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METHOD OF FORMING CORROSION RESISTANT FILMS ON STEEL PLATES

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ABSTRACT OF THE DISCLOSURE

A process for producing a surface-treated steel plate high in the anticorrosiveness, particularly adapted as a material for making cans, on the principle of the thermodecomposing plating, wherein the steel plate is coated with an aqueous solution containing nitrate and/or acetate of Ni as the main component thereof and of other metals such as Cr, Mn, Zn and Al as selective components and then heated at a certain range of temperature so as to cause the thermodecomposing reaction to cause thereby a strong film containing metallic nickel and at least one metal oxide to form on the surface of the steel plate.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a method of making surface-treated steel plates by thermodecomposing plating.

Description of the prior art

As well known, as a material for making cans, a tin-plated steel plate is used most today. However, tin has such problems that it is expensive, is not endurable to the use at a high temperature, is weak against corrosion in the atmosphere and further becomes black depending on the contents in case it is made a can. Furthermore, tin is so short as a resource in the world that its supply is unstable. As a result in the world that its support is unstable. As a result of making researches on surface-treated steel plates the present inventors have discovered that in order to produce surface-treated steel plates having no such defects as in the case of the above-mentioned tin-plated steel plate it is necessary to have a film, which is more stable than the steel plate to be plated and is to be formed on a technical idea different from the plating, such as tin-plating, for electrochemically protecting the steel plate in a corrosive liquid, on the surface of the steel plate.

Further, when using metal-plated surface-treated steel plates, including a tin-plated steel plate, as a material for making cans, it is usual to coat the metal-plating layer with well known lacquers of various kinds as, for example, an epoxy resin series paint for the necessity to prevent the metal-plating layer from being corroded and the metal ions from being melted-out by such contents in the can as, for example, a beverage, liquor, oil or fat.

Therefore, as for a metal-plated surface-treated steel plate the following conditions are required that not only it should be high in the antirusting property in the atmosphere but also, in case it is coated with a lacquer and is then dipped in the above described corrosive liquid, the lacquer coating film should not peel off, and moreover it should not interfere with the can-manufacturing operations, for instance, it should be easy to solder and mold.

As regards the peeling-off of such lacquer film, particularly the case of coating an Al- or Zn-plated steel plate with a lacquer can be taken as an example. When dipping said steel sheet in the above described corrosive liquid, the corrosion of the Al- or Zn-plating layer by said corrosive liquid proceeds faster than the corrosion of the iron

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base material on account of an anodic protective action of Al or Zn on the steel sheet, resulting in the peeling-off the lacquer film.

Different from the case of Al- or Zn-plated steel plate there occurs no peeling-off of a lacquer when applied on the surface of a Cr- or Ni-plated steel plate, because Cr or Ni is inherently high in the antirusting property and is more stable than the iron base when dipped in such corrosive liquid as above-mentioned, consequently the lacquer adheres firmly to the surface of the Cr- or Ni-plated steel plate. However, because the plating layer is thick, this plating method is not economic.

SUMMARY OF THE INVENTION

On the basis of such knowledge as is described above, the present inventors have developed a novel process for obtaining a surface-treated steel plate high in the anticorrosion by forming on a steel plate a film more stable than the iron base.

An object of the present invention is to provide surface-treated steel plates which are so high in the anticorrosiveness that they can sufficiently serve in place of tin-plated steel plates, particularly novel and economic steel plates to be used as material for manufacturing cans, generally called as tin-free steel plate and other steel plates to be used as materials for automobiles, constructions and toys.

In order to attain the object as above-mentioned the present invention is to provide methods which are characterized by the following features: that is, a method for obtaining surface-treated steel plate having an excellent anticorrosiveness wherein an aqueous solution of nitrate and/or acetate of Ni is applied on the surface of a steel plate previously subjected to a surface-cleaning treatment and is then heated in a nonoxidative gas atmosphere so as to cause the thermodecomposing reaction to thereby form a film containing metallic nickel on the surface of the steel plate, and a method for forming a further improved film, that is, a method for obtaining surface-treated steel plate having an excellent anticorrosiveness wherein an aqueous solution of nitrate and/or acetate of Ni with the addition of one or more of nitrates and acetates of Cr, Mn and Zn is applied on the surface of a steel plate previously subjected to a surface-cleaning treatment and is then heated in a nonoxidative gas atmosphere so as to cause the thermodecomposing reaction to thereby form a film containing metallic nickel and one or more of oxides of Cr, Mn and Zn, and further a method for forming a more excellent film, that is, a method for obtaining surface-treated steel plate having a particularly excellent anticorrosiveness wherein an aqueous solution of a nitrate and/or acetate of Ni with the addition of one or more of nitrates and acetates of Cr, Mn and Zn and with a further addition of a nitrate and/or acetate of Al is applied on the surface of a steel plate previously subjected to a surface-cleaning treatment and is then heated in a nonoxidative gas atmosphere so as to cause the thermodecomposing reaction to thereby form a film containing metallic nickel and one or more of oxides of Cr, Mn, Zn and Al in addition thereto.

