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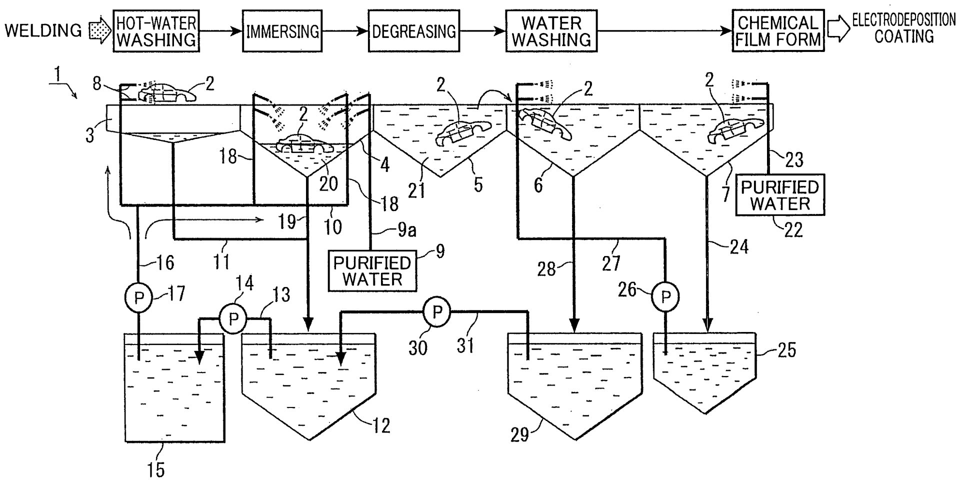
(54) Degreasing method and degreasing apparatus

(57) Prior to immersion of an object to be treated in a degreasing liquid, an aqueous solution 20 having a pH of 5.5 to 10. 0 is put into a sac-shaped portion of a vehicle body 2. Even when the vehicle body 2 is passed through the degreasing liquid, the aqueous solution 20 is not replaced with the degreasing liquid, and alkaline solid substances do not remain in the hemmed portion 2a. This prevents the water in the sac-shaped portion from having the high alkalinity even when water comes into the hemmed portion 2a later. The degreasing method can prevent the decrease in corrosion resistance of the joint portion of the object to be treated.

FIG.2



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Description

TECHNICAL FIELD

[0001] The present invention relates to a degreasing method and a degreasing apparatus.

BACKGROUND ART

[0002] In performing coating such as electrodeposition coating on an object, e.g., a vehicle body, a pretreatment is generally performed to remove oil and dust adhered to the object which has been subjected to welding or other processings, and to form a base coating on a surface of the object, as disclosed in Japanese Laid-Open Patent Publication No. 2004-238681. The pretreatment includes a hot-water washing step of immersing the object in hot water to remove dust and the like (e.g. iron powder) adhered to the object; a degreasing step of removing oil, dust and the like adhered to the object by a degreasing liquid; a water washing step of washing off the degreasing liquid adhered to the object in the degreasing step; a chemical film forming step of forming a chemical film on a surface of the object to enhance the coating adhesion after surface conditioning. After these steps are finished, electrodeposition coating is performed by immersing the object in a tank filled with a water-soluble coating material, and applying an electricity to the coating material in the tank to electrically form the object with a coating of the coating material.

[0003] However, it has been known that even in the case of electrodeposition coating, if the object has a joint portion such as a hemmed portion, a connection part between a flange and a corresponding member, corrosion or dissolution is likely to occur at the joint portion.

SUMMARY OF THE INVENTION

[0004] It is an object of the present invention to provide a degreasing method and a degreasing apparatus which both can prevent the corrosion resistance of a joint portion of a coated object from decreasing.

[0005] According to an aspect of the present invention, a degreasing method comprises allowing a joint portion of an object to be treated to have an aqueous solution having a pH of 5.5 to 10.0, and immersing the object in a degreasing liquid.

[0006] With this method, even when the object is immersed in the degreasing liquid, the aqueous solution in the joint portion of the object will not be replaced with the degreasing liquid. Accordingly, after the water of the aqueous solution evaporates in subsequent stages, alkaline solid substance does not remain in the joint portion. Accordingly, even if water comes into the joint portion during the use, the water in the joint portion will not have a strong alkalinity, thereby preventing the joint portion of the object from being corroded or dissolve by the water, that is, maintaining the corrosion resistance of the joint portion of the object.

[0007] It may be preferable that the immersing is performed before an electrodeposition coating is performed, and the aqueous solution contains a metal salt and metal ions of the metal salt at a concentration of 620 ppm or smaller when the metal salt is assumed to be converted to metal ions. In this modification, in the case where electrodeposition coating is conducted after the object is immersed in the degreasing liquid, aggregation (electrodeposition aggregation) of electrodeposition coating material liquid is likely to occur in the vicinity of the joint portion during the electrodeposition coating. However, the occurrence of electrodeposition aggregation can be prevented by the aqueous solution having a pH of 10 or lower and a concentration of 620 ppm or smaller when the metal salt is assumed to be converted to metal ions. Accordingly, in addition to the prevention of the corrosion of the joint portion of the object, electrodeposition aggregation can be prevented during the electrodeposition coating.

[0008] It may be preferable that the aqueous solution substantially contains no surfactant. This aqueous solution can more prevent the joint portion of the object from being corroded or dissolved.

[0009] It may be preferable that the degreasing liquid contains a surfactant at a first surfactant concentration, and the aqueous solution contains a surfactant at a second surfactant concentration that is equal to or smaller than 1/100 of the first surfactant concentration. In this modification, it is possible to use the aqueous solution containing the surfactant at the concentration equal to or smaller than 1/100 of the surfactant concentration of the degreasing liquid and having the pH of 5.5 to 10.0. Accordingly, the preparation of the aqueous solution can be easily industrialized, which thus makes it possible to industrially accomplish to maintain the corrosion resistance of the joint portion of the object. Further, the aqueous solution in the joint portion can suppress the degreasing of the joint portion to thus cause a noticeable amount of oil to remain in the joint portion. The remaining oil can further prevent corrosion of the joint portion.

[0010] It may be preferable that the joint portion of the object is shaped into a sac. In this modification, because the joint portion of the object is a sac-shaped portion, the existence of the aqueous solution in the sac-shaped portion can assuredly prevent another liquid from coming into the sac-shaped portion even when the object is immersed in another aqueous solution. If the degreasing liquid firstly exists in the sac-shaped portion, corrosion is likely to occur. On the other hand, if the aqueous solution having the pH of 5.5 to 10.0 firstly exists in the sac-shaped portion, the corrosion resistance of the sac-shaped portion can be effectively maintained.

[0011] It may be preferable that the object includes a plurality of plates which are jointed with each other, and the joint portion is at an overlapped part of plates. In this modification, because the object has a structure made up of a plurality of plates and the joint portion is constructed by stacking the plates to each other, the decrease in corrosion resistance of the plates forming the joint portion due to the degreasing liquid can be assuredly prevented.

[0012] It may be preferable to put the aqueous solution into the joint portion after the plurality of plates are joined to construct the object. In this modification, the aqueous solution is put into the joint portion after the plurality of plates are joined to construct the object, the aqueous solution can easily and reliably be present in the joint portion.

[0013] The joint portion may be preferably immersed in the aqueous solution contained in an immersing tank to put the aqueous solution into the joint portion. In this modification, because the joint portion is immersed in the aqueous solution contained in an immersing tank to put the aqueous solution into the joint portion, the aqueous solution can easily and reliably be present in the joint portion.

[0014] It may be preferable that the aqueous solution contains a surfactant at a concentration of 50 ppm to 190 ppm. In this modification, because the joint portion is immersed in the aqueous solution contained in an immersing tank to put the aqueous solution into the joint portion and the aqueous solution contains a surfactant concentration of 50 ppm to 190 ppm, the aqueous solution is provided with permeating power of the surfactant in addition to the maintaining of the corrosion resistance. Accordingly, the aqueous solution can be made to smoothly enter into the joint portion owing to the permeating power of the surfactant even if an amount of oil remains in the joint portion. In the case where the object is immersed in the aqueous solution in the immersing tank while being moved, the moving distance of the object in the immersing tank can be reduced, thereby reducing the volume of the immersing tank.

[0015] It may be preferable that the joint portion is immersed in the aqueous solution contained in an immersing tank to put the aqueous solution into the joint portion, the degreasing liquid contains a degreasing agent including a metal salt and a surfactant, and the aqueous solution in the immersing tank contains a part of used degreasing liquid, and has a degreasing agent concentration that is equal to or smaller than 1/10 of a degreasing agent concentration of the degreasing liquid. In this modification, the degreasing liquid contains the degreasing agent including a metal salt and a surfactant, and the aqueous solution in the immersing tank contains the used liquid recovered after being used in the immersing of the object with the degreasing liquid, and the metal ion concentration and the surfactant concentration are attained by adjusting the degreasing agent concentration of the aqueous solution that is equal to or smaller than 1/10 of the degreasing agent concentration of the degreasing liquid. Accordingly, the desired aqueous solution can be obtained by using the used liquid, and efficient use of water can be achieved while preventing the decrease in the corrosion resistance and the occurrence of the electrodeposition aggregation in the electrodeposition coating.

[0016] The aqueous solution may be preferably include ion-exchanged water. Because the ion-exchanged water is used for the aqueous solution, the aqueous solution does not contain chlorine ion, thereby preventing corrosion due to chlorine ion in addition to corrosion (dissolution) due to the degreasing liquid.

[0017] The aqueous solution may preferably include a buffer solution. Because the aqueous solution includes a buffer solution, the buffer solution component remains as solid substance in the joint portion after evaporation of the water. When water comes into the joint portion later, the water dissolves the solid substance, and provides a buffering effect (prevents the pH from changing to the alkaline side by dissolution of the object). Accordingly, due to the buffering effect, the joint portion can be prevented from being corroded.

[0018] The aqueous solution may preferably contain an anode reaction inhibitor. In this modification, because the aqueous solution contains the anode reaction inhibitor, the anode reaction inhibitor remains as solid substance in the joint portion after evaporation of the water. When water comes into the joint portion later, the anode reaction inhibitor (solid substance) dissolves in the water, captures metal ions (zinc ion, aluminum ion, and the like) eluding out from the object, and consequently forms a coating film. The coating film prevents further elusion of the metal ions. Accordingly, owing to this mechanism, the joint portion can be prevented from being corroded.

[0019] The aqueous solution may preferably contain a halogen capturing chemical element. In this modification, because the aqueous solution contains a halogen capturing chemical element (compound), the halogen capturing chemical element remains as solid substance in the joint portion after evaporation of the water. When water comes into the joint portion later, such rare earth element (solid substance) dissolves in the water, captures chlorine (halogen) contained in the entered water, and consequently forms a coating film. The coating film protects the object from chlorine. Accordingly, the corrosion of the joint portion due to chlorine can be prevented.

[0020] A surface of the object may be preferably made of an amphoteric metal. Because the surface of the object is made of an amphoteric metal, even if the object has a characteristic to dissolve in the strong alkalinity, the strong alkalinity is prevented. Accordingly, the object can be prevented from being dissolved or corroded.

[0021] According to another aspect of the invention, a degreasing apparatus comprises an aqueous solution supplier for supplying an aqueous solution to a joint portion of the object to be immersed in a degreasing liquid, the aqueous solution having a pH of 5.5 to 10.0.

[0022] With this apparatus, the aqueous solution is supplied into the joint portion of the object. The aqueous solution prevents another liquid from entering into the joint portion. Accordingly, after the water of the aqueous solution evaporates in subsequent stages , alkaline solid substance does not remain in the joint portion. Accordingly, even if water comes into the joint portion during the use, the water in the joint portion will not have a strong alkalinity, thereby preventing the joint portion of the object from being corroded or dissolve by the water.

[0023] The aqueous solution supplier may preferably include an immersing tank holding the aqueous solution containing a surfactant at a concentration of 50 ppm to 190 ppm. In this modification, the aqueous solution has a permeating power of the surfactant in addition to the maintaining of the corrosion resistance. Accordingly, the aqueous solution can be made to smoothly enter into the joint portion owing to the permeating power of the surfactant even if an amount of oil remains in the joint portion. The moving distance of the object in the immersing tank can be reduced, thereby reducing the volume of the immersing tank.

[0024] The aqueous solution supplier may preferably include an immersing tank holding the aqueous solution not containing a substantial amount of a surfactant. In this modification, the aqueous solution can more prevent the joint portion of the object from being corroded or dissolved.

