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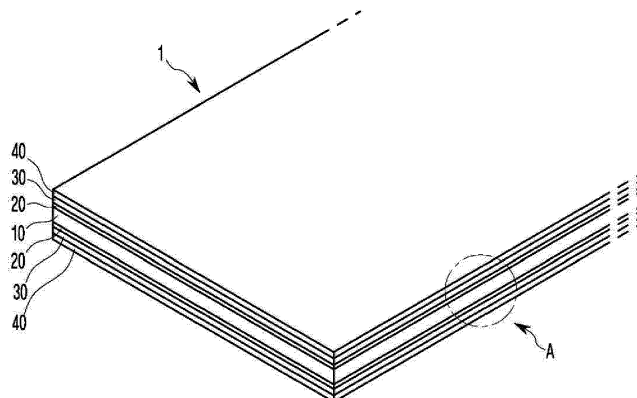
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(54) **SURFACE TREATMENT METHOD OF GALVANIZED STEEL SHEET PRODUCT AND GALVANIZED STEEL SHEET PRODUCT TREATED BY THE SAME**

(57) There is disclosed a surface treatment method of a steel sheet formed product including a first step of preparing a galvanized steel sheet formed product; a second step of performing surface-modification treatment for a galvanized layer of the prepared steel sheet formed product; a third step of coating a resin on the surface-modification-treated galvanized layer; and a fourth step of bring the resin coating layer into close contact on the galvanized layer. The second step may include a process of increasing a surface roughness by electrolytically etching the galvanized steel sheet formed product in a surface treatment composition solution. The surface

treatment composition may be an eco-friendly baking soda solution, and the baking soda solution may be prepared by dissolving 10wt% to 50wt% of baking soda in water. The electrolytic corrosion may be performed by using the galvanized steel sheet formed product as an anode and lead or copper as a cathode, and the electrolytic corrosion may be performed by a voltage of 10V to 36V DC at a temperature of 60°C to 85°C. The third step may perform a process of re-coating a resin by general coating once or twice or more on the base steel sheet coated with a resin by a first electrodeposition coating.

FIG. 1



Description

FIELD

[0001] This application claims priority to and the benefits of Korean Patent Application No. 10-2022-0131777 filed on October 13, 2022 and Korean Patent Application No. 10-2022-0144109 filed on November 02, 2022, the disclosure of which is incorporated herein by reference in its entirety.

[0002] The present disclosure relates to a surface treatment method of a galvanized steel sheet formed product and a galvanized steel sheet formed product treated by the same. More particularly, the present disclosure relates to a surface treatment method forming a resin coating layer after forming a steel sheet by rolling or pressing, galvanizing and modification a formed steel sheet product provided thereto, and a galvanized steel sheet formed product treated by the same.

BACKGROUND

[0003] Road structures such as guardrails, traffic lights, street lamps, and overpasses and construction structures, which are made of steel sheets, require aesthetic appearance, so galvanized steel sheets with excellent corrosion resistance are used. These galvanized steel sheets include hot-dip galvanized steel sheet forming products (i.e., GI steel), alloyed hot-dip galvanized steel sheet forming products (i.e., Galva-annealed (GA) steel) and electrolytic galvanized steel sheet forming products (i.e., EG steel), etc.

[0004] However, when metal components of such the galvanized steel sheet are exposed to a corrosive environment, especially a humid atmosphere, a rusting phenomenon called white rust could occur on a surface of the galvanized steel sheet. Accordingly, rust could occur on road structures or construction structures made of the galvanized steel sheets which are continuously exposed to rainwater and air.

[0005] In order to further increase the corrosion resistance of such a pure galvanized steel sheet, a steel sheet having a galvanized layer containing magnesium or aluminum is also being manufactured. Most of the surface of this steel sheet is made of zinc or zinc alloy.

[0006] However, since magnesium and aluminum included in the surface layer have higher oxygen affinity than zinc, a blackening phenomenon occurs due to the insufficient amount oxygen capable of bonding with zinc. That is, it is inevitable that such a blackening phenomenon also occurs in galvanized steel sheet formed products formed by a rolling forming method using a roller, a press forming method using a press or the like.

[0007] Therefore, colors of road structures and construction structures manufactured with these steel sheet formed products which are continuously exposed to acid rain and air gradually change to darker colors.

[0008] In order to prevent moisture from entering the

surface of the galvanized steel sheet from the outside, there has been an attempt to prevent the rusting or blackening of the galvanized steel sheet by applying painting treatment after galvanizing. However, the surface of the galvanized steel sheet easily absorbs moisture from the atmosphere and forms zinc hydroxide. Accordingly, if the galvanized steel sheet is exposed to the atmosphere between the galvanizing treatment and the painting treatment, it is difficult to prevent corrosion of the entire surface over a long period of time, despite the painting treatment.

[0009] As a result, the structures or construction structures manufactured by applying paint to galvanized products also have problems such as white rust occurring on the surface of zinc over time and peeling of the paint layer.

[0010] In addition, to improve the corrosion resistance of the galvanized steel sheet, which is vulnerable to corrosion due to moisture generated by the low density of the structure, a method of vacuum deposition of alumina thin film has been developed. However, this method has a problem in that the formability of the subsequent process is greatly reduced due to the high hardness and strength of the thin film.

[0011] In order to prevent rusting or blackening of the galvanized steel sheet, surface treatment using an inorganic phosphate-based or chromate-based pretreatment agent is performed after galvanizing to prevent inflow of moisture from the outside. Among them, the chromate-based pretreatment was performed by pretreating a metal surface with 5 to 100 mg/m² of chromate and then forming an organic film. This chromate-based pretreatment prevents oxidation of iron and zinc by the strong self-oxidizing power of 6+ chromium. Accordingly, it has an advantage of increasing the corrosion resistance of the galvanizing steel sheet and reducing the processing cost.

[0012] However, this method requires additional pretreatment facilities and additional processes due to heavy metals such as chromium contained in the pretreatment agent. Also, heavy metal wastewater might be generated, which causes a safety problem. In addition, the chromate-treated galvanized steel sheet has a problem in that chromium ions are eluted during use or disposal. In recent years, the seriousness of health and safety issues as well as environmental pollution has been increasingly highlighted worldwide. Consequently, there has been a growing demand for stricter environmental regulations. This has led to increased restrictions on the use of chromium components that are harmful to human health.

[0013] Traditional methods that have been applied to improve the corrosion resistance of galvanized steel sheets have problems of limited corrosion resistance, compromised formability of subsequent processes or raised environmental concern.

SUMMARY

[0014] Accordingly, one objective of the present dis-

closure is to solve the above-mentioned disadvantages and provide a new surface treatment method of a galvanized formed product that may improve corrosion resistance of the galvanized formed product.