The present invention is particularly very economical because it is possible to utilize a heating cycle of annealing conditions for the thermodecomposing reaction, and the method of the present invention is therefore very high in practical value.

Moreover, the thus obtained treated film is not only excellent in the anticorrosive activity but is also very excellent in the paint adhesiveness and mechanical workability. Therefore, the present invention is particularly adapted as a method of making steel plates for making cans.

The method of the present invention shall be detailed in the following.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The method which makes the foundation of the present invention is to form a very thin film of metallic nickel on the surface of a steel plate by applying an aqueous solution, for example, of nickel nitrate to coat the said surface of the steel plate and heating it in a reductive or inert non-oxidative atmosphere so as to cause the thermodecomposing reaction of the treating solution and the reduction (complete or partial) of nickel nitrate to metallic nickel.

Nickel nitrate or nickel acetate which is an essential component of the treating aqueous solution of the present invention is used alone or as mixed. However, any other Ni compound (particularly oxide) than this has a difficulty in the anticorrosiveness, paint adhesiveness and workability of the treated film and therefore should be avoided in the method of the present invention.

In the following, for the convenience of the explanation, the aqueous solution containing an Ni-salt prepared as described above shall be called a treating solution.

Depending on the kinds, some of such treating solutions are difficult to uniformly apply to coat steel plates. However, in such case, an improvement can be obtained by adding a proper amount of such surface active agent as, for example, a nonionic active agent. The deposited amount of the treating solution is so remarkably different depending on the method of coating the surface of the steel plate such as blowing a spray, applying with a roller or dipping the steel plate in the solution that the concentration of the treating solution is difficult to uniformly define but, if the effective quantitative range is to be defined in relation to the viscosity of the solution or the uniformity of the decomposing reaction, Ni ions are to be contained in an amount of 0.5 to 100 g./l. or preferably 1 to 20 g./l., later described Cr⁺⁺⁺ ions are less than 20 g./l. or preferably 10 g./l., Al ions are less than 20 g./l. or preferably less than 10 g./l., Zn ions are less than 40 g./l. or preferably less than 10 g./l. and Mn⁺⁺ ions are less than 20 g./l. or preferably less than 10 g./l.

Further, in order to improve the characteristics of the treated film, a nitrate or acetate of Mg, Ca or K may be added in an amount of about 1 g./l.

It is wise to prevent as much as possible the pH of the treating solution of the present invention from becoming excessively acidic to avoid an exchanging reaction with Fe. Therefore, in the industrial practice, it is desirable to make the pH of the treating solution 3 to 4.

As to a film which is heavily colored in its appearance after heat-treated, there is recognized a tendency of the lacquer adhesiveness being reduced and also the adhesion of the film itself to the base being reduced. Therefore, it is desirable to control the deposited amount of the film so that the appearance after the heat-treatment may have transparency of such a degree as will not substantially impair the luster of the cold-rolled steel plate or may have light tone of such a degree as can be barely recognized with the naked eye (that is, the metal thickness may be less than 1μ or, if possible, about 0.1μ or less).

Now, in the method of the present invention, the above described treating solution is applied and is then quickly heated to cause a thermodecomposing reaction at a temperature of 200 to 750° C. in a furnace of a gas atmosphere of such nonoxidative gas in which, for example, the H₂ content is 2 to 20% and the main component of the rest is N₂ as DX or NX gas used as a brightly annealing gas so that a strong metallic nickel film may be formed. When the content of H₂ in the gas atmosphere is less than 2%, the Ni salt is so hard to reduce that there is formed an undesirable film, because, the film having metallic nickel becomes lusterless and blackish. On the other hand, the content of H₂ of more than 20% is a great loss to the economy. In addition thereto such

a high content of H₂ is not desirable, particularly in the method, wherein salts of Al, Cr, Mn and Zn are added to a salt of Ni, because the reduction of salts of these metals proceeds too far with a result of that such a metallic nickel-plated film containing oxides of these metals as is intended in the present invention can not be obtained.