[0025] These and other objects, features, aspects, and advantages of the present invention will become more apparent from the following detailed description of the preferred embodiments/examples with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026]

FIG. 1 is a graph showing a dissolution speed of a zinc plating.
FIG. 2 is an illustration diagram of a pretreatment equipment according to a first embodiment of the present invention.
FIG. 3 is a partially enlarged sectional view of a hemmed portion at a periphery of an object to be treated.
FIG. 4 is a graph showing a relation between the pH of an aqueous solution and a plating dissolution rate.
FIG. 5 is a perspective view showing a test piece used for obtaining the result shown in FIG. 4.
FIG. 6 is a diagram showing properties of an aqueous solution for an immersing step.
FIG. 7 is a graph showing a durability comparison between a finished product with the solid substance of a degreasing liquid remaining thereon and a finished product without the solid substance of a degreasing liquid remaining thereon.
FIG. 8 is a sectional view showing an occurrence of coating-swelling rust or blister at the hemmed portion.
FIG. 9 is a sectional view showing a mechanism of occurrence of electrodeposition aggregation in an electrodeposition coating step.
FIG. 10 is a table diagram showing an effect of the pH and a converted metal ion concentration of the aqueous solution in the immersing step against electrodeposition aggregation.
FIG. 11 is a graph showing an effect of a surfactant concentration against a solution inflow speed or infiltration performance.
FIG. 12 is a graph showing a relation between a surfactant concentration of the aqueous solution and a plating dissolution rate in a joint portion.
FIG. 13 is a table diagram showing specific results or numerical values of the relation shown in FIG. 12.
FIG. 14 is a conceptual diagram showing a state of electrodeposition aggregation in the electrodeposition coating step.
FIG. 15 is a conceptual diagram showing a subsequent state advanced from the state shown in FIG. 14.
FIG. 16 is a conceptual diagram showing a further subsequent state advanced from the state shown in FIG. 15.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT OF THE INVENTION

[0027] Inventors of the present invention have studied the problems of the prior art, and obtained the following findings:

(1) An object to be treated is immersed in hot water in a hot-water washing step, but the hot water used in this step is likely to contain an amount of degreasing liquid. Specifically, for efficient use of water, a mixture of water used in the hot-water washing step and water used in a water washing step is repeatedly used for the hot-water washing step. The water used in the water washing step contains an amount of degreasing liquid because degreasing liquid comes into the object in the degreasing step. Accordingly, the hot water in the hot-water washing step contains an amount of degreasing agent at a concentration which is not as high as the degreasing agent concentration of the degreasing liquid in the degreasing step but considerably high.

(2) Hot water which has entered in the joint portion, especially in a sac-shaped joint portion, of the object in the hot-water washing step is hard to go out of the joint portion. It is very difficult to replace the hot water in the joint portion with another treatment liquid even if the object comes into subsequent immersing steps. At the very end, the hot

water evaporates in the electrodeposition coating step or baking step, and only solid substances contained in the hot water remain in the joint portion.

(3) A material which has at least a surface made up of an amphoteric element (e.g. a galvanized steel sheet, and an aluminum material) is often used for an object to be subject to electrodeposition coating. Such a material tends to corrode or dissolves both in strong acidity and in strong alkalinity as shown in FIG. 1 which is extracted from "Hot Dip Galvanization" written by Takayoshi Katsuyama. Accordingly, to prevent degreasing liquid from dissolving the object in the degreasing step, an upper pH limit of the degreasing liquid is set with respect to the alkalinity, e.g., pH of 10.9 to 11. 7 for a galvanized steel sheet. However, in the case where a liquid having a pH below the upper limit comes into the joint portion and only solid substances remain in the joint portion after evaporation of the water, it likely occurs that a small amount of water (moisture, dew condensation, or water infiltration) comes into the joint portion to thereby produce a degreasing liquid having a high concentration and a pH high enough to dissolve the object. Owing to the findings, the present inventions have been worked out.

[0028] An embodiment according to the present invention will be described with reference to the drawings. In this embodiment, as an example, an object to be treated is a vehicle body which includes a plurality of panels which are jointed with one another by means of spot welding and the like. The panel is made of a galvanized steel sheet which is plated with zinc. Zinc is an amphoteric element.

[0029] Between a welding of jointing panels with one another to thereby a vehicle body 2 and electrodeposition coating, a hot-water washing step, an immersing (degreasing pretreatment) step, a degreasing step, a water washing step, and a chemical film forming step including a surface conditioning are performed. As shown in FIG. 2, a coating pretreatment equipment 1 includes a hot-water washing tank 3, an immersing tank 4, a degreasing tank 5, first and second water washing tanks 6 and 7, and a chemical film forming tank (not shown) to accomplish the above-mentioned steps.

[0030] The hot-water washing tank 3 is provided with a high-pressure spray 8 above its upper opening to remove dust and the like (e.g. iron powder) adhered to the vehicle body 2 by a high-pressure spray 8 which is supplied with circulating water through a supply pipe 16 by a pump 17. The hot-water washing tank 3 is provided with a drain pipe 11 at a bottom thereof to thereby recover the used water from the hot-water washing tank 3 to a recovery tank 12 through the drain pipe 11. The used water in the recovery tank 12 is sent by a pump 14 through a pipe 13 to the iron powder removing apparatus 15 where iron powder is removed from the used water to produce the circulating water.

[0031] The circulating water is supplied from the iron powder removing apparatus 15 into the immersing tank 4 sequentially through the supply pipe 16, a branch pipe 10 and a branch pipe 18. The immersing tank 4 is connected at its bottom to the recovery tank 12 through a drain pipe 19, and the immersing tank 4 always holds an aqueous solution 20 at least at a certain volume which allows the vehicle body 2 to be fully immersed therein. The aqueous solution 20 in the immersing tank 4 is maintained at a predetermined quality which is defined as a concentration of degreasing agents of a part of the degreasing liquid which has come from the subsequent step, the degreasing agent including a surfactant and other substances. Specifically, the aqueous solution 20 is kept to have a degreasing agent concentration which is equal to or smaller than 1/100 of a decreasing agent concentration of the degreasing liquid used in the degreasing tank 5, and to have a PH of 5.5 to 10.0, and a water temperature near the room temperature, e.g., 25˚ C or lower.

[0032] In the present embodiment, the aqueous solution 20 contains a buffer solution or a buffer solution component (a weak acid salt or a weak alkali salt, e.g., ammonium acetate), an anode reaction inhibitor, and a halogen capturing chemical element capable of capturing chlorine. As the buffer solution or the buffer solution component, an acetic acid buffer solution (acetic acid and sodium acetate), a phosphate buffer solution (phosphoric acid and sodium phosphate), a citrate buffer solution (citric acid and sodium citrate), a boric acid buffer solution, a tartaric acid buffer solution, a tris buffer solution (tris(hydroxymethyl)ammonium), silica or the like is used. As the anode reaction inhibitor, a chelating agent which captures metal ion or a phosphate pigment is used. As the halogen capturing chemical element, a compound containing Pb, Ce, Bi or the like is used.

[0033] Although the quality of the aqueous solution 20 is controlled as described above, a purified water supply source 9 is further provided to adjust the degreasing agent concentration of the aqueous solution 20 in the immersing tank 4. The purified water supply source 9 supplies purified water into the immersing tank 4 through a purified water supply pipe 9a, and the purified water from the purified water supply source 9 is used mainly to adjust the degreasing agent concentration through dilution. In the present embodiment, the purified water supply source 9 sends out ion-exchanged water as the purified water by a pump. Obviously, the ion-exchanged water does not contain chlorine (hypochlorous acid; HOCl). HNO_3 or the like is used to adjust the pH of the aqueous solution 20 in the immersing tank 4. This water quality control is reflected in the quality of the circulating water in the iron powder removing apparatus 15, and the quality of the circulating water from the iron powder removing apparatus 15 is controlled so as to have the same degreasing agent concentration, pH and water temperature as the aqueous solution 20 in the immersing tank 4 based on this water quality control.

[0034] The degreasing tank 5 is filled with a degreasing liquid 21 to remove oil, dust and the like adhered to the vehicle body 2. The degreasing liquid 21 contains an alkaline builder (e.g. alkaline silicate, alkaline carbonate, and alkaline phosphate) and a surfactant (nonionic surfactant), and its pH is controlled so as to range from 10.9 to 11.7 to prevent the zinc plating of the vehicle body 2 (the panels) from being corroded. Although not shown, a blocking structure is provided between the degreasing tank 5 and the immersing tank 4 to prevent the degreasing liquid 21 from flowing into the immersing tank 4 when the vehicle body 2 is carried into the degreasing tank 5.

[0035] The first and second water washing tanks 6 and 7 are arranged adjacent to each other so as to make a line together with the other tanks in the step advancing direction, and filled with water for washing away the degreasing liquid 21 adhered to the vehicle body 2. Purified water is supplied from a purified water supply source 22 through a water supply pipe 23 into the second water washing tank 7, while the water in the second water washing tank 7 is drained from its bottom through a drain pipe 24 into a recovery tank 25. The recovered water in the recovery tank 25 is pumped out by a pump 26 through a supply pipe 27 into the first water washing tank 6, and the water in the first water washing tank 6 is drained from its bottom through a drain pipe 28 into a recovery tank 29. The recovered water in the recovery tank 29 is pumped out by a pump 30 through a pipe 31 into the recovery tank 12. Consequently, a considerable amount of degreasing liquid which is contained in the first and second water washing tanks 6 and 7 enters the recovery tank 12 and the powder iron removing apparatus 15, and comes into the circulating water from the powder iron removing apparatus 15. However, the water quality control is performed in the immersing tank 4 and the iron powder removing apparatus 15 as described above, and the purified water is supplied from the purified supply source 9 for dilution when the degreasing agent concentration of the degreasing liquid in each of the tanks 4 and 15 exceeds the aforementioned predetermined concentration.

[0036] The following will describe a coating pretreatment method together with a degreasing method included therein, using the coating pretreatment equipment 1.

[0037] When the welding is finished, the vehicle body 2 is carried above the upper opening of the hot-water washing tank 3 using a hanger (not shown) for the hot-water washing step. In this position, the vehicle body 2 receives water sprayed from the high-pressure spray 8 to thereby remove dust and the like (e.g. iron powder) adhered to the vehicle body 2.

[0038] When the hot-water washing step is finished, the vehicle body 2 is carried to the immersing tank 4 where the immersing step is performed as a degreasing pretreatment. The vehicle body 2 is passed through the immersing tank 4 such that at least a door window lower portion of the vehicle body 2 is immersed in the aqueous solution 20 in the immersing tank 4 (half dip). The aqueous solution 20 in the immersing tank 4 comes into a joint portion 2a of the vehicle body 2 for the first time. More specifically, the joint portion 2a of the vehicle body 2 includes a hemmed portion or a sac-shaped portion, which is formed by an outer panel 34 and an inner panel 35 along the periphery of a door as shown in FIG. 3 (the same numeral 2a as the joint portion is used for the hemmed portion) and a joint portion between a flange and its partner member. The aqueous solution 20 comes into these joint portions 2a.

[0039] When the immersing step is finished, the vehicle body 2 is carried into the degreasing liquid 21 in the degreasing tank 5 where the degreasing step is performed, thereby removing oil, dust and the like adhered to the vehicle body 2. However, the degreasing liquid 21 cannot replace the aqueous solution 20 which has entered into the hemmed portion 2a or the sac-shaped portion, and the aqueous solution 20 remains in the sac-shaped portion.

[0040] When the degreasing step is finished, the vehicle body 2 is led to the electrodeposition coating and baking after going through the water washing step and the chemical film forming step, and the aqueous solution 20 in the hemmed portion 2a of the vehicle body 2 evaporates during the electrodeposition coating step and the baking. Consequently, only the solid substance such as the buffer solution component and the anode reaction inhibitor remains in the hemmed portion 2a, but alkaline solid substance does not remain therein. Even after a vehicle is commercially supplied as a finished product, only the solid substance (such as the buffer solution component and the anode reaction inhibitor) of the aqueous solution 20 which has entered into the sac-shaped portion of the vehicle body 2 during the immersing step continues to remain therein.

[0041] In the vehicle manufactured through this coating pretreatment method, when water in the form of moisture, dew condensation or water infiltration comes into the joint portion 2a of the vehicle body 2 regardless of the presence of a waterproof seal, the solid substance in the joint portion 2a dissolves in the water. The solid substance does not include alkaline solid substance, and has just additives such as the buffer solution component. Accordingly, even when the solid substance dissolves in the water, its pH does not rise to a high alkaline pH which causes zinc plating to dissolve, thereby preventing the joint portion 2a of the vehicle body 2 such as the hemmed portion from being corroded.

[0042] On the other hand, if the above immersing step is not performed and the degreasing liquid comes into the joint portion 2a such as the hemmedportion during the degreasing step, the solid substance of the degreasing liquid left in the joint portion 2a such as the hemmed portion will react with water (in the form of moisture, dew condensation or water infiltration) as shown in Formula 1, and the pH of the water in the joint portion 2a such as the hemmed portion increases remarkably.