[0015] Another objective of the present disclosure is to provide a surface treatment method of a galvanized formed product and a galvanized formed product treated thereby that may meet the demands of the current environmental requirements.

[0016] A further objective of the present disclosure is to provide a surface treatment method of a galvanized formed product and coating technology that may use an environmentally friendly method, and a galvanized formed product using the same.

[0017] A still further objective of the present disclosure is to provide a surface treatment method of a galvanized formed product and a galvanized formed product using the same that may increase the adhesive strength of a coating layer coated on a galvanized layer of steel sheet, dramatically improve durability strength, long-term stability against corrosive substances, etc., and dramatically improve watertightness characteristics.

[0018] Aspects according to the present disclosure are not limited to the above ones, and other aspects and advantages that are not mentioned above can be clearly understood from the following description and can be more clearly understood from the embodiments set forth herein. Additionally, the aspects and advantages in the present disclosure can be realized via means and combinations thereof that are described in the appended claims.

[0019] To solve the above-mentioned problems, a surface treatment method of a steel sheet formed product and a steel sheet formed product using the same according to embodiments of the present disclosure may be applied to a steel sheet formed product provided after forming by rolling or pressing, galvanizing, and modifying.

[0020] The present disclosure may include a process of performing surface modification treatment for a galvanized layer of a galvanized steel sheet by using a baking soda solution.

[0021] The surface modification treatment may improve adhesion between a resin coating layer to be post-treated by electrodeposition coating, for example, and a galvanized layer.

[0022] The present disclosure may include a process of forming the resin coating layer on the surface-modification-treated galvanized layer by general coating or by electrodeposition coating.

[0023] This may include a process of coating a non-colorant resin on the surface of the surface-modified galvanized product and coating a general paint or a resin containing a colorant on the surface of the resin coating layer.

[0024] The present disclosure may provide the resin coating layer with various functions.

[0025] The surface treatment method of the present

disclosure including the process of performing the surface modification treatment and forming the resin coating layer may have an eco-friendly, harmless and highly reliable process.

[0026] The surface treatment method of a steel sheet formed product according to the present disclosure may include a first step of preparing a galvanized steel sheet formed product; a second step of performing surface-modification treatment for a galvanized layer of the prepared steel sheet formed product; a third step of coating a resin on the surface-modification-treated galvanized layer; and a fourth step of bring the resin coating layer into close contact on the galvanized layer.

[0027] Preferably, the first step may include a process of galvanizing the steel sheet formed product.

[0028] Preferably, the first step may include a process of storing the galvanized steel sheet formed product. The second step may include a process of increasing a surface roughness by electrolytically etching the galvanized steel sheet formed product in a surface treatment composition solution.

[0029] Preferably, the surface treatment composition may be an eco-friendly solution.

[0030] Preferably, the surface treatment composition may be a baking soda solution.

[0031] Preferably, the baking soda solution may be prepared by dissolving 10wt% to 50w% of baking soda in water.

[0032] Preferably, the electrolytic corrosion may be performed by using the galvanized steel sheet formed product as an anode and lead or copper as a cathode.

[0033] Preferably, the electrolytic corrosion may be performed by a voltage of 10V to 36V DC at a temperature of 60°C to 85°C.

[0034] Preferably, after the second step, before the third step, a process of coating the galvanized steel sheet formed product in a solution containing zirconium compounds may be further performed.

[0035] Preferably, the zirconium compound solution may be prepared by dissolving 0.5 wt% to 3.0 wt% of titanate, 1.0 wt% to 5.0 wt% of hexafluorozirconic acid, and 0.1 wt% to 2.0 wt% of amino methyl substituted polyvinylphenol in water.

[0036] Preferably, the zirconium compound coating process may be performed at a temperature of 100°C or more and 200°C or less.

[0037] The third step and the fourth step are performed once or more than once with alternating. For example, the third step and fourth step of the surface treatment method may be performed once respectively. For example, the third step and fourth step of the surface treatment method may be performed once respectively and may be performed once respectively again.

[0038] Preferably, the third step may include a process of coating the base steel sheet with a resin by a first electrodeposition coating.

[0039] Preferably, the first electrodeposition coating may be performed while maintaining the preheated tem-

perature of the steel sheet formed product subjected to the surface modification treatment in the second step.

[0040] Preferably, the first electrodeposition coating may be performed at 150°C to 300°C.

[0041] More preferably, the first electrodeposition coating may be performed at 200°C to 250°C.

[0042] Preferably, the third step may further include a process of re-coating a resin on the base steel sheet coated with the resin by the first electrodeposition coating by a second general coating.

[0043] Preferably, the third step may further include a process of re-coating a resin on the base steel sheet coated with the resin by the second general coating by a third general coating.

[0044] Preferably, the third step may further include a process of re-coating a resin on the base steel sheet coated with the resin by the third general coating by a fourth general coating.

[0045] Preferably, the fourth step may include a process of heating the base steel sheet coated by the first electrodeposition coating.

[0046] Preferably, the fourth step may include a process of heating the base steel sheet coated with the resin by the general coating.

[0047] Preferably, the fourth step further may include a process of cooling the heated steel sheet coated with the resin.

[0048] The present disclosure provides a steel sheet formed product subjected to the surface treatment by the surface treatment method.

[0049] The steel sheet formed product subjected to the surface treatment method may include a formed base steel sheet; a galvanized layer formed on the base steel sheet and surface-modification-treated through the second step of the surface treatment method; and resin coating layers coated on the galvanized layer through the third step and the fourth step of the surface treatment method.

[0050] The surface treatment method of the steel sheet formed product according to the present disclosure can have excellent coatability, and is eco-friendly and mass produced, thereby becoming very economical.

[0051] The steel sheet formed product subjected to the surface treatment method according to the present disclosure can have excellent durability and coatability of the disposed resin coating layer, and excellent corrosion resistance and blackening resistance of the steel sheet.

[0052] The steel sheet formed product subjected to the surface treatment method according to the present disclosure can be prevented from peeling of the resin coating layer, which might occur due to rainwater, polluted air, etc., even when installed on the open ground.

[0053] According to the surface treatment method of the steel sheet formed product, since the surface modification treatment of the galvanized steel sheet formed product may be performed by using the baking soda solution, exhaust and water treatment facilities are unnecessary and it is eco-friendly to the extent that there is no

problem with microbial cultivation.

[0054] According to the surface modification treatment process of the surface treatment method, after the process, there is almost no loss of zinc, and by increasing the surface roughness, excellent coatability can be obtained compared to the conventional formed products.