The above described nonoxidative gas may contain a slight amount of carbon dioxide, carbon monoxide or water. However, the heating atmosphere must not be oxidative by containing oxygen in such a degree as will have a bad influence on the reduction of the salt of nickel to metallic nickel, because otherwise the salt of nickel applied on the surface of a steel plate may not be reduced to metallic nickel of a required amount within the time of the annealing condition and may remain as nickel oxide on the surface of the steel plate, which does not suit with the object of the present invention.

When the heating temperature is less than 200° C., no effective thermodecomposition takes place. On the contrary, when it is more than 750° C., there are produced undesirable results that all the metallic nickel produced by the thermodecomposition will alloy with the iron base to form a hard film which is not only low in the adhesiveness but also low in the anticorrosiveness, and further even mechanical properties of the steel plate itself, which is to be treated, are often impaired thereby.

In the foregoing an example of applying a treating solution composed of an Ni-salt only has been explained. The surface film obtained by this method is thought to be a two-layer film high in the anticorrosiveness, consisting of an Fe-Ni alloy in the lower layer and metallic nickel in the upper layer. As a result of making further investigations, however, the present inventors have succeeded in developing an improved method of forming on the surface of a steel plate a film which is more excellent than the above described film. This film is thought to be formed of two layers, wherein the lower layer is made of an Fe-Ni alloy and the upper layer is a mixture of oxides of Cr, Mn and Zn and metallic nickel, of which the mixture, however, is mainly composed.

That is, the improved method is that, wherein an aqueous solution (which shall be called a treating solution with additive for the convenience of the explanation hereinafter) obtained by adding one or more of nitrates and acetates of Cr, Mn and Zn to a nitrate and/or acetate of Ni is applied to coat the surface of a steel plate and is heated in a non-oxidative gas atmosphere furnace to form a film consisting of one or more of oxides of Cr, Mn and Zn and metallic nickel. The above-mentioned treating solution with additive may be prepared by adding one or more of carbonates, oxalates and hydroxides of Cr, Mn and Zn to an aqueous solution of Ni nitrate and/or acetate.

In the foregoing, there have been shown examples of dissolving a nitrate or acetate of Ni and carbonates, oxalates, hydroxides and oxides of Cr, Mn and Zn in an aqueous solution of nitric acid and/or acetic acid. However, the present invention is not limited to them except the Ni salts. Any salts of Cr, Mn and Zn may be used, if they leave no anion in an aqueous solution of nitric acid or acetic acid when they are dissolved in it.

As to the method of applying said treating solution with additive any of methods adopted when applying the abovementioned treating solution, such as the spraying method, roller-coating method and dipping method, may be likewise used. If necessary, also a surface active agent may be further added.

Also the heating can be carried out under exactly the same conditions and in the same manner, that is, in a temperature range of 200 to 750° C. in a furnace of a non-oxidative gas atmosphere in which, for example, the H₂ content is 2 to 20% and the rest is mostly N₂. However, the thus obtained film is higher in the anticorrosive-

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ness than in the case of the above mentioned treating solution composed of the Ni salt only.

Further, as a result of making further investigations the present inventors have discovered that when an Al salt is further added to the above-mentioned treating solution with additive a film having more excellent anticorrosiveness and workability can be obtained.

For example, when a treating solution prepared by adding an Al salt to the above-mentioned treating solution with additive, which contains one or more of Cr, Mn and Zn salts in addition to Ni, is subjected to the thermodecomposition in a temperature range of from 200 to 750° C. in a furnace of a nonoxidative gas atmosphere, in which the H₂ content is 2 to 20%, there can be formed on the surface of a steel plate a very thin film which has been proved to be all the more improved

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No. 13 in the same table was prepared by subjecting a steel to a cold-rolling with the above-mentioned continuous strip rolling apparatus, thereupon to alkali-defatting and pickling and then to an annealing in the above-mentioned gas atmosphere (this referential steel shall be called a nontreated steel plate hereinafter for the convenience of the explanation).

In the rusting test by an indoor exposure the nontreated steel plate rusted within one month, while samples Nos. 1, 2 and 3 did not rust in 3 to 5 months in the same indoor exposure. Further, in the corrosion test, in which samples were dipped in a carbonic acid beverage after being coated with an epoxy resin series paint, samples Nos. 1, 2 and 3 showed results much superior to the nontreated sample in the anticorrosiveness, but somewhat inferior in the paint adhesiveness.

