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(54) Method of chemical conversion coating for low-lead electrodeposition coating

(57) A method of pretreatment for low-lead electrodeposition with no lead or with a low lead content is provided, which comprises the step of forming a zinc phosphate film on a metal surface so that a corrosion resistance value according to the AC impedance method is not less than 2,500 Ω cm^2, and then subjecting the substrated metal with a cationic electrodeposition coating with a lead concentration of not more than 300 ppm.

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Description

Field of the Invention

[0001] The present invention relates to a method of surface-treating a substrate metal to be subjected to electrodeposition coating. More particularly, the present invention relates to a method of surface-treating a substrate metal for electrodeposition coating on a metal surface by means of an electrodeposition coating bath containing no lead or with low lead content.

Background Art

[0002] Recently, cationic electrodeposition coating is widely employed as a method for coating a metal of an automobile body and the like. Generally, such a major cationic electrodeposition coating composition contains an epoxy-resin-based film-forming resin as an amino group containing resin and a blocked polyisocyanate as a cross-linking agent. To this composition, an anti-corrosion pigment is added to retain the durability of the coating film after the coating treatment. A major anti-corrosion pigment is a lead compound such as a basic lead pigment. Contrary to the fact that this coating composition has an excellent anti-corrosion property, the use of lead is becoming more and more restricted from the view point of its toxicity and, in future, the electrodeposition coating bath should not contain lead. Meanwhile, in order to ensure adhesion and durability of the coating film, a surface of a metal (hereafter referred to as "substrate metal") to be subjected to an electrodeposition coating process is pretreated as shown in Fig. 1 with a chemical conversion treatment solution before carrying out the electrodeposition coating process. The chemical conversion treatment solution typically contains zinc, manganese, nickel, fluoride, and the like. By this pretreatment, a zinc phosphate film is formed on the surface of the substrate metal.

[0003] Such a chemical conversion treatment solution is prepared on the presupposition that the electrodeposition coating bath contains lead. Therefore, in the case where the electrodeposition coating process is carried out using an electrodeposition coating bath containing no lead or containing lead at less than a predetermined concentration, a sufficient durability of the coating film cannot be obtained by the conventional chemical conversion treatment solution.

DISCLOSURE OF THE INVENTION

[0004] A purpose of the present invention is to provide a method of pretreatment for a low-lead electrodeposition coating process, which is carried out in an electrodeposition coating bath containing no lead or a low lead.

[0005] Accordingly, the present invention provides a method of chemical conversion treating a substrate metal useful for a cationic electrodeposition coating process with an electrodeposition coating bath containing a lead at a concentration of not more than 300 ppm, which comprises the step of forming a zinc phosphate film on the metal surface so that a corrosion resistance value according to the AC impedance method is not less than 2,500 Ω cm^2.

[0006] Especially, the present invention concerns a method of chemical conversion treating the substrate metal which is useful for a cationic electrodeposition coating process substantially with zero lead concentration in the electrodeposition coating bath.

[0007] More specifically, the present invention concerns a method of chemical conversion treating the substrate metal by subjecting the metal surface to an immersion-treatment with a chemical conversion treatment solution containing 0.5 to 1.5 g of zinc ions, 5 to 30 g of phosphate ions, 0.1 to 4 g of nickel ions, 0.6 to 3 g of manganese ions, 0.05 g or more of fluoride ions, 5 to 20 ppm of copper ions, and a chemical conversion promoter as major components in one liter of the chemical conversion treatment solution.

[0008] By treating, by the chemical conversion treating method of the present invention, the surface of the substrate metal to be subjected to the cationic electrodeposition coating process, an acidic zinc phosphate film having a corrosion resistance value of not less than 2,500 Ω cm^2 according to the AC impedance method can be formed on the surface. Since the film having such a corrosion resistance value is formed, it is possible to form a coating film having an excellent durability even if the electrodeposition coating process is carried out by means of a cationic electrodeposition coating bath with low lead content.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The above and further objects and features of the invention will more fully be apparent from the following detailed description with accompanying drawings, in which,

Fig. 1 is a view illustrating steps for a chemical conversion treatment; and
Fig. 2 is a view illustrating an AC impedance equivalent circuit.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The chemical conversion treatment of the present invention provides a method suitable for surface treatment of a metal to be subjected to substrate treatment, prior to cationic electrodeposition coating substantially with no lead content.

[0011] An electrodeposition coating composition containing no lead for use in the present invention may be, for example, the following composition.

[0012] A representative low-lead electrodeposition coating composition may be, for example, a cathode electrodeposition coating composition containing components of (A) 40 to 95 wt% of a film-forming resin with an average molecular weight of 500 to 20,000 containing both an amino group and a hydroxyl group and being water-dilutable by acid neutralization and (B) 5 to 60 wt% of a blocked polyisocyanate cross-linking agent.