[0055] According to the surface modification treatment process of the surface treatment method, it is possible to control the non-uniform corrosion of the coating lower layer, which cannot be controlled in the conventional conversion treatment and coating treatment process, so that the galvanized surface can exhibit a uniform and constant size of the surface roughness.

[0056] The process of forming the resin coating layer according to the present disclosure can freely express colors while securing durability and corrosion resistance. Accordingly, the steel sheet formed product manufactured by using the surface treatment method according to the present disclosure can be widely used for various purposes, such as products requiring color or design to ensure safety, and products beautifully decorating the aesthetic of cities.

[0057] The steel sheet formed product applying the surface treatment method thereto can require no separate coating after being installed on site, have excellent workability and corrosion resistance, and are easy to maintain and repair.

[0058] Specific effects are described along with the above-described effects in the section of Detailed Description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0059]

FIG. 1 is a sectional view of a galvanized steel sheet according to the present disclosure.

FIG. 2 is an enlarged view showing 'A' of the galvanized steel sheet of FIG. 1.

FIG. 3 shows an optical microscope photograph of a galvanized steel sheet according to embodiments of the present disclosure and comparative embodiments.

FIG. 4 is a scanning electron microscope (SEM) photograph of galvanized steel sheets according to embodiments of the present disclosure and comparative embodiments.

FIG. 5 is a photograph showing the results of corrosion tests on galvanized steel sheets according to embodiments of the present disclosure and comparative embodiments.

FIG. 6 is a photograph showing the results of cross-cut experiments on the galvanized steel sheets according to embodiments of the present disclosure and comparative embodiments.

DETAILED DESCRIPTION

[0060] Description will now be given in detail according to exemplary embodiments disclosed herein, with reference to the accompanying drawings.

[0061] The present disclosure may be applied to sheet metal formed products by rolling, pressing or the like and then galvanizing.

[0062] The present disclosure may include a process of surface-modification the galvanized layer, coating the surface-modified galvanized layer with a resin and adhering it. According to the present disclosure, the adhesive strength between the galvanized layer and the resin layer may be increased and durability may be improved. As a result, the steel sheet formed product manufactured by the present disclosure may have improved physical properties such as corrosion resistance, durability and formability.

[0063] A steel sheet formed product, to which the surface treatment method of the present disclosure can be applied, may be provided by forming a normal steel sheet using a conventional roller, die, press, etc. and galvanizing the formed steel sheet.

[0064] Such the steel sheet formed product, which has been galvanized in the above-mentioned way, may be outsourced and stored.

[0065] First, the surface treatment method of the steel sheet formed product according to the present disclosure may proceed a surface modification treatment process of immersing the received galvanized steel sheet product in an eco-friendly surface treatment composition solution and performing electrolytic corrosion by using the galvanized steel sheet formed product as an anode and lead or copper as a cathode, to increase surface roughness. Accordingly, water washing treatment, surface modification treatment and degreasing treatment may be performed simultaneously.

[0066] Next, there may be a process of coating a resin on the galvanized layer corroded by the surface modification treatment process and a process of heating the resin-coated coating layer to bring it into close contact with the galvanized steel sheet formed product.

[0067] Accordingly, the steel sheet formed product manufactured by the above-described surface treatment method may include a formed base steel sheet 10; a galvanized layer 20 formed on the base steel sheet 10 and subjected to the surface modification treatment; and a resin coating layer 30 and 40 formed on the galvanized layer.

[0068] While being manufactured through the above-described surface treatment method, such the steel sheet formed product can be efficiently produced by passing through an electrolytic device for immersing the galvanized steel sheet formed product in a surface treatment composition solution and electrolytically etching, a first electrodeposition resin coating device, a second general coating resin coating device, a post-heating device, and a cooling device.

[0069] As a result, the steel sheet formed product having been through the surface treatment method may have a structure in which the first and second resin coating layers are coated in multiple layers on the surface of the steel sheet formed product.

[0070] As described in the background art, corrosion or oxidation is likely to occur in steel sheet formed products of road structures such as guardrails, traffic lights, streetlights, overpasses, etc., which are formed from steel sheets and galvanized by the conventional galvanizing method. Due to this, there is a problem in that the durability is lowered and the service life is then rapidly shortened.

[0071] For this purpose, in normal cases, a method of plating the surface of the base steel sheet or a method of coating the plated surface with a resin are used. However, the adhesive strength between the plating layer plated on the surface of the base steel sheet and the resin coating layer to protect it is not high, corrosion could occur on the galvanized surface and then the base steel sheet and the resin coating layer could be easily separated.

[0072] According to the present disclosure, by applying the surface treatment method of the embodiments to the conventional galvanized steel sheet formed product, it is possible to obtain an effect of improving the adhesive strength and mechanical properties while forming the coating layer. In addition, according to the present disclosure, it is also possible to manufacture a galvanized steel sheet formed product in which a coating layer exhibiting such an effect is coated in a multi-layered structure.

[0073] Hereinafter, the surface treatment method of the steel sheet formed product according to the present disclosure will be described in detail.

[A step of preparing a galvanized steel sheet formed product]

[0074] First of all, a type of a base steel plate constituting the steel sheet is not particularly limited. The type of the base steel sheet may be a hot-rolled steel sheet or a cold-rolled steel sheet. A type of metal constituting the steel sheet is not particularly limited. The type of metal may include a steel sheet using carbon steel, alloy steel or stainless steel and the like.

[0075] A plating layer formed on the steel sheet formed product may include aluminum and magnesium, in addition to zinc. If necessary, the plating layer may further include one or more selected from the group consisting of Si, Be, Ni and Zr.

[0076] As one example, the plating may be formed by using a hot-dip galvanizing method (GI) in which a steel sheet is deposited in a molten zinc, and an alloy hot-dip galvanizing method (GA) in which a steel sheet is immersed in the molten zinc and then subjected to a heat treatment process to induce alloying, or an electrogalvanizing method (EG) using an electrolytic method. The

hot-dip galvanizing method GI, the ally hot-dip galvanizing method GA and the electrogalvanizing method EG are well-known knowledge in the art to which the present disclosure pertains, and detailed description thereof will be omitted accordingly.

[0077] The galvanized steel sheet formed product may be outsourced and supplied. In embodiments, the use of the steel sheet formed product to which the hot-dip galvanizing method is applied is exemplified.

[An electrolytic corrosion processing step of simultaneous performing washing treatment, surface modification treatment and degreasing treatment of the prepared galvanized steel sheet formed product]

[0078] The prepared galvanized steel sheet formed product may undergoes the electrolytic corrosion processing step in a predetermined surface treatment composition solution, thereby a washing treatment, a surface modification treatment to increase a surface roughness, and a degreasing treatment therefor may be performed simultaneously.