PERFORMANCE TEST COMPARISON TABLE

Sample No.	Treating solution composition	Treating process	Performance tests		
			(1) Antirusting property	(2) Corrosion resistance below the coating film	(3) Paint adhesiveness
1.....	Nickel nitrate (60 g./l.).....	Dip-coating.....	5.0	3	4
2.....	Nickel acetate (30 g./l.).....	Heating atmosphere (H ₂ :6%, N ₂ :rest).	4.0	3	4
3.....	Nickel nitrate (10 g./l.) plus nickel acetate (10 g./l.).....	Heating temperature, 600° C.	2.5	2	4
4.....	Nickel nitrate (20 g./l.) plus chromium acetate (10 g./l.).....	Roller-coating.....	7.0	4	5
5.....	Nickel acetate (20 g./l.) plus manganese nitrate (10 g./l.).....	Heating atmosphere (H ₂ :10%, N ₂ :rest).	6.0	3	4
6.....	Nickel nitrate (20 g./l.) plus zinc nitrate (10 g./l.).....	Heating temperature 600° C.	4.5	3	4
7.....	Nickel acetate (20 g./l.) plus chromium acetate (5 g./l.) plus manganese nitrate (5 g./l.).....		9.5	5	5
8.....	Nickel nitrate (20 g./l.) plus manganese nitrate (5 g./l.) plus zinc nitrate (5 g./l.).....		8.5	4	3
9.....	Nickel nitrate (20 g./l.) plus aluminium nitrate (5 g./l.) plus chromium acetate (5 g./l.).....	Dip-coating.....	11.5	5	5
10.....	Nickel nitrate (20 g./l.) plus aluminium nitrate (5 g./l.) plus zinc nitrate (5 g./l.).....	Heating atmosphere (H ₂ :6%, N ₂ :rest).	10.0	5	5
11.....	Nickel acetate (20 g./l.) plus aluminium nitrate (5 g./l.) plus zinc nitrate (5 g./l.).....	Heating temperature 250° C.	9.0	5	5
12.....	Nickel acetate (10 g./l.) plus aluminium nitrate (5 g./l.) plus chromium nitrate (5 g./l.) plus manganese nitrate (5 g./l.).....		12.5	5	5
13.....	(Nontreated steel plate).....		0.5	1	5

in the anticorrosiveness and workability, as are shown in the following examples.

As will be understood from the foregoing, the method of the present invention can provide cheaply a steel plate having a strong inactive film, just like the surface of a stainless steel, which is particularly suitable as a material for manufacturing cans therefrom because of being high in the anticorrosiveness and excellent in the paint adhesiveness.

Examples shall be detailed in the following.

Example 1

A cold-rolled steel plate of a thickness of 0.26 mm., which had been cold-worked by a well known method, that is, by using a continuous strip rolling apparatus, but had not yet been annealed, was subjected to a well known pretreatment, for example, such surface adjustments as alkali-defatting and sulfuric acid-pickling, was then dipped in an aqueous solution of nickel nitrate or nickel acetate so that nickel salt might be deposited on the surface, was immediately thereupon heated at a temperature of 600° C. in an annealing gas atmosphere of an H₂ content of 6% and the rest being N₂, so as to effect a strain-removing annealing and at the same time to form a nickel film and was then rolled for refining at a rate of reduction of 1%. The comparison of the performances was made on the antirusting property, the corrosion resistance below the coating film and the paint adhesiveness. The samples Nos. 1, 2 and 3 in the below-mentioned performance test comparison table are steel plates having a film composed of metallic nickel prepared by the above-mentioned method respectively. On the other hand, a referential sample

Example 2

The same cold-rolled steel plate as in Example 1 was defatted with an alkali and pickled with sulfuric acid, was then coated with a treating solution prepared by adding one or more of chromium acetate, manganese nitrate and zinc nitrate into an aqueous solution of nickel acetate or nickel nitrate by using a roller and was then immediately heated at a temperature of 600° C. in a brightly annealing gas atmosphere of an H₂ content of 10%, the rest being N₂, to form a film. The samples Nos. 4 to 8 in the above-mentioned performance test comparison table were steel plates prepared by the above-mentioned process. It is obviously seen that the film obtained by applying a treating solution containing one or more of Cr, Mn and Zn salts in addition to an Ni salt has performances more excellent than of the film by Example 1. That is, they showed no rusting in 4 to 10 months in the rusting test by indoor exposure and were very high in the corrosion resistance below the coating film in a carbonic acid beverage after being coated with a lacquer.