Formula 1 $$Na_2O \cdot nSiO_2 + 2H_2O \rightarrow 2NaOH + Si_nO_{2n-1}(OH)_2$$

[0043] Due to the increase of the pH, the reaction shown in Formula 2 occurs, and the zinc plating of the panels (the galvanized steel sheets) dissolves (corrodes).

Formula 2 $Zn+2NaOH \rightarrow Na_2ZnO_2+H_2$ $Zn(OH)_2+2NaOH \rightarrow Na_2ZnO_2+2H_2O$

[0044] FIG. 4 shows experiment results that leads to the pH range of 5.5 to 10.0 described above. The experiment results show the effect of pH in the aqueous solution 20 in the immersing step with respect to dissolution or corrosion of the joint portion 2a of the vehicle body 2. For this experiment, as shown in FIG. 5, a test piece 37 was produced by welding two galvanized steel sheets 38 in a state of being spaced apart at a distance of 200 μm. Each of the pH-adjusted aqueous solutions 20 was put into the joint portion 2a of the two galvanized steel sheets 38, and the test piece 37 was baked at a temperature of 160˚C for 30 minites (a solid substance appears in the joint portion 2a). Then, 1 ml of water was infiltrated into the joint portion 2a of each test piece 37, and the plating dissolution rate (%) in the joint portion 2a was measured after a predetermined time (3 days in this experiment). The results were that, when the aqueous solution 20 infiltrated into the joint portion 2a has a pH lower than 5.5 or higher than 10.0, the dissolution rate is higher than an allowable limit, thereby indicating that the pH range of 5.5 to 10.0 is appropriate for preventing corrosion. The pH range of 5.5 to 10.0 is based on this experiment. Regarding the alkaline side causing the above-mentioned problem, the upper pH limit (10.0) is lower than the pH at which a zinc plating generally starts to dissolve (see FIG. 1 for comparison). This is thought to be because the water that comes into the joint portion 2a and dissolves the solid substance is a small amount, resulting in a highly concentrated solution of the solid substance, accordingly, the pH of the water reaches a level which causes the zinc plating to dissolve.

[0045] In the present embodiment, the aqueous solution 20 in the immersing step contains the buffer solution component, and this buffer solution component remains as solid substance in the joint portion 2a due to evaporation of the water during the electrodeposition coating step. Accordingly, when water comes into the joint portion 2a later as in the above case, the water dissolves the buffer solution component (solid substance), and functions as a buffer solution. This solution prevents pH change in the joint portion 2a when the zinc plating starts to corrode, thereby preventing the corrosion from advancing.

[0046] In FIG. 4, plots P1 and P3 are data points of the above experiment for the test pieces 37 using acetate and borate, respectively, as the buffer solution component in the aqueous solution 20. These results (P1, P3) show more excellent corrosion resistance than in the case of purified water (P2).

[0047] In the present embodiment, the aqueous solution 20 in the immersing step contains, in addition to the buffer solution component, a chelating agent and/or a phosphate pigment as anode reaction inhibitors, and these anode reaction inhibitors remain as solid substance in the joint portion 2a due to the evaporation of the water during the electrodeposition coating step. Accordingly, when water comes into the joint portion 2a later, these anode reaction inhibitors (solid substance) dissolve in the water, capture zinc ion dissolving from the zinc plating of the vehicle body 2, and form a coating film. This coating film prevents the zinc plating from being ionized. Accordingly, the anode reaction inhibitors can prevent the joint portion 2a from being corroded.

[0048] Further, in the present embodiment, the aqueous solution 20 used in the immersing step contains Pb, Ce, Bi and the like as the halogen capturing chemical elements, and these halogen capturing chemical elements remain as solid substance in the joint portion 2a due to the evaporation of the water during the electrodeposition coating step. Accordingly, when water comes into the joint portion 2a later, these halogen capturing chemical elements are ionized by the water, capture chlorine (halogen) contained in the water which has entered into the joint portion 2a, and form a coating film. The coating film protects the joint portion 2a from chlorine.

[0049] In the coating pretreatment method according to the present embodiment, the quality of the aqueous solution 20 in the immersing step is controlled so as to have a pH of 5.5 to 10.0, and a degreasing agent concentration which is equal to or smaller than 1/100 of the degreasing agent concentration of the degreasing liquid 21 used in the degreasing step. Accordingly, the aqueous solution 20 can be considered not having a very high pH and substantially not containing the degreasing liquid 21, and Accordingly industrial action can be taken while making an efficient use of water. Further, the presence of the aqueous solution 20 substantially not containing the degreasing liquid 21 in the joint portion 2a during the degreasing step will prevent oil from being removed out of the joint portion 2a, and this oil can be utilized to prevent the zinc plating in the joint portion 2a from dissolving. By realizing the fact that it is difficult to adhere coating in the joint portion 2a, especially, in the hemmed portion as the sac-shaped portion, of the door, the present invention intends to protect the zinc plating from dissolving by the oil which is left rather than being removed before the coating step.

[0050] In FIG. 4, plots P4 to P6 are data points of the above experiment when using an aqueous solution 20 containing a degreasing liquid, and plots P4' and P5' are data points of the above experiment when using an aqueous solution 20 containing a degreasing liquid which does not have surfactant. More specifically, plot P6 is a data point when using an aqueous solution 20 containing the degreasing liquid in the degreasing step, plot P5 is a data point when using an aqueous solution 20 obtained by 1/10-dilution of the degreasing liquid at plot P6, and plot P4 is a data point when using an aqueous solution 20 obtained by 1/100-dilution of the degreasing liquid at plot P6. Plot P5' is a data point when using an aqueous solution 20 by 1/10-dilution of the degreasing liquid at plot P6 but without surfactants, and plot P4' is a data point when using an aqueous solution 20 obtained by 1/100-dilution of the degreasing liquid at plot P6 but without surfactants.

[0051] According to FIG. 4, the comparison of plots P4 to P6 (the aqueous solutions 20 containing the degreasing liquid with the surfactant) with plots P4' and P5' (the aqueous solutions 20 containing the degreasing liquid without the surfactant) shows that the plating dissolution rate is higher even at the same pH, and that the smaller amount of the degreasing liquid 21 provides a lower plating dissolution rate. This is because less degreasing liquid (especially degreasing liquid containing a surfactant) makes more oil to remain, and the plating in the joint portion 2a is prevented from dissolving based on the increased oil left. This is supported by FIG. 6 showing properties of the aqueous solutions 20. FIG. 6 shows that less alkaline builder and surfactant as components of the degreasing liquid 21 lead to less plating corrosion, a result similar to the result from FIG. 4.

[0052] In the immersing step, the purified water supplied by the immersing tank 4 is ion-exchanged water, and does not contain chlorine ion. Accordingly, the aqueous solution 20 coming into the joint portion 2a of the vehicle body 2 does not contain chlorine ion, thereby preventing corrosion due to chlorine ion in addition to corrosion (dissolution) due to the degreasing liquid 21.

[0053] FIG. 6 shows a characteristic regarding water type (water purity) as one of the properties of the aqueous solution 20, wherein the plating corrosion ratio (S/N ratio) in the joint portion 21a is shown when ion-exchanged water, tap water, and industrial water are used as the aqueous solution 20 put into the joint portion 2a in the above experiment. This shows that the ion-exchanged water not containing chlorine ion provides a smaller corrosion ratio than the tap water and the industrial water.

[0054] FIG. 6 shows a characteristic regarding a water temperature as one of the properties of the aqueous solution 20, wherein the plating corrosion ratio (S/N ratio) in the joint portion 21a is shown at various temperatures of the aqueous solution 20 put into the joint portion 2a. This shows that a lower temperature results in a smaller corrosion ratio. This is thought to be because the oil in the joint portion 2a is more difficult to remove at a lower temperature of the aqueous solution 20.

[0055] FIG. 7 shows the result of a durability test of finished products (coating and the like has been performed thereon) produced with the immersing step (the case where the solid substance of the degreasing liquid does not remain in the sac-shaped portion) and without the immersing step (the case where the solid substance of the degreasing liquid remains in the sac-shaped portion). For this experiment, a GA material (available from Nippon Steel Corporation; coating amount: 48.8 g/m^2, degree of alloying: 10.4 Fe%) was used as a test material, and the durability test was carried out under a constant conditions with one cycle approximately corresponding to three cycles of JISK5600-7-9 cycle A. In this case, 10 cycles corresponds to approximately one year in the marketed use. As shown in FIG. 8, coating-swelling rust (blister) 40 occurs at a coating 42 adjacent to a coating sealer 44 by development of rust from a starting point S1 in the sac-shaped portion as indicated by the arrow, and the width of the swelling of the coating 40 is indicated by LB. In FIG. 8, the numerals 41 and 43 designate a coating on the outer panel 34 and an AD sealer, respectively.

[0056] According to FIG. 7, the finished product which was produced without the immersing step and in which the solid substance of the degreasing liquid remained in the sac-shaped portion shows the durability equivalent to about two years in the marketed use, but the finished product which was produced through the immersing step and in which the solid substance of the degreasing liquid did not remain in the sac-shaped portion shows the durability equivalent to further two years in the marketed use.

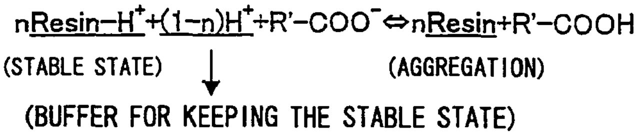
[0057] FIGS. 9 to 16 show a second embodiment of the present invention which is basically identical to the first embodiment except for some parts. Accordingly, only characteristic parts of the second embodiment will be described. For the other parts, the like elements to those of the first embodiment are designated by the same numerals, and the description thereof will be omitted.

[0058] The second embodiment prevents corrosion of a joint portion 2a of a vehicle body 2 such as a hemmed portion as well as occurrence of abnormal aggregation or electrodeposition aggregation of an electrodeposition coating material liquid in the vicinity of the joint portion 2a during the electrodeposition coating step. A method for preventing electrodeposition aggregation is based on a mechanism of electrodeposition aggregation which has been discovered by the inventors. First, the discovered mechanism of electrodeposition aggregation will be described.

[0059] A degreasing liquid 21 for a degreasing step (in a degreasing tank 5) contains an alkaline builder and a surfactant as described above, and metal salts such as sodium silicate (Na_2SiO_3), sodium carbonate (Na_2CO_3), and sodium hydrogen carbonate ($NaHCO_3$) are generally used as the alkaline builder. Such metal salts enter treat water in first and second water washing tanks 6 and 7 during a water washing step after the degreasing step, and further enters an aqueous solution 20 in an immersing tank 4 because of reuse of the used water (see FIG. 2). The aqueous solution 20 containing the dissolved metal salts (ionized and non-ionized metal salts) comes into the joint portion 2a of the vehicle body 2 during the immersing step, and the vehicle body 2 having the joint portion 2a is advanced to the electrodeposition coating step after going through the degreasing step, the waterwashing step, and the chemical film forming step while holding the aqueous solution 20 in the joint portion 2a. During the electrodeposition coating step, the vehicle body 2 is immersed in a cationic electrodeposition coating material liquid in a tank, and an electric voltage is applied between the tank as an anode and the vehicle body 2 as a cathode.

[0060] In the electrodeposition coating material liquid, chemical equilibration is maintained as shown by Formula 3. Accordingly, in the electrodeposition coating material liquid, a resin (electrodeposition coating material) becomes water soluble by lowering the pH (by acid being present therein), and generally this situation does not cause electrodeposition aggregation to occur. However, in the electrodeposition coating step, electrodeposition aggregation is actually observed in the vicinity of the joint portion 2a, and it is necessary to repair the joint portion 2a.

Formula 3



$$n\underline{\text{Resin}-H^+}+\underline{(1-n)H^+}+R'-COO^- \Leftrightarrow n\underline{\text{Resin}}+R'-COOH$$

[0061] When the inventors studied this in view of such circumstances, the inventors found that during the electrodeposition coating step, the temperature of the vehicle body 2 rises due to the application of the electric voltage, and the aqueous solution 20 thermally expands in the joint portion 2a such as the hemmed portion and overflows into the electrodeposition coating material liquid as shown in FIG. 9. Based on this, the mechanism of electrodeposition aggregation, which is shown in FIG. 9, was found. The mechanism will be described specifically with one metal salt, Na_2SiO_3, being taken as an example.