[0013] The film-forming resin of the component (A) is a resin with an average molecular weight of 500 to 20,000 containing an amino group (for example, a primary amino group, a secondary amino group, or a tertiary amino group) and a (primary or secondary) hydroxyl group and being water-dilutable with an acid. In this case, the amount of amino groups is usually represented by an amino value, which is typically within the range of 30 to 150, preferably within the range of 45 to 80. If the amino value is insufficient, the water-dilution property will decrease. The amount of hydroxyl groups is represented by a primary hydroxyl value, which is typically within the range of 20 to 200, preferably within the range of 50 to 120. The hydroxyl group acts as a cross-linking site. A secondary hydroxyl group, a primary amino group, or a secondary amino group are used as a cross-linking reaction group in addition to a primary hydroxyl group. Such a film-forming resin is typically formed by introducing an amino group to an epoxy resin, an epoxy-containing acrylic copolymer resin, a polyurethane resin, or the like.

[0014] The blocked isocyanate cross-linking agent (B) is typically obtained by blocking isocyanate groups in a multifunctional isocyanate.

[0015] The multifunctional isocyanate may be, for example, an aliphatic, alicyclic, and/or aromatic polyisocyanate having two or more isocyanate groups with respect to one molecule. Examples of the multifunctional isocyanate include isomers or isomer mixtures of toluylene diisocyanate, toluylene triisocyanate, 4,4'-diphenylmethane diisocyanate, isophorone diisocyanate (IPDI), xylylene diisocyanate (XDI), norbornene diisocyanate (NBDI), hexamethylene diisocyanate (HMDI), biphenyl tetraisocyanate, and/or naphthyl tetraisocyanate, and hydrogenated products thereof, such as dicyclohexylmethane diisocyanate.

[0016] A usable blocking agent is well-known in the art, and examples of the usable blocking agent include aliphatic alcohols such as n-butanol, 2-ethylhexanol, ethylene glycol monobutyl ether, and cyclohexanol; phenols such as phenol, nitrophenol, cresol, and nonylphenol; oximes such as dimethyl ketoxime, methyl ethyl ketoxime, and methyl isobutyl ketoxime; and lactams such as caprolactam.

[0017] Preparation of a cationic electrodeposition coating material composition such as mentioned above can be carried out by blending a metal compound and an optional cross-linking agent to a cationic electrodeposition resin before or after neutralization of the cationic electrodeposition resin and then, after the neutralization if not neutralized yet, conducting a water-dispersion, i.e. an emulsification, or by blending a metal compound and an optional cross-linking agent to an emulsified cationic electrodeposition resin, or by the like method. The neutralization can be carried out by means of a water-soluble organic acid such as formic acid, acetic acid, lactic acid, propionic acid, citric acid, malic acid, tartaric acid, acrylic acid, or sulfamic acid, or an inorganic acid such as hydrochloric acid or phosphoric acid.

[0018] Further, the cationic electrodeposition coating composition of the present invention may optionally contain ordinary coating material additives, for example, a coloring pigment such as titanium white, carbon black, or red oxide; an extender pigment such as talc, calcium carbonate, mica, clay, or silica; an anti-corrosive pigment, for example a non-pollutant anti-corrosive agent such as zinc phosphate or aluminum phosphomolybdate, and optionally basic lead silicate and the like dispersed in a pigment-grinding resin and used as a paste. Also, an anti-cissing agent, a solvent, a curing catalyst, and the like may be allowed to be contained therein.

[0019] The cationic electrodeposition coating can be carried out in accordance with a known method, generally by diluting the above-mentioned electrodeposition coating composition with deionized water so that a solid component concentration will be about 5 to 40 wt%, preferably 15 to 25 wt%, adjusting an electrodeposition coating bath, with pH adjusted within the range of 5.5 to 8.0, usually at a bath temperature of 15 to 35°C, and using a substance to be coated as a cathode under the condition of a load voltage of 100 to 450 V.

[0020] The film thickness of the coating material to be formed by the electrodeposition coating process is not specifically limited, and may be suitably within the range of 5 to 60 μm, preferably within the range of 10 to 40 μm, based on the cured coating film. Also, it is suitable that a baking curing temperature of the coating film is generally 100 to 200°C, preferably 160 to 180°C, and the baking is carried out for about 10 to 30 minutes.

[0021] On the substrate metal surface treated with the chemical conversion treating method of the present invention, there is formed a zinc phosphate film having a corrosion resistance value of the metal surface of not less than 2,500 $\Omega\,cm^2$ according to the AC impedance method. The inventors of the present invention have found out that, by forming a zinc phosphate film having an AC impedance within this range on the metal surface, a coating film being excellent in durability can be formed by the electrodeposition coating process even if the cationic electrodeposition coating bath does not contain lead ions.

[0022] The chemical conversion treating method of the present invention is characterized in that an aqueous solution of acidic zinc phosphate containing copper ions is used as a chemical conversion treating agent.