[0079] The prepared galvanized steel sheet formed product may be electrolytically corroded in a baking soda solution which is the surface treatment composition. This can be used as a method of immersing the galvanized steel sheet formed product in the prepared baking soda solution and corroding it electrolytically. For example, when the corrosion process is performed, the temperature of the baking soda solution whose main solvent is water may be 0°C to 60°C, more preferably 5°C to 40°C. After forming the electrolytic corrosion process on the galvanized steel sheet product in the baking soda solution as described above, the steel sheet formed product is washed.

[0080] According to the present disclosure, the baking soda solution which is the surface treatment composition is prepared by dissolving baking soda in water and a solution of 10wt% to 50wt% is used. If the concentration of the baking soda solution is less than 10wt%, the reaction rate is slowed down, and the surface of the galvanized steel sheet formed product is not corroded, which is the main cause of peeling of the coated resin layer which would be coated in the subsequent process. If the concentration of the baking soda solution is 50wt% or more, the baking soda is no longer dissolved at room temperature and precipitated.

[0081] The prepared galvanized steel sheet formed product is immersed in the baking soda solution and used as an anode. Copper or lead is used as a cathode.

[0082] The higher the temperature of the baking soda solution, the faster the reaction rate. However, the appropriate temperature is 60 °C ~ 85 °C, and the appropriate voltage is 10V ~ 36V DC. Preferably, the voltage may be 12V to 24V DC. In the embodiment, it is exemplified that the voltage is 24V DC.

[0083] This electrolytic corrosion process is intended to form an optimal surface roughness to greatly improve

adhesion between the galvanized layer and the first electrodeposition resin coating layer of the steel sheet formed product to be followed. The electrolytic corrosion process is a kind of an etching process to obtain uniform and sufficiently deep surface roughness. If the surface roughness of the galvanizing during the electrolytic corrosion process is not sufficient, the adhesion between the resin layer formed by the first electrodeposition coating which is the subsequent process and the surface of the steel sheet formed product is reduced. If the adhesion between the first electrodeposition coating resin coating layer is reduced, there is a significant effect on adhesion and close contact strength of a second general coating which is the subsequent process.

[0084] According to the present disclosure, after the electrolytic corrosion process, a process of coating the galvanized steel sheet formed product in a solution containing zirconium compounds may be further performed.

[0085] The zirconium compound solution, which is the surface treatment composition, may be manufactured by containing 0.5 to 3.0 g/L of hexafluorotitanic acid, 1.0 to 5.0 g/L of hexafluorozirconic acid, 0.1 to 2.0 g/L of aminomethyl-substituted polyvinylphenol, and water as the remainder.

[0086] A coating film may be formed by immersing the hot-dip galvanized steel sheet formed product in the zirconium compound solution. Heat treatment of the coating film may be performed at a temperature 100°C or higher.

[0087] Then, the galvanized steel sheet formed product coated with the zirconium compounds may exhibit sufficient color development and excellent processability, and may provide a colored painted metal surface that prevents discoloration or fading of a colored film due to light irradiation over time.

[A step of coating a resin on the galvanized layer of the surface-modified steel sheet product]

[0088] In a state where the surface-modified steel sheet formed product is heated at a predetermined temperature, the first electrodeposition coating resin coating and the second general coating resin coating are performed for double-coating on the galvanized layer provided in an inner or outer surface of the steel sheet formed product.

[0089] Accordingly, compared to the case of performing only the general resin coating without the electrodeposition coating, the close contact strength and adhesion between the galvanized layer and the resin coating layer of the steel sheet formed product may be further improved. For example, peeling strength is improved, durability and abrasion resistance are improved, and antibacterial properties, oxidation resistance and ductility can be exhibited by the coating layer in the multilayered structure. Accordingly, the use and utilization of the final product can be greatly expanded.

① 1st Electrodeposition Coating Resin Coating Process

[0090] As a primer for the galvanized steel sheet formed product, electrodeposition coating is applied. The electrodeposition is performed to form the resin coating layer thick and improve the close contacting strength between the galvanized layer and the second general coating resin coating layer of the steel sheet formed product. the electrodeposition is performed by immersing a coating target in an electrodeposition paint so that the coating target may be uniformly painted on the inner surface as well as the outer surface.

[0091] In such the electrodeposition, after immersing the galvanized steel sheet formed product in a tank containing the electrodeposition paint, a voltage is applied between the galvanized steel sheet formed product and an electrode to form the electrodeposition coating layer on the surface of the galvanized steel sheet formed product. specifically, by applying a voltage to the electrodeposition paint to cause current to flow, positive ion particles move to the negative electrode and negative ion particles move to the positive electrode. This phenomenon is used to form a coating layer, that is, the first electrodeposition coating resin coating layer on the surface of the galvanized steel sheet formed product.

[0092] The electrodeposition paint used in the electrodeposition coating process may use both a cationic paint and an anionic paint. Preferably, a cationic epoxy-based paint having excellent corrosion resistance may be used. In addition, depending on the purpose, it is of course possible to use all kinds of electrodeposition paints such as cationic acrylic paints and anionic epoxy paints.

[0093] In an embodiment of the present disclosure, an acrylic electrodeposition coating resin and an epoxy-based electrodeposition coating resin are used in the first electrodeposition coating.

[0094] The components of the paint used for the acrylic electrodeposition coating are propylene glycol methyl ether: 1-5%, propylene glycol phenyl ether: 1-5%, hexone: 0.1-1%, 2-butoxyethanol: 0.1 ~%, α -[3-[3-(2H-benzotriazol-2-yl)]derivatives: 0.1~%, and dibutyltin diacetate: 0.1~1vol%.

[0095] The components of the paint used in the epoxy-based electrodeposition coating may be titanium dioxide: 10-20 vol%, 2-butoxyethanol: 10-20%, kaolin: 5-10%, dibutyl tin oxide: 1- 5%, Poly[oxy(methyl-1,2-ethanediyl)] α -(methylphenyl)- ω -hydroxy: 1~%, Hexon: 0.1-1%, Trimethylolpropane: 0.1-1%, and Carbon black : 0.1~1%. Bis(2-(2-butoxyethoxy)ethoxy)methane: 1-5%, 4,4'-Isopropylidenediphenol: 1-5%, and mixture of 2-methyl-3(2H)-isocyanate zolones and 5-chloro-2-methyl-3(2H)-isothiazolone: not more than 0.1% may be composed as a binder.

