention Example
18	A	spray	60	4	5.5	2.3	2.1	-	-	4.6	3.8	5.7	5.8	Invention Example
19	A	immersion	60	4	4.3	12.1	0.9	-	-	4.8	3.9	5.9	5.9	Invention Example
20	A	immersion	60	4	3.8	4.2	5.1	-	-	4.9	3.8	5.8	5.9	Invention Example
21	A	immersion	60	4	9.2	3.5	1.5	5.5	-	4.7	3.9	5.8	6.0	Invention Example
22	A	immersion	60	4	13.9	4.6	2.1	-	5.2	4.8	3.9	5.9	5.8	Invention Example
23	A	immersion	60	4	21.9	7.2	0.4	-	-	4.8	3.8	5.8	5.9	Invention Example
24	A	immersion	60	4	4.2	5.8	1.5	-	-	6.3	5.9	7.2	8.1	Comparative Example

(continued)

Test No.	Steel No.	Water washing condition								Ratio of yellowing after pickling (%)	Maximum peeling full width after corrosion test (mm)			Remarks	
		immersion or spray	temperature (°C)	time (s)	ion concentration in washing water (g/L)				temperature of phosphating solution : 35°C		33°C				
					iron ion	nitric acid ion	chloride ion	fluoride ion	sulfuric acid ion			hot salt water immersion test	salt water spray test		composite cycle corrosion test
25	A	immersion	60	4	4.1	5.6	2.3	-	-	65	4.9	4.0	5.9	6.3	Comparative Example
26	A	immersion	60	4	20.4	5.6	2.3	-	-	75	5.0	4.5	6.2	6.9	Comparative Example

INDUSTRIAL APPLICABILITY

[0077] The technique of the invention is not limited to high-strength cold rolled steel sheets containing a greater amount of Si or Mn and is applicable to all steel sheets for manufacturing products by pickling.

Claims

1. A method for prevention of yellowing on a surface of a steel sheet subjected to re-pickling, washing with water and drying after a surface of a continuously annealed steel sheet is pickled to remove Si-containing oxide layer from a surface layer of the steel sheet, **characterized in that** the surface of the steel sheet is held at a wet state between the pickling and the re-pickling and between the re-pickling and the washing.
2. The method for prevention of yellowing on a surface of a steel sheet according to claim 1, wherein the washing is carried out with washing water having an iron ion concentration decreased to not more than 20 g/L.
3. The method for prevention of yellowing on a surface of a steel sheet according to claim 2, wherein the washing water is further **characterized by** decreasing a concentration of nitric acid ion to not more than 10 g/L, a concentration of chloride ion to not more than 5 g/L, a concentration of fluoride ion to not more than 5 g/L and a concentration of sulfuric acid ion to not more than 5 g/L.
4. The method for prevention of yellowing on a surface of a steel sheet according to any one of claims 1-3, wherein the washing is conducted by immersing into washing water at a temperature of not lower than 20°C for not less than 3 seconds.
5. The method for prevention of yellowing on a surface of a steel sheet according to any one of claims 1-4, wherein the re-pickling is conducted with a re-pickling solution having an iron ion concentration decreased to not more than 40 g/L.
6. The method for prevention of yellowing on a surface of a steel sheet according to claim 5, wherein the re-pickling solution is further **characterized by** decreasing a concentration of nitric acid ion to not more than 20 g/L.
7. The method for prevention of yellowing on a surface of a steel sheet according to any one of claims 1-6, wherein the re-pickling is conducted with a non-oxidizing acid.
8. The method for prevention of yellowing on a surface of a steel sheet according to claim 7, wherein the non-oxidizing acid is characterized to be any one of hydrochloric acid, sulfuric acid, phosphoric acid, pyrophosphoric acid, formic acid, acetic acid, citric acid, hydrofluoric acid, oxalic acid and a mixture of these two or more acids.
9. The method for prevention of yellowing on a surface of a steel sheet according to claim 7, wherein the non-oxidizing acid is hydrochloric acid having a concentration of 0.1-50 g/L, sulfuric acid having a concentration of 0.1-150 g/L or a mixture of hydrochloric acid having a concentration of 0.1-20 g/L and sulfuric acid having a concentration of 0.1-60 g/L.
10. The method for prevention of yellowing on a surface of a steel sheet according to any one of claims 1-9, wherein the pickling is conducted with nitric acid, hydrochloric acid, hydrofluoric acid, sulfuric acid or a mixture of these two or more acids as a pickling solution.
11. The method for prevention of yellowing on a surface of a steel sheet according to any one of claims 1-9, wherein the pickling is conducted with a mixture of nitric acid and hydrochloric acid or a mixture of nitric acid and hydrofluoric acid as a pickling solution.
12. The method for prevention of yellowing on a surface of a steel sheet according to any one of claims 1-11, wherein the steel sheet is a cold rolled steel sheet containing Si: 1.0-2.0 mass%.
13. The method for prevention of yellowing on a surface of a steel sheet according to any one of claims 1-12, wherein the steel sheet contains C: 0.01-0.20 mass%, Mn: 1.0-3.0 mass%, P: not more than 0.05 mass%, S: not more than 0.005 mass% and Al: not more than 0.06 mass% in addition to Si: 1.0-2.0 mass%.

14. The method for prevention of yellowing on a surface of a steel sheet according to any one of claims 1-13, wherein a content ratio (Si/Mn) of Si to Mn exceeds 0.4.

5

10

15

20

25

30

35

40

45

50

55

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2013/050678

A. CLASSIFICATION OF SUBJECT MATTER

C23G1/08(2006.01)i, C22C38/00(2006.01)i, C22C38/06(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)

C23G1/08, C22C38/00, C22C38/06

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 1996-2013

Kokai Jitsuyo Shinan Koho 1971-2013 Toroku Jitsuyo Shinan Koho 1994-2013

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 2011-21240 A (Mitsubishi-Hitachi Metals Machinery, Inc.), 03 February 2011 (03.02.2011), (Family: none)	1-14
A	WO 2009/145353 A1 (Nippon Steel Corp.), 03 December 2009 (03.12.2009), & KR 10-2011-0003556 A & EP 2302102 A1 & US 2011/0079244 A1 & CN 102046850 A & JP 4714800 B	1-14
A	JP 2009-221586 A (JFE Steel Corp.), 01 October 2009 (01.10.2009), (Family: none)	1-14

☒ 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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

17 April, 2013 (17.04.13)

Date of mailing of the international search report

07 May, 2013 (07.05.13)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2013/050678

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 2006-322028 A (Nippon Steel Corp.), 30 November 2006 (30.11.2006), & CA 2605488 A & US 2009/0211668 A1 & KR 10-0968620 B & US 2013/0008569 A1	1-14
A	JP 2005-314725 A (Sumitomo Metal Industries, Ltd.), 10 November 2005 (10.11.2005), (Family: none)	1-14
A	JP 7-258873 A (Sumitomo Metal Industries, Ltd.), 09 October 1995 (09.10.1995), (Family: none)	1-14

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2011177861 A [0008] [0033]
- JP 2004204350 A [0011]
- JP 2004244698 A [0011]
- JP 2007217743 A [0011]
- JP 2007246951 A [0011]
- JP 2000178775 A [0011]
- JP 2006131924 A [0011]
- JP 2003193275 A [0011]
- JP H02270977 A [0011]