[0062] In the electrodeposition coating material liquid, as shown in FIG. 14, R'-COOH is present around the electrodeposition coating material to provide water solubility to the resin. When the aqueous solution 20 overflows and Na_2SiO_3, Na^+, and SiO_3^{2-} enter the electrodeposition coating material liquid in such a situation, they enter an ionization equilibrium state in accordance with the condition of the electrodeposition coating material liquid as shown by Formula 4. Na^+ and the O atom (negatively-charged) in R'-COOH attract each other, while Na^+ and the H atom (positively-charged) in R'-COOH repel each other. Accordingly, the OH bond in a carboxyl group -COOH is broken (R'-COOH is ionized), and $R'\text{-}COO^-$ moves away from the electrodeposition coating material, following Na^+ as shown in FIG. 15. Although H^+ increases around the electrodeposition coating material due to the ionization of R'-COOH, because SiO_3^{2-} is present in the electrodeposition coating material liquid, H^+ reacts with SiO_3^{2-}, and chemical equilibrium shifts in a direction so as to decrease H^+ as shown in FIGS. 15 and 16. As a result, the provision of water solubility to the resin by R'-COOH becomes difficult, and the resin condenses to form electrodeposition aggregation as shown in FIG. 16.

[0063] From this revealed mechanism of electrodeposition aggregation, the inventors found that more Na+ present in the electrodeposition coating material liquid increases the ionization degree of R'-COOH and a larger ionization degree of R'-COOH increases the amount of electrodeposition aggregation. Based on this finding, the inventors conclude that an upper limit is needed for the Na+ concentration in the electrodeposition coating material liquid in order to prevent the occurrence of electrodeposition aggregation.

[0064] It is thought that a reaction other than the above reaction proceeds simultaneously. As described above, when the aqueous solution 20 overflows into the electrodeposition coating material liquid and Na_2SiO_3, Na^+, and SiO_3^{2-} enter the electrodeposition coating material liquid, they enter an ionization equilibrium state in accordance with the condition of the electrodeposition coating material liquid as shown in Formula 4. However, in the electrodeposition coating material liquid, R'-COOH is ionized, and equilibrium is maintained as shown by Formula 5. This results in the coexistence of SiO_3^{2-} and H^+ in the electrodeposition coating material liquid. Accordingly, equilibrium shown by Formula 6 also needs to be maintained in the electrodeposition coating material liquid.

Formula 4 $Na_2SiO_3 \Leftrightarrow 2Na^+ + SiO^{2-}{}_3$

Formula 5 $R'\text{-}COOH \Leftrightarrow R'\text{-}COO + H^+$

Formula 6 $H_2SiO_3 \Leftrightarrow 2\,H^+ + SiO^{2-}{}_3$

[0065] In this case, because silicic acid H_2SiO_3 is a weak acid, in order to have Formula 6 occur, the reaction must take place from the right to the left in Formula 6 to produce H_2SiO_3. For that reason, H^+ must decrease. When H^+ decreases in the electrodeposition coating material liquid as described, the equilibrium of Formula 5 shifts from the left to the right, supplying H^+. The supplied H^+ binds with SiO_3^{2-} to produce non-ionized H_2SiO_3. It is considered that such reaction continues until Formula 5 and Formula 6 both come to the equilibrium. The above-mentioned facts can be summed up as equilibrium Formula 7 wherein SiO_3^{2-} reacts with -COOH to produce silicic acid molecules H_2SiO_3 and $R'\text{-}COO^-$.

Formula 7 $2\ R'\text{-}COOH + SiO^{2-}_3 \rightleftharpoons 2\ R'\text{-}COO^- + H_2SiO_3$

[0066] On the other hand, although Na^+ which is ionized from Na_2SiO_3 and $R'\text{-}COO^-$ which is produced by the reaction of Formula 7 are left in the electrodeposition coating material liquid, they remain ionized as shown by Formula 8 because they attract each other. Accordingly, it is thought that the presence of more $Na^+(Na_2SiO_3)$ increases the amount of $R'\text{-}COO^-$. It is assumed that such a phenomenon occurs similarly for other metal salts, such as Na_2CO_3 and $NaHCO_3$ shown by Formulas 9 and 10 (see FIG. 9).

Formula 8 $2\ R'\text{-}COOH + SiO^{2-}_3 + 2Na^+ \rightleftharpoons 2\ R'\text{-}COO^- + H_2SiO_3 + 2Na^+$

Formula 9 $R'\text{-}COOH + CO^{2-}_3 + 2Na^+ \rightleftharpoons R'\text{-}COO^- + H\ CO^-_3 + 2\ Na^+$

Formula 10 $R'\text{-}COOH + H\ CO^-_3 + Na^+ \rightleftharpoons R'\text{-}COO^- + H_2CO_3 + Na^+$

[0067] The inventors perceive that electrodeposition aggregation takes place owing to the fact that the abundance of $R'\text{-}COO^-$ shifts the equilibrium state of the electrodeposition coating material liquid toward the side in which the electrodeposition coating material condenses, as shown in Formula 11

Formula 11

$$\text{Resin-}H^+ + R'\text{-}COO^- \longrightarrow \underset{\text{(AGGREGATION)}}{\text{Resin}} + R'\text{-}COOH$$

[0068] FIG. 10 shows results of a test carried out by the inventors based on the above findings and conclusions (prediction that the pH and the concentration of metal salts and its ions in the aqueous solution 20 are linked to electrodeposition aggregation).

[0069] In the test, a test liquid of each condition shown in FIG. 10 was poured into a petri dish, and a drop of a cationic electrodeposition coating material liquid (PN1020 available from Nippon Paint Co. , Ltd.) was put into each petri dish to check whether or not aggregation of the electrodeposition coating material liquid occurs under each condition. Evaluation of the test results was based on whether the phenomenon of electrodeposition aggregation was visually confirmed or not. In FIG. 10, the mark "○" means that the phenomenon of electrodeposition aggregation was not confirmed, and the mark "× " means that the phenomenon of electrodeposition aggregation was confirmed. In this case, as shown in FIG. 10, a "converted metal ion concentration" ("converted Na^+ concentration") is used as a total concentration of the metal salts (Na_2SiO_3, Na_2CO_3, $NaHCO_3$) and their ions (Na^+) which are held in equilibrium in the aqueous solution 20. The "converted metal ion concentration" is a total metal ion concentration (Na^+ concentration) when all the metal salts including the non-ionized metal salts are assumed to be fully ionized in the aqueous solution 20. This conversion is needed because the metal ion concentration in the electrodeposition coating material liquid is determined based on the chemical equilibrium state in the electrodeposition coating material liquid, and even if the metal ion concentration in the immersing step (immersing tank 4) is determined, the metal ion concentration in the immersing step is not necessarily the same as that in the electrodeposition coating material liquid in the electrodeposition coating step, thereby lacking accuracy. In other words, by using the total concentration of all the elements which can become metal ions, the total concentration of metal ions among the immersing step and the electrodeposition coating step can be considered as constant, and this approximation is advantageous in identifying a condition to prevent the occurrence of electrodeposition aggregation. Further, in the case of defining the metal salt concentration, because there are many types of metal salts, the final metal ion concentration after full ionization will differ even at the same metal salt concentration depending on the type of metal salt and the ratio among these.

[0070] According to the results shown in FIG. 10, even if the pH of the aqueous solution 20 is lowered, the occurrence of electrodeposition aggregation cannot be prevented when the converted Na^+ concentration of the aqueous solution 20 is high. Accordingly, to prevent the occurrence of electrodeposition aggregation, in addition to the pH control of the aqueous solution 20, it is necessary to lower the concentrations of the metal salts and their metal ions (Na_2CO_3, $NaHCO_3$, Na_2SiO_3, Na^+) in the aqueous solution 20 as concluded or predicted by the inventors.

[0071] Further, as in the first embodiment, when taking into consideration that the upper pH limit of the aqueous solution 20 must be set at pH 10 (pH adjustment by an agent such as HNO_3) to prevent corrosion, the converted Na^+

concentration of the aqueous solution 20 which can prevent the occurrence of electrodeposition aggregation must be set equal to or smaller than 620 ppm, as shown in the result in FIG. 10. Accordingly, in the present embodiment, in addition to the prevention of the corrosion of the joint portion 2a, in order to prevent the occurrence of electrodeposition aggregation, the quality of the aqueous solution 20 in the immersing step is controlled such that its pH is equal to or lower than pH 10 and its converted Na^+ concentration is equal to or smaller than 620 ppm. The dilution by the purified water supply source 9, the pH adjustment by an agent such as HNO_3, and the like may be used as means for accomplishing this adjustment.

[0072] Further, in the present embodiment, the quality of the aqueous solution 20 in the immersing tank 4 is controlled so as to have a pH of 5.5 to 10.0, a converted Na^+ concentration equal to or smaller than 620 ppm, and a surfactant concentration of 50 ppm to 190 ppm (preferably from 50 ppm to 100 ppm). Although it is generally difficult for the aqueous solution 20 to enter into the joint portion 2a due to the presence of oil prior to the degreasing step, the permeating power of the surfactant of the aqueous solution 20 is utilized to cause the aqueous solution 20 to easily and rapidly enter into the joint portion 2a, thereby reducing the volume or the lateral length of the immersing tank 4. The reason why the preferable concentration of the surfactant ranges from 50 ppm to 100 ppm is to obtain the maximum permeating power effect (the effect of inflow into the joint portion 2a) with the minimum amount of surfactant contained while preventing the corrosion of the joint portion 2a.

[0073] FIG. 11 shows the results of the test which provides the preferable conditions about the surfactant concentration of the aqueous solution in the immersing step (immersing tank 4) ranging from 50 ppm to 190 ppm, more preferably, ranging from 50 ppm to 100 ppm. This test aims at measuring the effect of the surfactant concentration on the inflow speed of the aqueous solution 20 into the hemmed portion (joint portion) 2a. Press washing oil was applied into colorless and transparent tubes each having a length of 300 mm and an inner diameter of 1 mm to prepare test tubes. These tubes were fully immersed into aqueous solutions having different surfactant concentrations, a pH of 9.0, and a temperature of 30°C at different angles (with respect to the water surface) to measure the infiltration speed (inflow speed) of the aqueous solution into the respective tubes.

[0074] The test results shown in FIG. 11 show that the inflow speed increases in a range of the surfactant concentration from 0 ppm to just above 50 ppm (60ppm), while the inflow speed does not increase in a range of the surfactant concentration from 100 ppm to 190 ppm. The identical results were obtained at the different immersion angles of the test tubes.

[0075] FIGS. 12 and 13 show results of an experiment which was carried out to measure the effect of surfactant with respect to corrosion. The experiment was carried out based on the experiment method shown in FIG. 4 in the first embodiment. FIGS. 12 and 13 show that corrosion preventing performance deteriorates with an aqueous solution 20 containing surfactant. However, when the pH of the aqueous solution 20 is appropriately adjusted at pH 10 or lower (adjustment by HNO_3 and the like) and the surfactant concentration is equal to or smaller than 190 ppm, the corrosion preventing performance reduces to some extent (to the extent which slightly exceeds the allowable reference line in FIG. 4) as compared with the case of the aqueous solution 20 not containing a surfactant (substantially not containing a surfactant (about 20 ppm)), but this reduction lies in a practically allowable level (the dissolution rate is 20 % or lower) (see P4 to P6 in FIG. 4 where onlywater dilution is performed and pH adjustment is not performed). According to the experiment results of FIGS. 11 to 13, the surfactant concentration is set in the range of 50 ppm to 190 ppm as described above.

[0076] In the present embodiment, the surfactant contained in the recovered liquid (the surfactant which has been used in the degreasing step) is reused in the immersing step. In consideration of the use of the surfactant (utilization of the permeating power performance) in the immersing step, it is preferable to use a nonionic surfactant such as alkyl ethoxylate as the surfactant. The degreasing liquid in the degreasing tank 5 has the converted Na^+ concentration of 6200 ppm and the surfactant concentration of 1900 ppm. The degreasing liquid is diluted to 1/10 or smaller (preferably 1/40, more preferably 1/100) of the degreasing agent concentration of the degreasing liquid in the degreasing tank 5, and then reused in the immersing tank 4. Obviously, the pH of the reused degreasing liquid is adjusted to be equal to or lower than 10 by HNO_3 or the like.

[0077] It should be noted that although only the significant parts of the second embodiment has been described, the other parts than the surfactant and the metal ion are identical to those of the first embodiment, and are applicable to the second embodiment.

[0078] The present invention is not limited to the above-described embodiments, the following modifications may be made.

(1) In the above embodiments, on the assumption that the degreasing liquid comes into the joint portion 2a of the vehicle body 2 (an object to be treated) during the degreasing step, the aqueous solution 20 is put into the joint portion 2a of the vehicle body 2 in the immersing step before the degreasing step. However, in the case where a vehicle body 2 is immersed into the hot-water washing tank 3 into which an amount of degreasing liquid is likely to flow, it is preferable to put the aqueous solution 20 into the joint portion 2a of the vehicle body 2 prior to the hot-

water washing step.