[0096] As another epoxy resin, an epoxy resin having a number average molecular weight of 3,000 to 7,000 dispersed or emulsified in water, in particular, diglycidyl ether type epoxy resin may be used. At this time, it is

preferred that the resin dispersed or emulsified in water has a maximum particle diameter of 10 microns or less. If the number average molecular weight of the epoxy resin is less than 3,000, it reacts with amines or amides rather than reacting with melamine resin, which is a curing agent. If the number average molecular weight exceeds 7,000, the time required to dissolve the epoxy resin in a solvent to make it a water-soluble resin increases, making it difficult to manufacture the resin.

[0097] In addition, the smaller the particle diameter of the epoxy resin dispersed or emulsified in water, the better. If the maximum resin particle diameter exceeds 10 microns, the reactivity with melamine resin is reduced, and when coating a resin composition containing metal powder, the film becomes non-uniform due to the large resin particles. Accordingly, there is a risk of occurrence of incompletely covered spots.

[0098] The process of forming the first electrodeposition coating resin coating layer on the surface of the product coated with the galvanized layer may be performed at 150°C to 300°C. Preferably, the process may be performed at 200°C to 250°C. In order to uniformly form the first electrodeposition coating resin coating layer on the top of the galvanized steel sheet product, it is effective to maintain a preheating temperature of the galvanized steel sheet formed product.

[0099] At this time, if the formation temperature of the first electrodeposition coating resin coating layer is less than 150°C, the first electrodeposition coating resin coating layer is not sufficiently melted, so that a uniform electrodeposition coating resin coating layer cannot be formed on the surface of the steel sheet. When the temperature exceeds 300°C, the resin coating layer is thermally decomposed and the adhesive strength may be greatly reduced.

[0100] Preferably, the thickness of the first electrodeposition coating resin coating layer is 0.1 mm to 0.4 mm, more preferably 0.1 mm to 0.2 mm.

[0101] In conclusion, the first electrodeposition coating resin coating layer may play a role of preventing peeling between the resin coating layer and the galvanized steel sheet molded product caused by the difference between the components of the base portion of the steel sheet and the outermost second general coating resin coating layer.

② 2nd General Coating Resin Coating Process

[0102] The second general coating resin coating process is a process of re-coating a second general resin on the base steel sheet coated with the first electrodeposition coating resin. The composition used in the second general resin coating process can be used with all types of resins such as acrylic, urethane, and epoxy resins, and can also be implemented in various colors depending on use.

[0103] If necessary, a process of re-coating a third general coating resin may be further performed on the base

steel sheet coated with the second general coating resin. If necessary, a process of re-coating a fourth general coating resin on the base steel sheet coated with the third general coating resin. That is, the general coating process may be performed twice or more.

[0104] If necessary, the second general coating resin coating process may be omitted.

[A step of heating the resin-coated coating layers and bringing them into close contact with the galvanized steel sheet formed product]

[0105] After the second general coating resin coating, the resin coating layers, a post-treatment heating process for smoothing an irregular fusion of the resin coating layers on the surface of the galvanized steel sheet formed product may be performed at 50°C to 100°C, preferably 70°C to 90°C.

[0106] This process may be a process in which the first and second resin coating layers formed on the inner surface and the outer surface of the galvanized steel sheet are simultaneously fused by pressing and frictionally driving the steel sheet formed product, which has the first electrodeposition coating resin coating layer and the second general coating resin coating layer formed therein, with a roller or the like, thereby forming uniform and smoothed resin coating layers with a predetermined thickness.

[0107] After performing the post-treatment heating process, a process of may be performed in which the heated galvanized steel sheet product is water-cooled while passing through cooling water or aircooled.

[0108] Through such post-treatment heating and cooling processes, the adhesion and close contacting strength between the galvanized steel sheet formed product and the electrodeposition coating resin coating may be further secured, and then corrosion resistance and durability may be secured accordingly.

[0109] Meanwhile, the resin coating process and the coating layer close contacting process described above may include a process of coating the surface of the base steel sheet with a resin in the second general coating without electrodeposition coating and a process of heating and cooling the base steel sheet coated with the second general coating resin.

[0110] The resin coating process and the coating layer close contacting process may include a process of coating a second general coating resin on the surface of the base steel sheet and re-coating a third general coating resin on the base steel sheet coated with the second general coating resin; and a process of re-heating and cooling the re-coated base steel sheet.

[0111] As such, the process of coating the upper and lower surfaces of the galvanized steel sheet formed product in triple, quadruple or more layers of resin coating may be easily modified and carried out by those skilled in the art.

[0112] Since the resin coating galvanized steel sheet

formed product according to the present disclosure uses the steel sheet formed product galvanized on the base steel sheet, it basically has an integrated coating structure in which the resin layer is coated on the surface of the galvanized layer in multiple layers. The first electrodeposition resin coating layer is fused to the heated metal component and has excellent adhesion, and at the same time, it has excellent adhesive performance, and is firmly bonded to another material, that is, the second general coating resin coating layer, so that the adhesion of the coating is excellent.

[0113] In addition, the baking soda solution, which is the surface treatment composition for the galvanized steel sheet of the present disclosure, contains no chrome, so it is eco-friendly and harmless to human bodies. Meanwhile, when performing the surface modification treatment for the galvanized steel sheet formed product by using the baking soda solution, excellent corrosion resistance and excellent close contacting strength of the coating layer may be exhibited compared to the conventional surface treatment method.

[0114] Hereinafter, the present disclosure will be described in detail based on embodiments and comparative embodiments.

<Embodiment>

[0115] The present disclosure performs degreasing → pickling → washing with water → flux → drying → plating → cooling processes.

[0116] Specifically, ① The degreasing process is performed as a dipping process for 3 to 5 minutes with a 99% concentration of chloric methane solution at a temperature of 2°C ~ 38°C,

② The pickling process is performed as a dipping process for 20 to 120 minutes with hydrochloric acid (HCl) at a temperature of 8°C to 38°C and a concentration of 4% to 25%,

(3) The water washing process is performed by primary and secondary immersion in a solution of pH: 1 to 6 at room temperature for 30 seconds,

④ The flux process is performed as an immersion process for 2 to 3 minutes at a temperature of 50°C ~ 90°C and a concentration of 11Be ~ 25Be,

⑤ The drying process is performed by air cooling,

⑥ The hot-dip galvanizing process is a process in which the temperature of the hot-dip galvanizing bath is immersed in a short time at 450°C ± 10°C, and then lifted for 30 seconds to 600 seconds,

⑦ The cooling process is performed by air cooling for 30 seconds, immersion at a temperature of 35°C to 45°C for 1 minute, and then cooling,

[0117] The hot-dip galvanized steel plate molded product is manufactured through those processes.