Example 3

A cold-rolled steel plate of a thickness of 0.26 mm. which had been cold-worked by a well known method, for example, by using a continuous strip rolling apparatus, thereafter alkali-defatted, sulfuric acid-pickled and then annealed in a reductive atmosphere was once more surface-treated with alkali-defatting and sulfuric acid-pickling, was then dip-coated with a treating solution prepared by adding one or more of chromium acetate, manganese nitrate and zinc nitrate into an aqueous solution of a mixture of nickel nitrate and aluminium nitrate and was then

immediately heated at a temperature of 250° C. in a heated gas atmosphere of an H₂ content of 6%, the rest being N₂, to form a film.

The samples Nos. 9 to 12 in the above-mentioned performance test comparison table which correspond to this example, did not rust in 9 to 13 months in a rusting test by indoor exposure, were not corroded at all below the lacquer-coated film in a carbonic acid beverage after being coated with a lacquer and were high also in the paint adhesiveness.

In all the Examples 1, 2 and 3 the heating time was very short, amounting to several seconds, though there was a slight difference according to the temperature in the range of 200 to 750° C.

The numerals in the above-mentioned performance test comparison table are defined as follows:

(1) Antirusting property

The period until a rust recognizable by observation with the naked eye was generated on the surface of the steel plate by the indoor exposure test was represented by the number of months.

(2) Corrosion resistance below the coating film

The steel plate was coated with an epoxy resin series lacquer, had then a scratch of a width of 0.1 mm. made on it and was dipped for one month in a cola series carbonic acid beverage kept at such fixed temperature as 38° C. in the example and then the degree of corrosion below the coating film in the scratched part was observed. The numerals in the table were defined as follows by dividing the evaluations into five grades:

- 5—When no coating film peeling was recognized at all.
- 4—When a coating film peeling of about 0.1 to 0.2 mm. was recognized.
- 3—When a coating film peeling of about 0.2 to 0.4 mm. was recognized.
- 2—When a coating film peeling of about 0.4 to 0.8 mm. was recognized.
- 1—When a coating film peeling of about 0.8 to 2.0 mm. was recognized.

(3) Paint adhesiveness

A lacquer was applied and was then bonded with a binder and then the tensile strength was measured and was evaluated by making the maximum value 5 and the minimum value 1 as a scale of the lacquer adhesiveness.

What is claimed is:

1. A method of imparting anti-corrosive properties to surface-treated steel plates comprising applying to the surface of a steel plate an aqueous solution consisting essentially of at least one compound selected from the group consisting of nitrates and acetates of Cr, Mn and Zn in admixture with at least one compound selected from the group consisting of a nitrate and acetate of Ni to coat the surface thereof said steel plate having been previously subjected to a surface-cleaning pretreatment and then heating the thus-coated steel plate in a nonoxidative gas atmosphere to cause a thermodecomposing reaction to form a film containing metallic nickel and at least one oxide selected from the group consisting of oxides of Cr, Mn and Zn.

2. A method of imparting anti-corrosive properties to surface-treated steel plates comprising applying to the surface of a steel sheet an aqueous solution consisting essentially of at least one compound selected from the group consisting of nitrates and acetates of Cr, Mn and Zn in admixture with at least one compound selected from the group consisting of a nitrate and acetate of Ni and further containing at least one compound selected from the group consisting of a nitrate and acetate of Al to coat the surface thereof, said steel plate having been previously subjected to a surface-cleaning pretreatment and then heating the thus-coated steel plate in a nonoxidative gas atmosphere to cause a thermodecomposing reaction to

form a film containing metallic nickel, an oxide of aluminum and at least one oxide selected from the group consisting of oxides of Cr, Mn, and Zn.