(2) It may be appreciated to provide the immersing step (immersing tank 4) before the hot-water washing step (hot-water washing tank 3) for further preventing the decrease in the corrosion resistance of the joint portion 2a of the vehicle body 2.

(3) In order to prevent the occurrence of electrodeposition aggregation, the concentration of metal ions other than Na^+ may be preferably controlled.

Claims

1. A degreasing method comprising the steps of:

allowing a joint portion (2a) of an object (2) to be treated to have an aqueous solution (20) having a pH of 5.5 to 10.0; and
immersing the object (2) in a degreasing liquid (21).

2. The degreasing method according to claim 1, wherein the immersing is performed before an electrodeposition coating is performed, and the aqueous solution (20) contains a metal salt and metal ions of the metal salt at a concentration of 620 ppm or smaller when the metal salt is assumed to be converted to metal ions.

3. The degreasing method according to claim 1 or 2, wherein the aqueous solution (20) substantially contains no surfactant.

4. The degreasing method according to claim 1 or 2, wherein,
the degreasing liquid (21) contains a surfactant at a first surfactant concentration; and
the aqueous solution (20) contains a surfactant at a second surfactant concentration that is equal to or smaller than 1/100 of the first surfactant concentration.

5. The degreasing method according to any one of claims 1 to 4, wherein the joint portion (2a) of the object (2) is shaped into a sac.

6. The degreasing method according to any one of claims 1 to 5, wherein,
the object (2) includes a plurality of plates which are jointed with each other, and
the joint portion (2a) is at an overlapped part of plates.

7. The degreasing method according to claim 6, wherein the aqueous solution (20) is put into the joint portion (2a) after the plurality of plates are joined to construct the object (2).

8. The degreasing method according to any one of claims 1 to 7, wherein the joint portion (2a) is immersed in the aqueous solution (20) contained in an immersing tank (4) to put the aqueous solution (20) into the joint portion (2a).

9. The degreasing method according to claim 2, wherein the aqueous solution (20) contains a surfactant at a concentration of 50 ppm to 190 ppm.

10. The degreasing method according to claim 9, wherein, the joint portion (2a) is immersed in the aqueous solution (20) contained in an immersing tank (4) to put the aqueous solution (20) into the joint portion (2a),
the degreasing liquid (21) contains a degreasing agent including a metal salt and a surfactant, and
the aqueous solution (20) in the immersing tank (4) contains a part of used degreasing liquid, and has a degreasing agent concentration that is equal to or smaller than 1/10 of a degreasing agent concentration of the degreasing liquid (21).

11. The degreasing method according to any one of claims 1 to 10, wherein the aqueous solution (20) includes ion-exchanged water.

12. The degreasing method according to any one of claims 1 to 11, wherein the aqueous solution (20) includes a buffer solution.

13. The degreasing method according to any one of claims 1 to 12, wherein the aqueous solution (20) contains an anode reaction inhibitor.

14. The degreasing method according to any one of claims 1 to 13, wherein the aqueous solution (20) contains a halogen capturing chemical element.

15. The degreasing method according to any one of claims 1 to 14, wherein a surface of the object (2) is made of an amphoteric metal.

16. A degreasing apparatus comprising:

an aqueous solution supplier (4) for supplying an aqueous solution to a joint portion (2a) of the object (2) to be immersed in a degreasing liquid (21), the aqueous solution having a pH of 5.5 to 10.0.

17. The degreasing apparatus according to claim 16, wherein the aqueous solution (20) contains a metal salt and metal ions of the metal salt at a concentration of 620 ppm or smaller when the metal salt is assumed to be converted to metal ions.

18. The degreasing apparatus according to claim 17, wherein the aqueous solution supplier (4) includes an immersing tank (4) holding the aqueous solution (20) containing a surfactant at a concentration of 50 ppm to 190 ppm.

19. The degreasing apparatus according to claim 16, wherein the aqueous solution (20) does not contain a substantial amount of a surfactant.

20. The degreasing apparatus according to claim 19, wherein the aqueous solution supplier (4) includes an immersing tank (4) holding the aqueous solution (20) not containing a substantial amount of a surfactant.

21. The degreasing apparatus according to any one of claims 16 to 20, wherein the aqueous solution (20) includes ion-exchanged water.

FIG.1

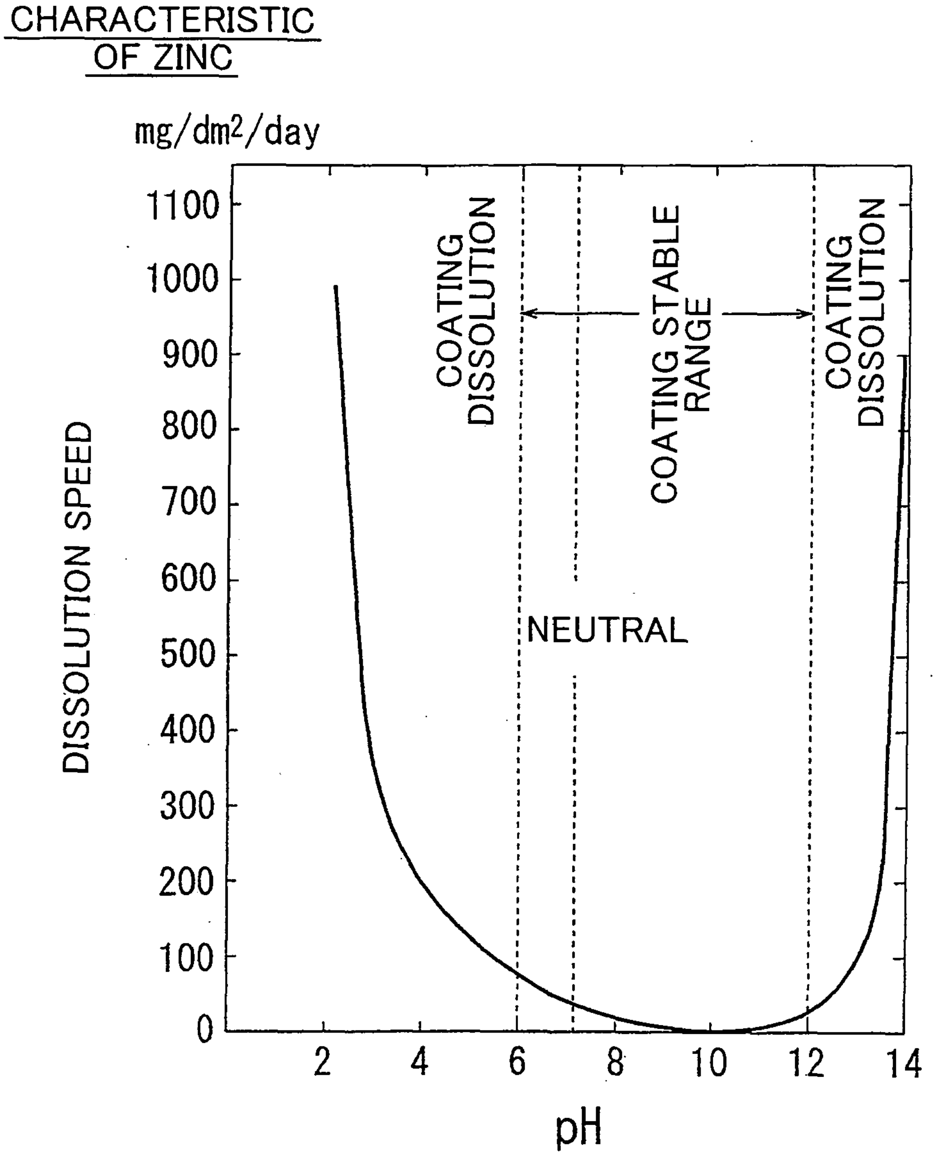

CHARACTERISTIC OF ZINC
mg/dm2/day
DISSOLUTION SPEED
1100
1000
900
800
700
600
500
400
300
200
100
0
2
4
6
8
10
12
14
pH
COATING DISSOLUTION
COATING STABLE RANGE
COATING DISSOLUTION
NEUTRAL

FIG.2

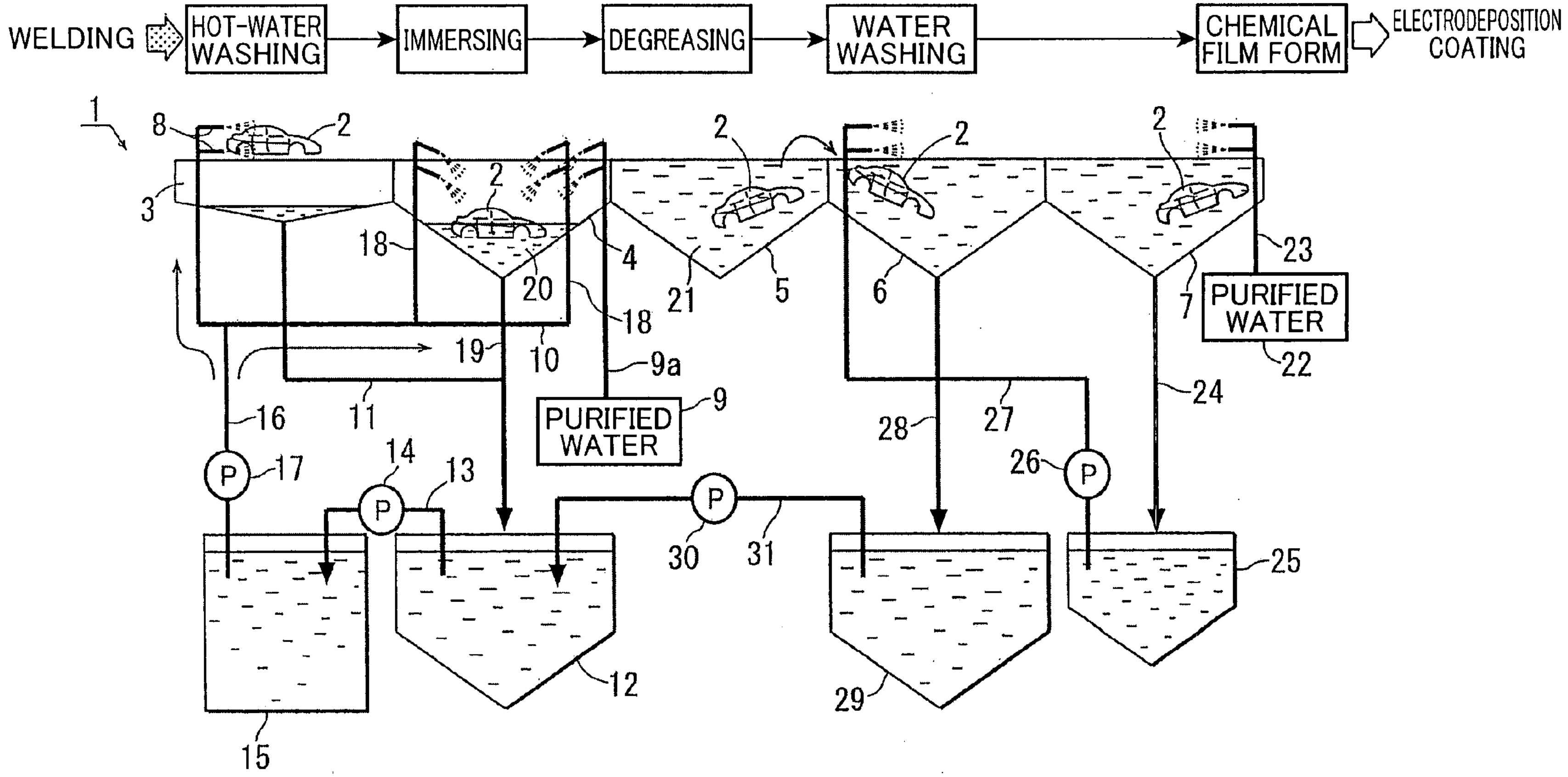

WELDING
HOT-WATER WASHING
IMMERSING
DEGREASING
WATER WASHING
CHEMICAL FILM FORM
ELECTRODEPOSITION COATING
1
8
2
3
18
20
4
21
5
6
7
23
PURIFIED WATER
22
19
10
18
9a
PURIFIED WATER
9
16
11
28
27
24
P
17
14
13
P
30
31
26
25
15
12
29