[0118] This hot-dip galvanized steel sheet formed product was washed with water and pickled using distilled

water and dilute acid to perform a cleaning process. After taking a specimen of 1.8 dm² of the washed galvanized steel sheet, electrolytic corrosion in which copper or lead is used as the cathode and the hot-dip galvanized steel sheet is used as the anode in a 10 wt% solution of baking soda at 60°C is performed at 10V DC for 60 seconds. Then, it is washed twice with industrial water, and coated with Zr Phosphate at room temperature to increase paint adhesion. As a post-treatment heating process, the drying step was performed in a drying furnace at 150 to 230°C. for 20 to 60 minutes, followed by air cooling at room temperature.

<Comparative Embodiment>

[0119] A galvanized steel sheet formed product without the surface modification treatment of the embodiment is selected as a comparative embodiment. That is, in the Comparative Example, a galvanized steel sheet formed product is manufactured by a process of a conventional phosphate coating treatment which the process of electrolytic corrosion with the baking soda solution in the example was replaced with, and the rest of the process was performed by the same process as the above example.

[0120] FIG. 3 shows a 500-magnification microscopic image of a galvanized steel sheet according to embodiments of the present disclosure and comparative embodiments.

[0121] The cross section of the galvanized steel sheet formed product surface-treated with the baking soda solution shown in (a) shows a shape corroded with the same or similar surface roughness while being homogeneous as a whole. The phosphate surface-treated galvanized steel sheet formed product shown in (b) shows an inhomogeneous corrosion shape deeply corroded in each part.

[0122] The surface roughness was measured by the KTR Korea Testing & Research Institute KS B ISO 4287 method. The surface roughness of the galvanized steel sheet treated with the baking soda solution was average roughness (Ra): 1.55 μm, 10-point average roughness (Rz): 11.05 μm, whereas the surface roughness of the phosphate-coated galvanized steel sheet was average roughness (Ra): 1.25 μm, 10-point average roughness (Rz): 10.36 μm. That is, both Ra and Rz of hot-dip galvanized steel sheet surface treated with baking soda solution were higher than Ra and Rz of surface roughness of phosphate-coated galvanized steel sheet.

[0123] FIG. 4 is scanning electron micrographs of Examples and Comparative Examples, and like the result of FIG. 3, this is clearly demonstrated even at 1,000 magnification or 5,000 magnification. In other words, in the hot-dip galvanized steel sheet formed product subjected to phosphate surface treatment shown in (b), corrosion of the galvanized layer appears unevenly in each part, as observed in the optical micrograph. On the other hand, the scanning electron micrograph of the present invention surface-treated with a baking soda solution shown

in (a) shows a tendency of surface roughness showing a relatively uniform shape and depth even at 1,000 or 5,000 magnifications.

[0124] As a result, it can be confirmed that the surface roughness is increased due to the interaction of the hot-dip galvanizing surface layer and the baking soda solution in the baking soda solution electrolytic corrosion treatment process, and it has a characteristic of being corroded at a uniform and equal depth. Accordingly, it can be expected that various physical properties such as adhesion and corrosion resistance of the electrodeposition coating resin coating layer formed by the subsequent process are improved.

[0125] Figure 5 is a photograph showing the results of a corrosion resistance test on a hot-dip galvanized steel sheet formed product after the first electrodeposition coating resin coating according to Examples of the present invention and Comparative Examples.

[0126] The corrosion resistance test was performed for 30 minutes under the condition of 25 V DC in 30% saline.

[0127] It can be confirmed that while the surface condition of the hot-dip galvanized steel sheet formed product of Example treated with the baking soda solution shown in (a) was very good, the phosphate surface-treated hot-dip galvanized steel sheet formed product shown in (b) was corroded and red rust was generated.

[0128] FIG. 6 is a photograph showing the results of a cross-cut test after the first electrodeposition coating and the second general coating resin coating on galvanized steel sheet formed products according to Examples of the present invention and Comparative Examples.

[0129] While the surface condition of the hot-dip galvanized steel sheet formed product of Example treated with the baking soda solution shown in (a) was very good, it can be confirmed that the coating layer of the hot-dip galvanized steel sheet formed product subjected to surface treatment shown in (b) is peeled off while the painted surface is scratched.

[0130] As can be seen from the cross-cut test results, the adhesion strength between the hot-dip galvanized steel sheet formed product subjected to electrolytic corrosion with a baking soda solution as in the example of the present invention and the resin coating layer is superior to the adhesive strength of a hot-dip galvanized steel sheet formed product with phosphate surface treatment without electrolytic corrosion and a resin coating layer.

[0131] In conclusion, it can be confirmed that as the surface roughness increases by the baking soda solution treatment, the adhesion between the hot-dip galvanized steel sheet formed product and the resin coating layer also increases.

[Description of Symbols]

[0132]

10: Base steel sheet

20: Galvanized layer
 30: First electrodeposition coating resin coating layer
 40: Second electrodeposition coating resin coating layer

Claims

1. A surface treatment method of a steel sheet formed product comprising:

a first step of preparing a galvanized steel sheet formed product;
 a second step of performing surface-modification treatment for a galvanized layer of the prepared steel sheet formed product;
 a third step of coating a resin on the surface-modification-treated galvanized layer; and
 a fourth step of bringing the resin coating layer into close contact on the galvanized layer,
characterized in that
 the second step comprises a process of increasing a surface roughness by electrolytically etching the galvanized steel sheet formed product in a surface treatment composition solution.

2. The surface treatment method of the steel sheet formed product of claim 1, wherein the surface treatment composition comprises a baking soda solution.

3. The surface treatment method of the steel sheet formed product of claim 2, wherein the baking soda solution is prepared by dissolving 10wt% to 50wt% of baking soda in water.

4. The surface treatment method of the steel sheet formed product of claim 3, wherein the electrolytic corrosion is performed by using the galvanized steel sheet formed product as an anode and lead or copper as a cathode.

5. The surface treatment method of the steel sheet formed product of claim 4, wherein the electrolytic corrosion is performed by a voltage of 10V to 36V DC at a temperature of 60°C to 85°C.

6. The surface treatment method of the steel sheet formed product of any one of preceding claims, wherein after the second step, before the third step, a process of coating the galvanized steel sheet formed product in a solution containing zirconium compounds is further performed.

7. The surface treatment method of the steel sheet formed product of claim 6, wherein the zirconium compound solution is prepared by dissolving 0.5 wt% to 3.0 wt% of titanate, 1.0 wt% to 5.0 wt% of hexafluorozirconic acid, and 0.1 wt% to 2.0 wt% of amino

methyl substituted polyvinylphenol in water, and the zirconium compound coating process is performed at a temperature of 100°C or more and 200°C or less.