3. A method of imparting anti-corrosive properties to surface-treated steel plates comprising applying to the surface of a steel plate an aqueous solution consisting essentially of at least one compound selected from the group consisting of nitrates and acetates of Cr, Mn and Zn in admixture with at least one compound selected from the group consisting of a nitrate and acetate of Ni containing 0.5 to 100 g./l. of Ni ions whereby less than 20 g./l. of Cr⁺⁺⁺, less than 40 g./l. of Zn ions and less than 20 g./l. of Mn ions are present in the solution and further containing at least one compound selected from the group consisting of a nitrate and acetate of Al so that the content of Al ions is less than 20 g./l. to coat the surface of the steel plate, said steel plate having been previously subjected to a surface-cleaning pretreatment and then heating the thus coated steel plate in a nonoxidative gas atmosphere to cause a thermodecomposing reaction to form a film containing metallic nickel, an oxide of aluminum and at least one oxide selected from the group consisting of oxides of Cr, Mn, and Zn.

4. A method of imparting anti-corrosive properties to surface-treated steel plates comprising applying to the surface of a steel plate an aqueous solution consisting essentially of at least one compound selected from the group consisting of nitrates and acetates of Cr, Mn and Zn in admixture with at least one compound selected from the group consisting of a nitrate and acetate of Ni containing 1 to 20 g./l. of Ni ions whereby less than 10 g./l. of Cr⁺⁺⁺, less than 10 g./l. of Zn ions and less than 10 g./l. of Mn ions are present in the solution and further containing at least one compound selected from the group consisting of a nitrate and acetate of Al so that the content of Al ions may be less than 10 g./l. to coat the surface of the steel plate, said steel plate having been previously subjected to a surface-cleaning pretreatment and then heating the thus coated steel sheet in a nonoxidative gas atmosphere to cause a thermodecomposing reaction to form a film containing metallic nickel, an oxide of aluminum and at least one oxide selected from the group consisting of oxides of Cr, Mn, and Zn.

5. A method of imparting anti-corrosive properties to surface treated steel plates according to claim 1 wherein the pH of said treating aqueous solution is 3 to 4.

6. A method of imparting anti-corrosive properties to surface treated steel plates according to claim 1 wherein the thickness of the treated film is less than 1μ.

7. A method of imparting anti-corrosive properties to surface-treated steel plates according to claim 1 wherein the thickness of the treated film is less than 1μ and an organic coating film is formed directly on said film and is heated and dried.

8. A method of imparting anti-corrosive properties to surface treated steel plates according to claim 1, wherein the pH of said treating aqueous solution is 3 to 4 and wherein the thickness of the film formed by the coating treatment is less than 1μ.

9. A method of imparting anti-corrosive properties to surface treated steel plates according to claim 2, wherein the pH of said treating aqueous solution is 3 to 4 and wherein the thickness of the film formed by the coating treatment is less than 1μ.

10. A method of imparting anti-corrosive properties to surface treated steel plates according to claim 3, wherein the pH of said treating aqueous solution is 3 to 4 and wherein the thickness of the film formed by the coating treatment is less than 1μ.

11. A method of imparting anti-corrosive properties to surface treated steel plates according to claim 4, wherein the pH of said treating aqueous solution is 3 to 4 and wherein the thickness of the film formed by the coating treatment is less than 1μ.

12. A method of imparting anti-corrosive properties to surface-treated steel plates according to claim 1 wherein the steel plate is a cold-rolled steel sheet and the coated cold-rolled steel sheet is heated at 200 to 750° C. in a non-oxidative gas atmosphere composed of 2 to 20% H₂ and the rest being nitrogen gas to form the film on the surface of the sheet and to remove strains in the steel sheet.

13. A method of imparting anti-corrosive properties to surface-treated steel plates according to claim 2 wherein the steel plate is a cold-rolled steel sheet and the coated cold-rolled steel sheet is heated at 200 to 750° C. in a non-oxidative gas atmosphere composed of 2 to 20% H₂ and the rest being nitrogen gas to form the film on the surface of the sheet and to remove strains in the steel sheet.

14. A method of imparting anti-corrosive properties to surface-treated steel plates according to claim 3 wherein the steel plate is a cold-rolled steel sheet and the coated cold-rolled steel sheet is heated at 200 to 750° C. in a non-oxidative gas atmosphere composed of 2 to 20% H₂ and the rest being nitrogen gas to form the film on the surface of the sheet and to remove strains in the steel sheet.

15. A method of imparting anti-corrosive properties to surface-treated steel plates according to claim 4 wherein the steel plate is a cold-rolled steel sheet and the coated cold-rolled steel sheet is heated at 200 to 750° C. in a non-oxidative gas atmosphere composed of 2 to 20% H₂ and

the rest being nitrogen gas to form the film on the surface of the sheet and to remove strains in the steel sheet.

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