FIG.3

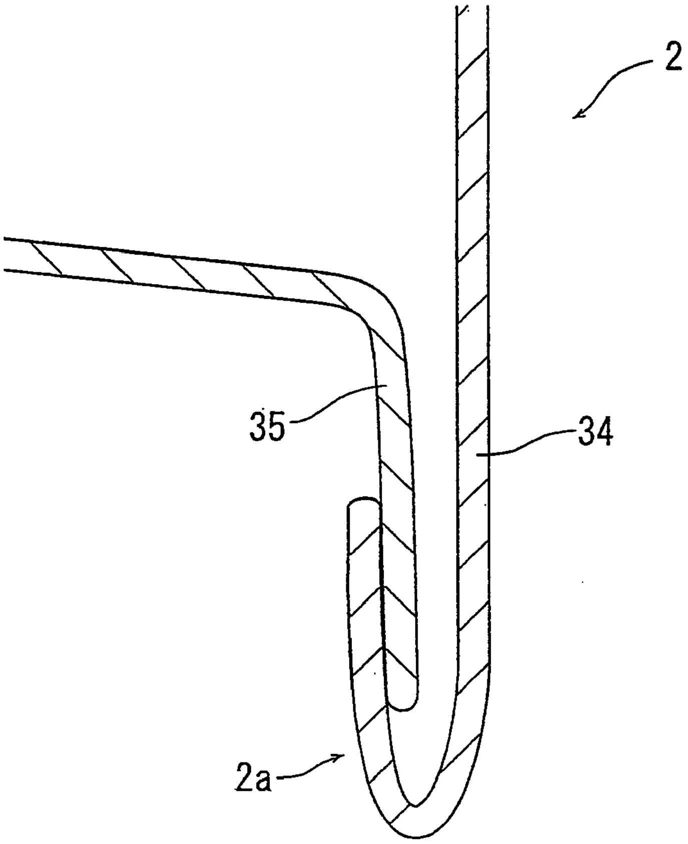


FIG.4

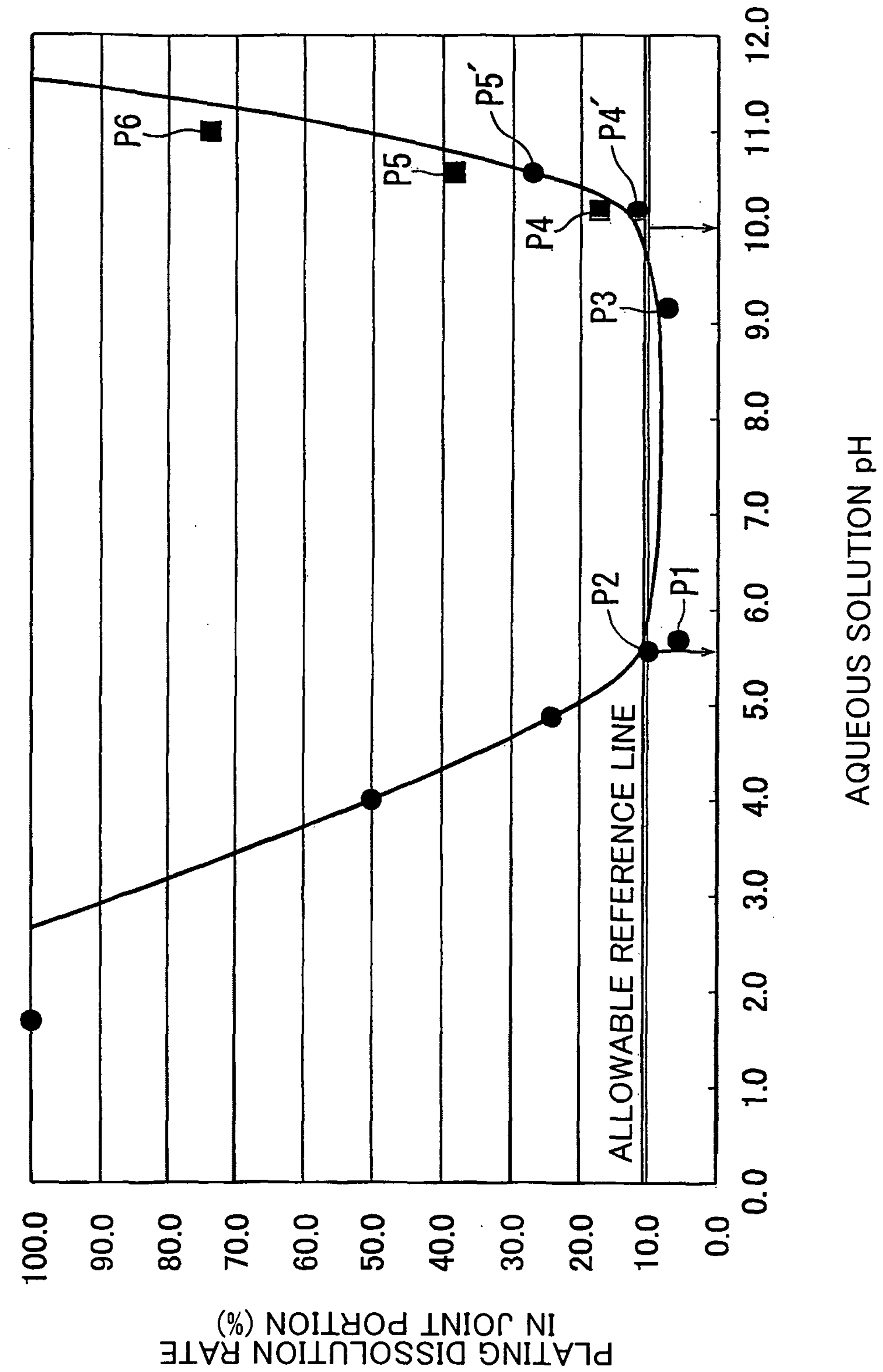

PLATING DISSOLUTION RATE IN JOINT PORTION (%)
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
AQUEOUS SOLUTION pH
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
ALLOWABLE REFERENCE LINE
P1
P2
P3
P4
P4´
P5
P5´
P6

FIG.5

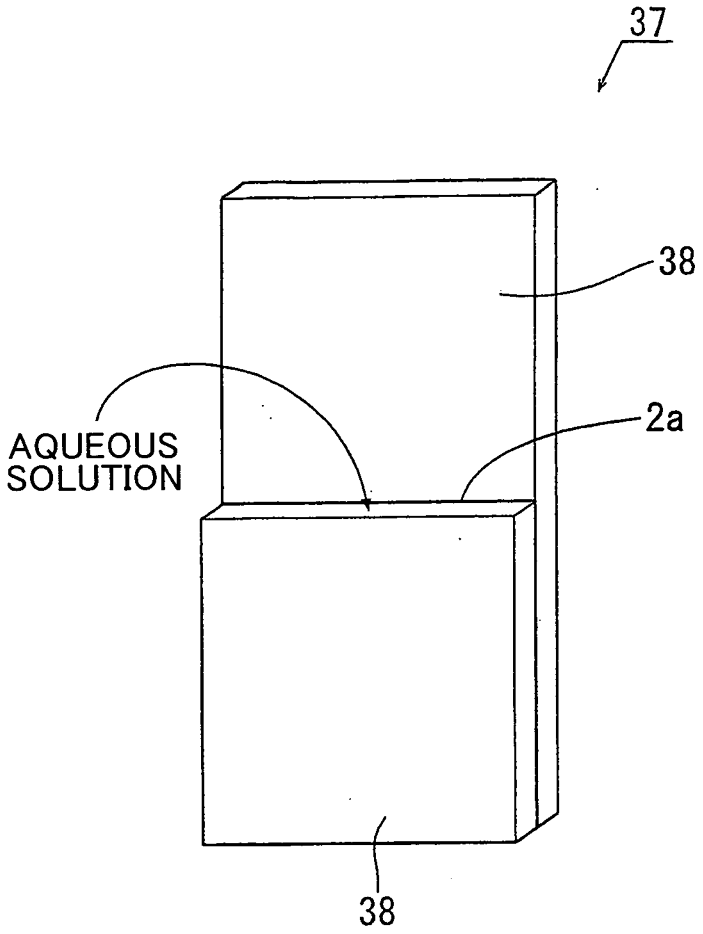


FIG.6

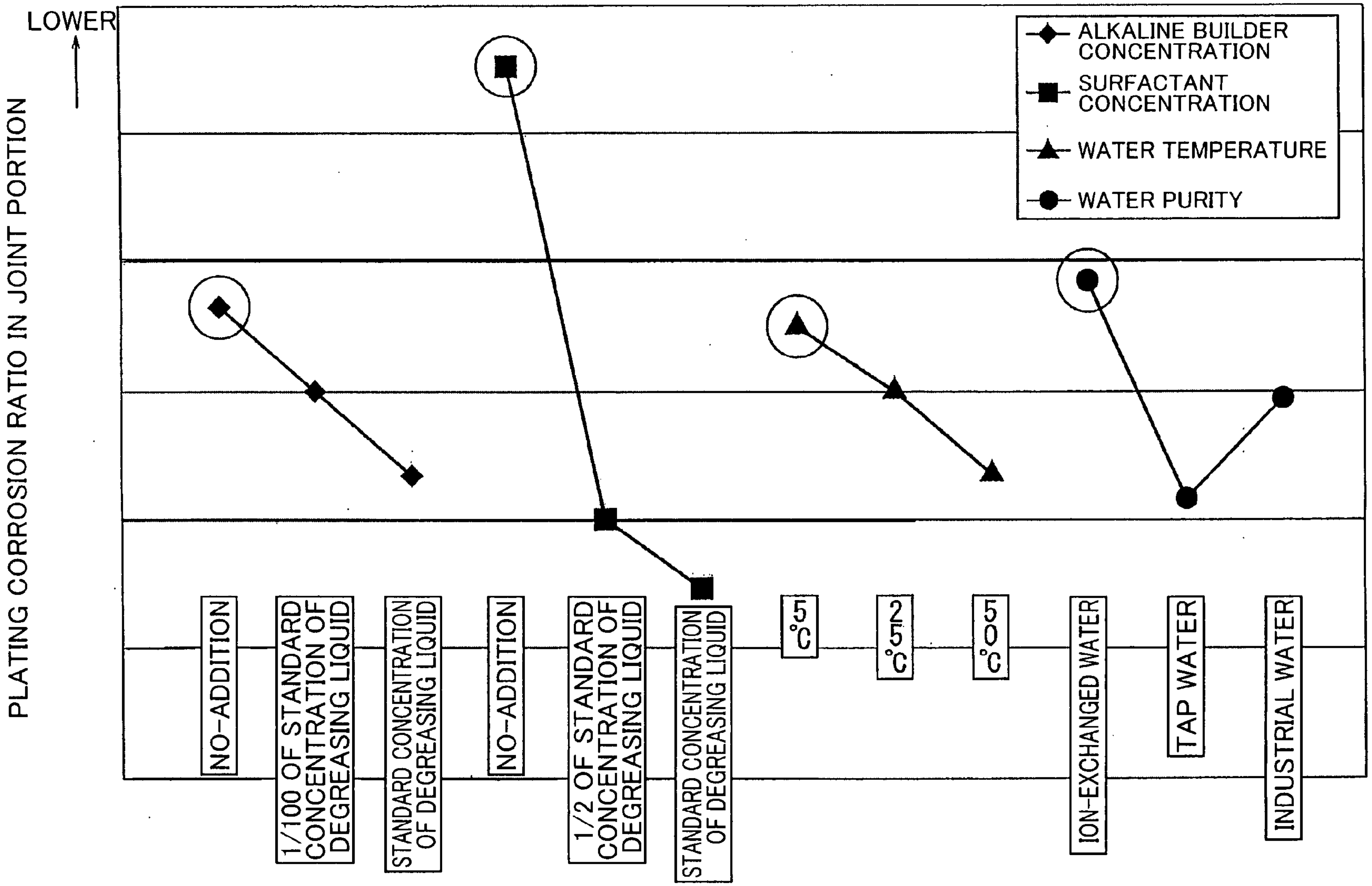

LOWER
PLATING CORROSION RATIO IN JOINT PORTION
ALKALINE BUILDER CONCENTRATION
SURFACTANT CONCENTRATION
WATER TEMPERATURE
WATER PURITY
NO-ADDITION
1/100 OF STANDARD CONCENTRATION OF DEGREASING LIQUID
STANDARD CONCENTRATION OF DEGREASING LIQUID
NO-ADDITION
1/2 OF STANDARD CONCENTRATION OF DEGREASING LIQUID
STANDARD CONCENTRATION OF DEGREASING LIQUID
5°C
25°C
50°C
ION-EXCHANGED WATER
TAP WATER
INDUSTRIAL WATER