8. The surface treatment method of the steel sheet formed product of any one of preceding claims, wherein the third step comprises a process of coating the base steel sheet with a resin by a first electrodeposition coating.

9. The surface treatment method of the steel sheet formed product of claim 8, wherein the first electrodeposition coating is performed at 150°C to 300°C.

10. The surface treatment method of the steel sheet formed product of claim 8 or 9, wherein the third step performs a process of re-coating a resin by general coating once or twice or more on the base steel sheet coated with the resin by the first electrodeposition coating.

11. The surface treatment method of the steel sheet formed product of any one of preceding claims, wherein the fourth step comprises a process of heating the base steel sheet coated with the resin.

12. The surface treatment method of the steel sheet formed product of claim 11, wherein the fourth step further comprises a process of cooling the heated resin steel sheet.

13. The surface treatment method of the steel sheet formed product of any one of preceding claims depending on claim 8, wherein the fourth step comprises a process of heating the base steel sheet coated by the first electrodeposition coating process.

14. The surface treatment method of the steel sheet formed product of any one of preceding claims depending on claim 10, wherein the fourth step comprises a process of heating the base steel sheet re-coated with the resin by the general coating.

15. A steel sheet formed product comprising:

a formed base steel sheet (10);
 a galvanized layer (20) formed on the base steel sheet and surface-modification-treated through the second step of the surface treatment method of any one of preceding claims; and
 resin coating layers (30) and (40) coated on the galvanized layer (20) through the third step and the fourth step of the surface treatment method of any one of preceding claims.