FIG.7

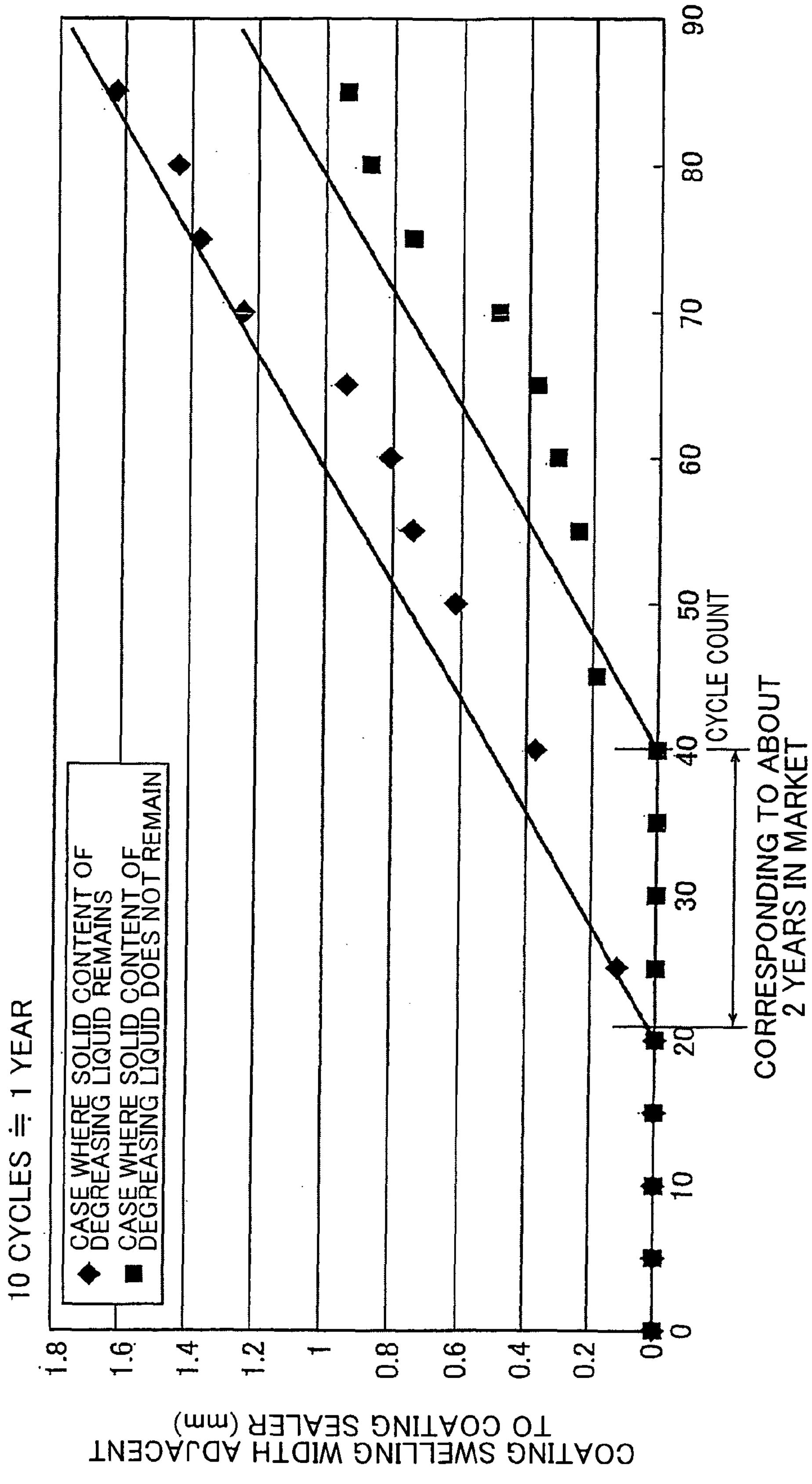

10 CYCLES ≒ 1 YEAR
◆ CASE WHERE SOLID CONTENT OF DEGREASING LIQUID REMAINS
■ CASE WHERE SOLID CONTENT OF DEGREASING LIQUID DOES NOT REMAIN
COATING SWELLING WIDTH ADJACENT TO COATING SEALER (mm)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
0
10
20
30
40
50
60
70
80
90
CYCLE COUNT
CORRESPONDING TO ABOUT 2 YEARS IN MARKET

FIG.8

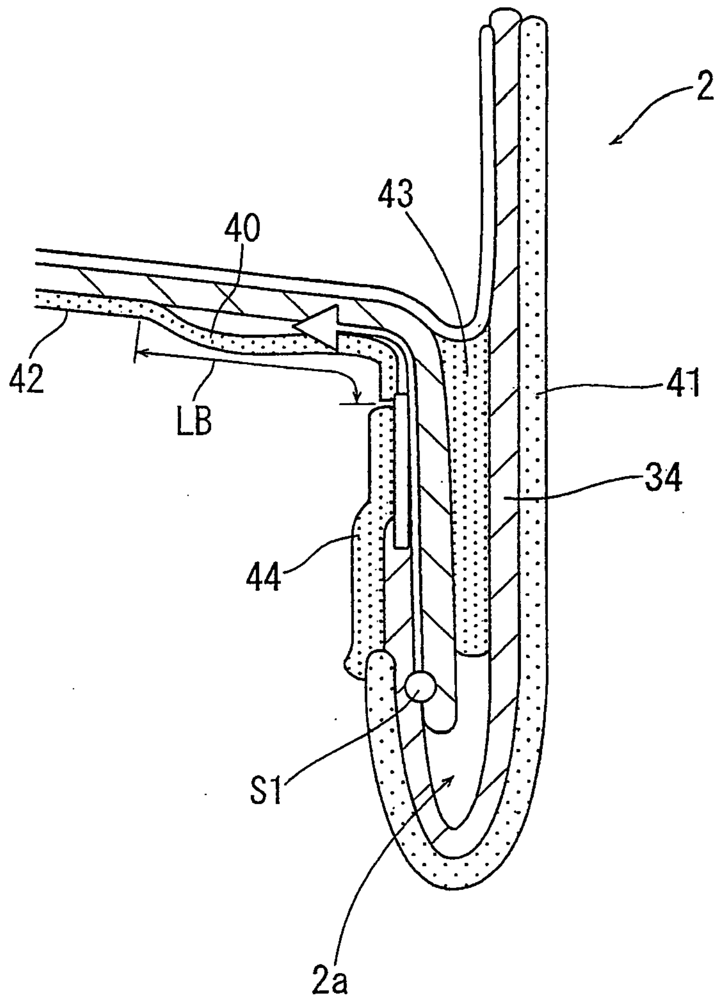


FIG.9

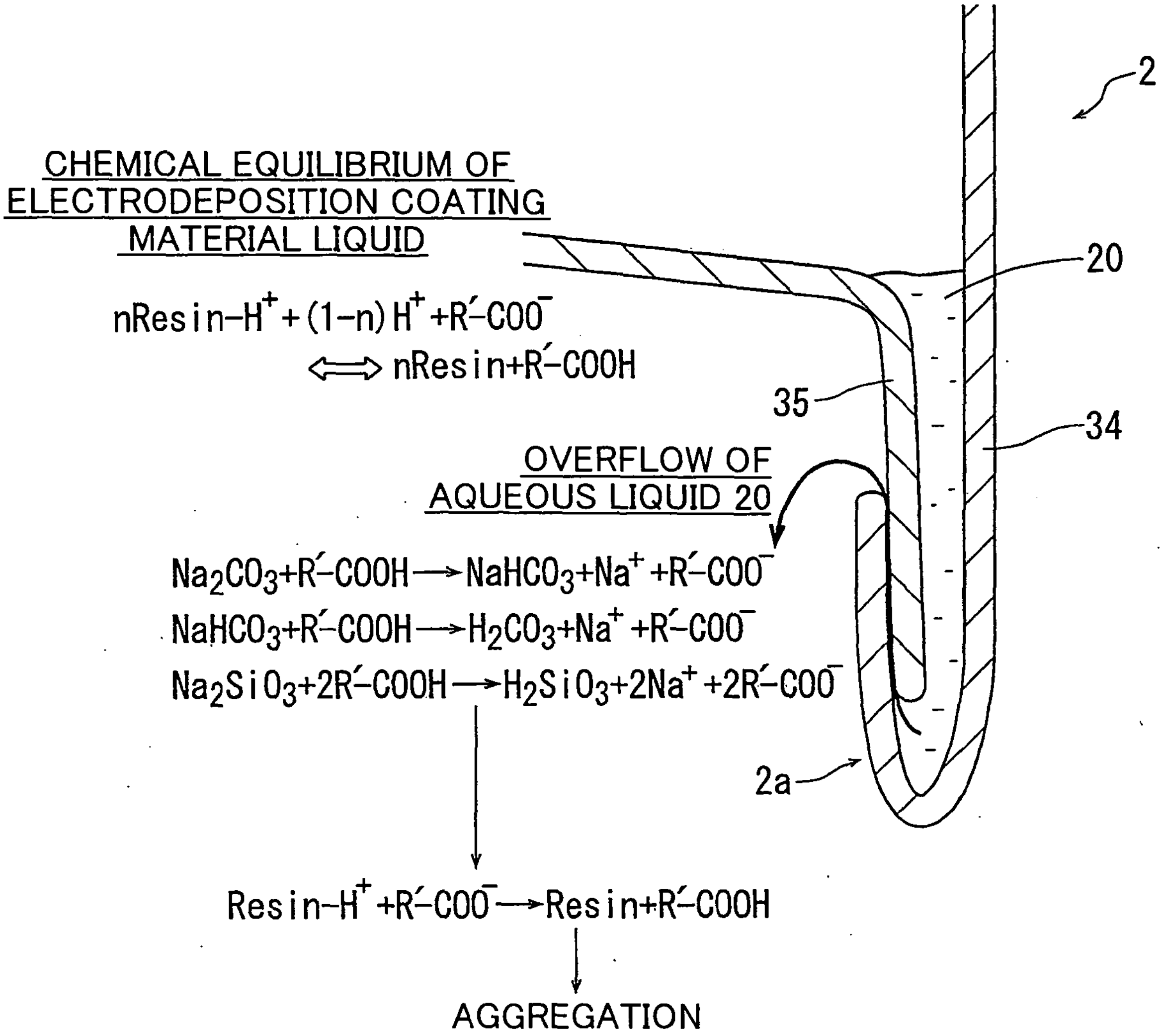

2
CHEMICAL EQUILIBRIUM OF ELECTRODEPOSITION COATING MATERIAL LIQUID
$n\mathrm{Resin{-}H^+} + (1-n)\mathrm{H^+} + \mathrm{R'{-}COO^-} \Longleftrightarrow n\mathrm{Resin} + \mathrm{R'{-}COOH}$
20
35
34
OVERFLOW OF AQUEOUS LIQUID 20
$\mathrm{Na_2CO_3 + R'{-}COOH \rightarrow NaHCO_3 + Na^+ + R'{-}COO^-}$
$\mathrm{NaHCO_3 + R'{-}COOH \rightarrow H_2CO_3 + Na^+ + R'{-}COO^-}$
$\mathrm{Na_2SiO_3 + 2R'{-}COOH \rightarrow H_2SiO_3 + 2Na^+ + 2R'{-}COO^-}$
2a
$\mathrm{Resin{-}H^+ + R'{-}COO^- \rightarrow Resin + R'{-}COOH}$
AGGREGATION

FIG.10

		CONVERTED METAL ION (Na$^+$) CONCENTRATION (ppm)				
		6200 (1/1 DILUTION)	620 (1/10 DILUTION)	62 (1/100 DILUTION)	12.4 (1/500 DILUTION)	6.2 (1/1000 DILUTION)
pH	11. 20	×				
	11. 16	×	×			
	10. 75	×	×	×		
	10. 30	×	×	○	○	
	9. 95	×	○	○	○	○

FIG.11

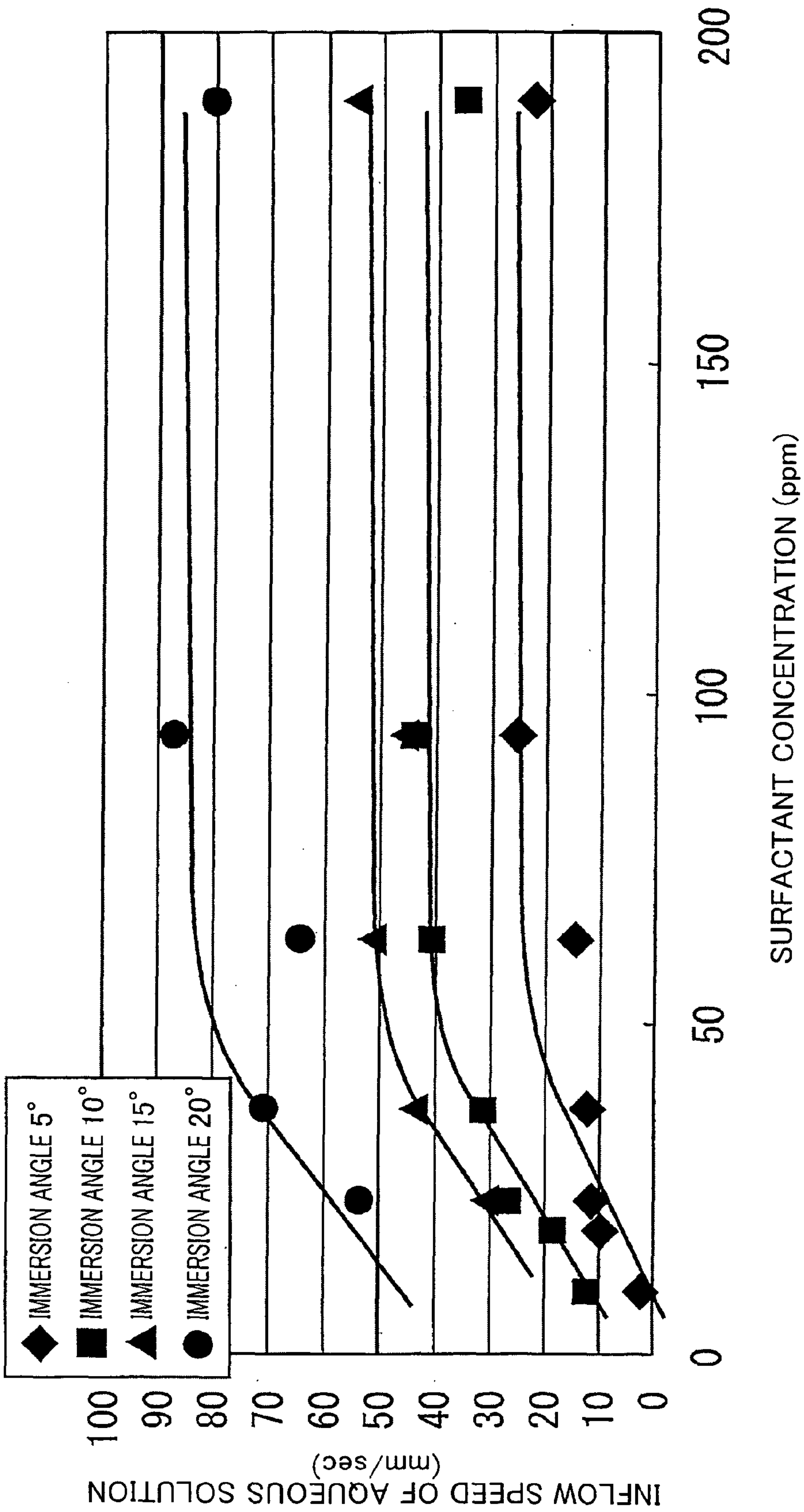

IMMERSION ANGLE 5°
IMMERSION ANGLE 10°
IMMERSION ANGLE 15°
IMMERSION ANGLE 20°
INFLOW SPEED OF AQUEOUS SOLUTION (mm/sec)
100
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
SURFACTANT CONCENTRATION (ppm)

FIG.12

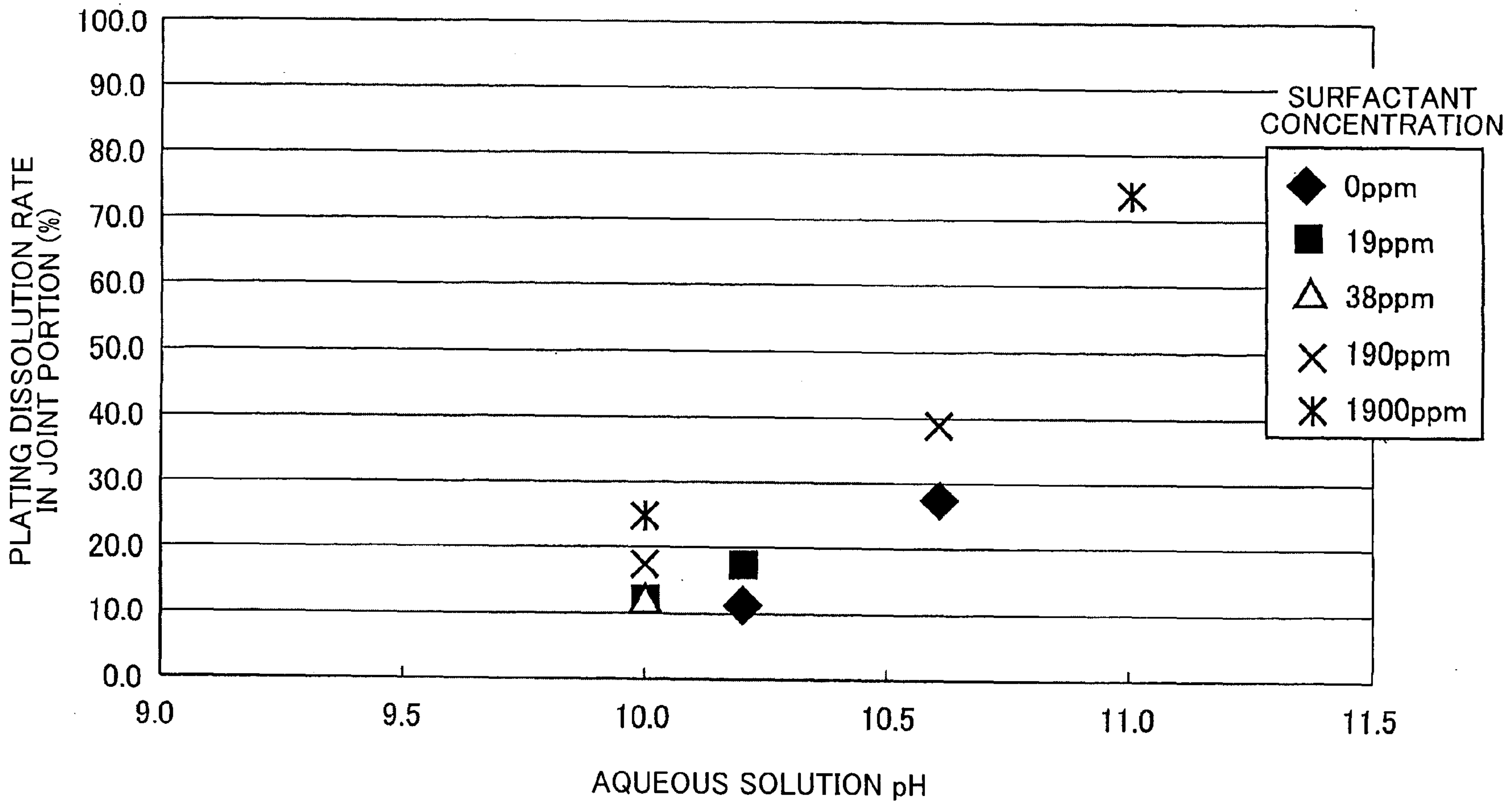

PLATING DISSOLUTION RATE IN JOINT PORTION (%)
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
9.0
9.5
10.0
10.5
11.0
11.5
AQUEOUS SOLUTION pH
SURFACTANT CONCENTRATION
◆ 0ppm
■ 19ppm
△ 38ppm
× 190ppm
✳ 1900ppm

FIG.13

		SURFACTANT CONCENTRATION				
		0ppm	19ppm (1/100 DILUTION)	38ppm (1/50 DILUTION)	190ppm (1/10 DILUTION)	1900ppm (1/1 DILUTION)
pH	10.0	–	11.5	12.1	17.3	24.7
	10.2	11.4	17.1	–	–	–
	10.5	27.1	–	–	38.6	–
	11.0	–	–	–	–	74.3

FIG.14

CHEMICAL EQUILIBRIUM OF
ELECTRODEPOSITION COATING MATERIAL

$n\underline{Resin{-}H^+}+\underline{(1-n)H^+}+R'{-}COO^- \Leftrightarrow n\underline{Resin}+R'{-}COOH$

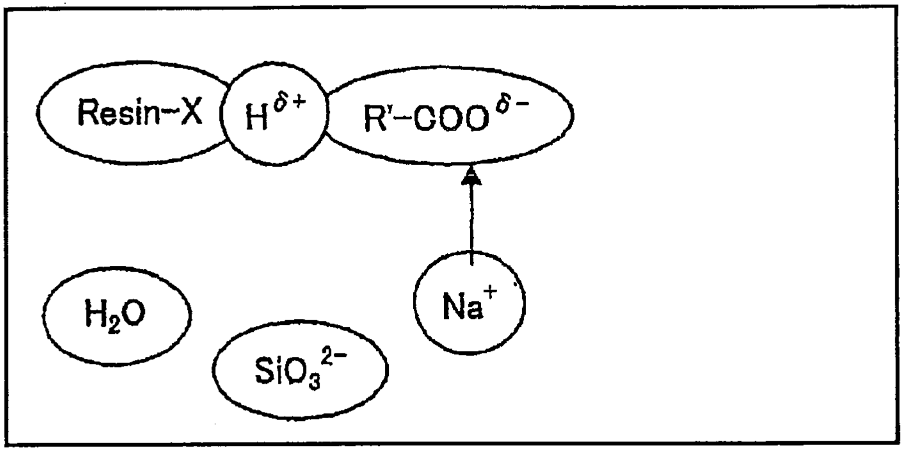


FIG.15

$Na_2SiO_3+2R'{-}COOH \rightarrow H_2SiO_3+2Na^++2R'{-}COO^-$

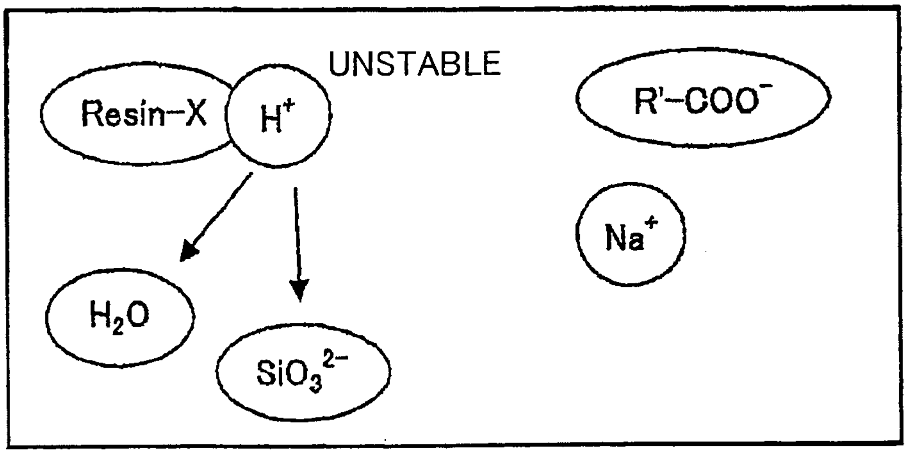
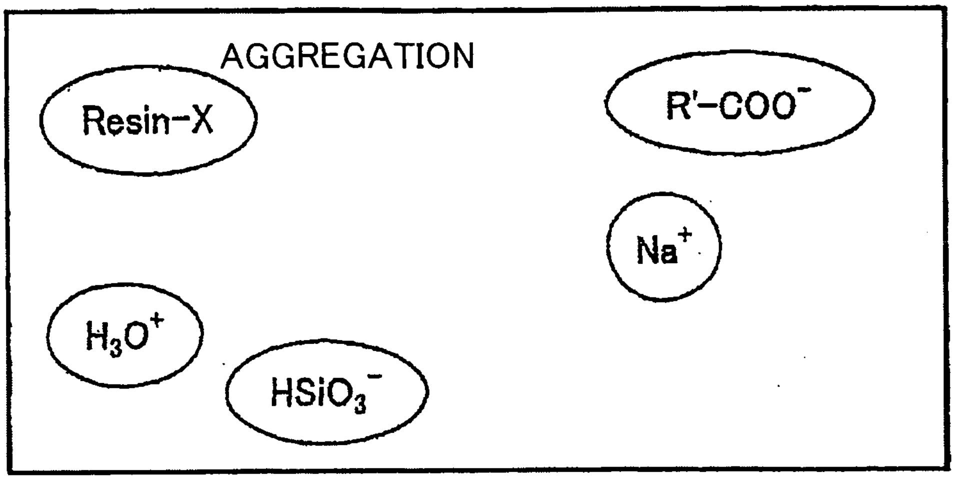


FIG.16

$\text{Resin}-\text{H}^{+}+\text{R}'-\text{COO}^{-}\rightarrow\underline{\text{Resin}}+\text{R}'-\text{COOH}$



REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2004238681 A **[0002]**