FIG.1

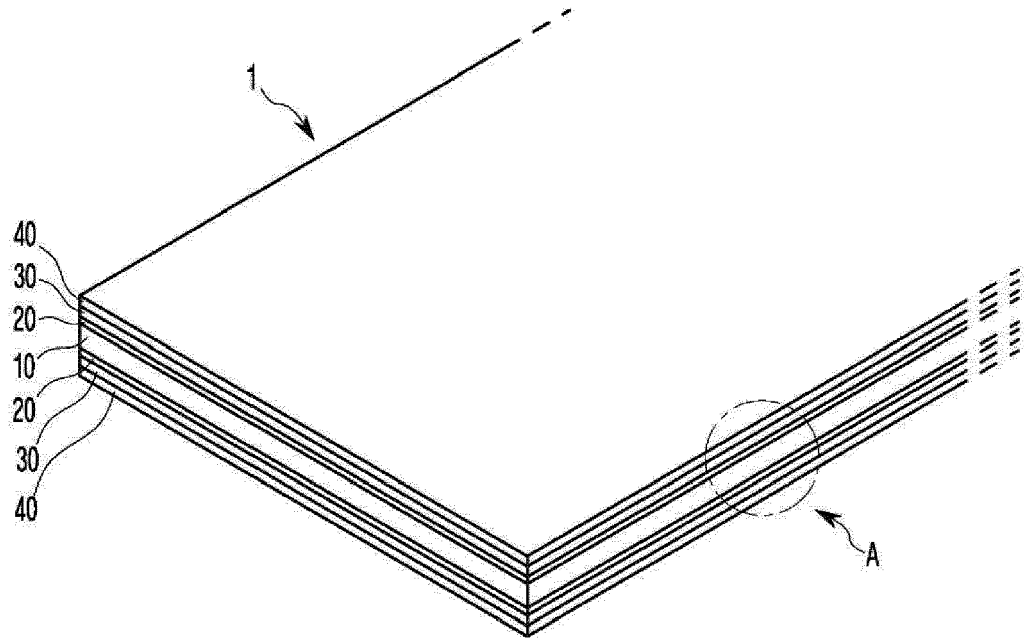


FIG.2

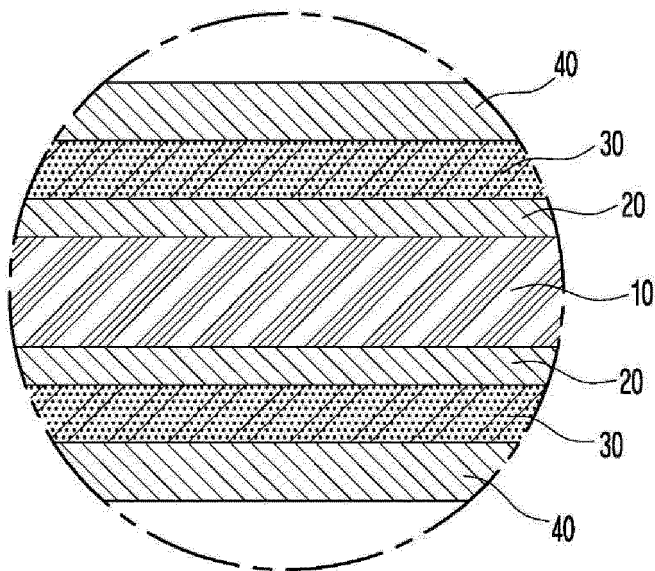


FIG. 3

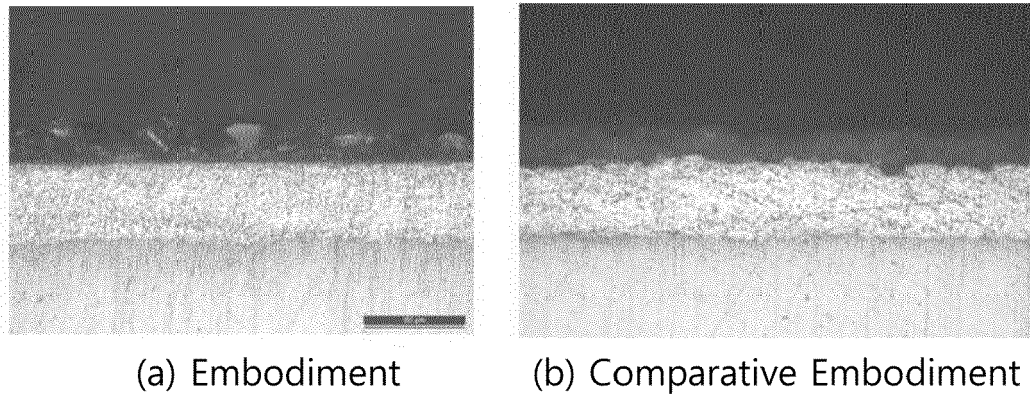


FIG. 4

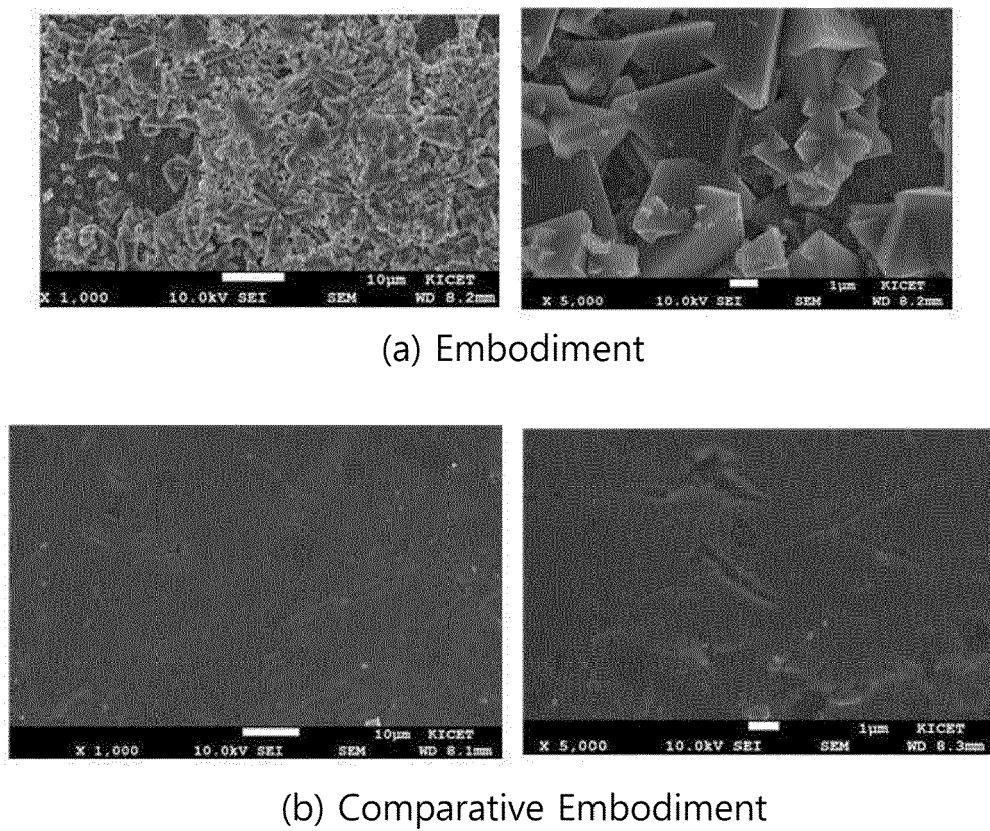


FIG. 5

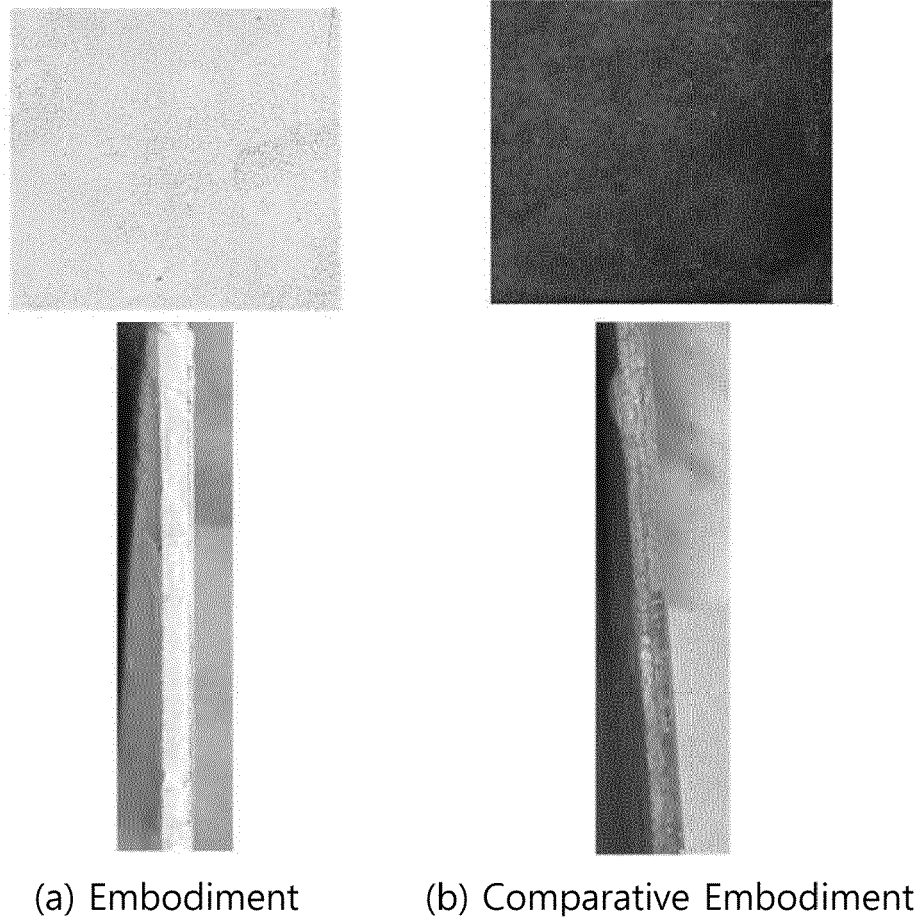
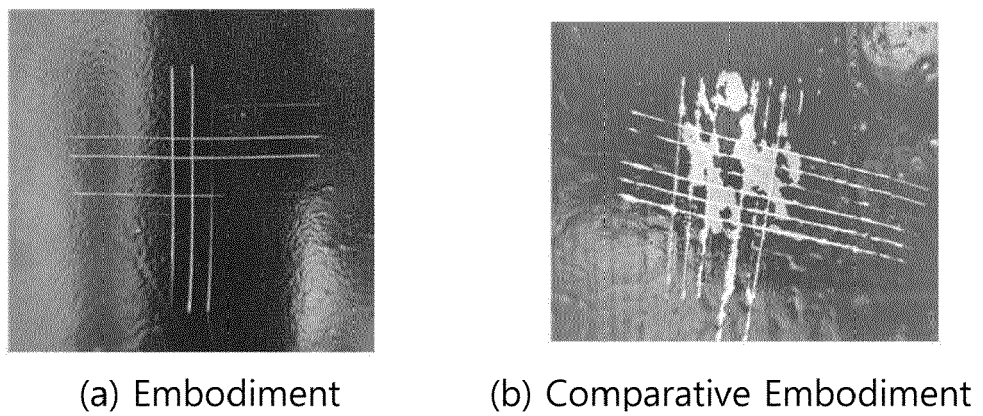


FIG. 6



REFERENCES CITED IN THE DESCRIPTION

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