[0023] The aqueous solution of acidic zinc phosphate according to the present invention contains 0.5 to 1.5 g/liter of zinc ions, 5 to 30 g/liter of phosphate ions, 0.1 to 4 g/liter of nickel ions, 0.6 to 3 g/liter of manganese ions, 0.05 g/liter or more of fluoride ions, 5 to 20 ppm of copper ions, and a chemical conversion promoter as major components.

[0024] The chemical conversion treatment solution of the present invention contains 0.5 to 1.5 g/liter, preferably 0.7 to 1.2 g/liter, of zinc ions as an essential component. If the zinc ion content is less than 0.5 g/liter, a uniform phosphate film is not formed on an iron-based surface, partially generating a blue-color-like film. On the other hand, if the zinc ion content exceeds 1.5 g/liter, the film on the iron-based surface is likely to be a leaf-like crystal such as generated by a spraying treatment, although a uniform phosphate film is formed, so that it is not suitable as a substrate for cationic electrodeposition coating. (In the above, the concentration unit g/liter means that the component is contained in gram units per one liter of the chemical conversion treatment solution. Hereafter, the concentration unit g/liter is used in the same sense throughout the specification.)

[0025] The phosphate ions are contained at 5 to 30 g/liter, preferably 10 to 20 g/liter. If the phosphate ion content is less than 5 g/liter, a non-uniform film is likely to be formed. If the phosphate ion content exceeds 30 g/liter, it is not possible to expect an effect that exceeds that of the present invention, and the amount of drugs to be used increases, so that it is economically disadvantageous.

[0026] The nickel ions are contained at 0.1 to 4 g/liter, preferably 0.3 to 2 g/liter. Nickel ions in the presence of manganese ions further improve the formation film performance, and improve the close adhesion and the anti-corrosion property after the cationic electrodeposition coating process. If the nickel ion content is less than 0.1 g/liter, the effect of adding the nickel ions does not appear. On the other hand, if the nickel ion content is more than 4 g/liter, the amount of the zinc phosphate film decreases, causing adverse effects on the anti-corrosion property.

[0027] The manganese ions are contained at 0.6 to 3 g/liter, preferably 0.8 to 2 g/liter. If the manganese ion content is less than 0.6 g/liter, the manganese content in the coating film generated on a zinc-based surface decreases, so that the close adhesion between the substrate and the coating film after the cation electrodeposition coating process will be insufficient. If the manganese ion content exceeds 3 g/liter, it is not possible to expect an effect that exceeds that of the present invention, so that it is economically disadvantageous.

[0028] The fluoride ions are contained at not less than 0.05 g/liter, preferably 0.1 to 2 g/liter. If the fluoride ion content is less than 0.05 g/liter, it is not possible to achieve miniaturization of the crystal of the phosphate film, improvement of the anti-corrosion property after the coating process, and a low-temperature formation process. In the meantime, even if the fluoride ions are allowed to be present in an excessive amount, it is not possible to expect an effect that exceeds that of the present invention, so that it is economically disadvantageous. The fluoride ions are preferably used as complex fluoride ions.

[0029] The copper ions are contained at 5 to 20 ppm, preferably 10 to 15 ppm. If the copper ion content is less than 5 ppm, the close adhesion of the coating film and the adhesion durability of the coating film are insufficient. On the other hand, if the copper ion content exceeds 20 ppm, the outer appearance changes, so that it is not preferable.

[0030] At least one kind selected from the group consisting of 0.01 to 0.2 g/liter, preferably 0.04 to 0.15 g/liter of nitrite ions, 0.05 to 2 g/liter, preferably 0.1 to 1.5 g/liter of m-nitrobenzenesulfonate ions, 0.5 to 5 g/liter, preferably 1 to 4 g/liter of hydrogen peroxide (as converted to 100% H_2O_2), and 0.1 to 5 g/liter, preferably 0.5 to 2 g/liter, of hydroxylamine is used as the chemical conversion promoter. If these promoters are contained below a prescribed amount, it is not possible to carry out a sufficient chemical conversion on an iron-based surface, thereby producing yellow rusts and the like. If the promoters are contained above the prescribed amount, a non-uniform blue-color-like film is likely to be formed on the iron-based surface.

[0031] As a source for these major components, it is possible to use, for example, zinc oxide, zinc carbonate, zinc nitrate or the like as a source for zinc ions; phosphoric acid, zinc phosphate, manganese phosphate or the like as a source for phosphate ions; nickel carbonate, nickel nitrate, nickel chloride, nickel phosphate or the like as a source for nickel ions; manganese carbonate, manganese nitrate, manganese chloride, manganese phosphate or the like as a source for manganese ions; hydrofluoric acid, borohydrofluoric acid, silicohydrofluoric acid, a metal salt thereof (for example, zinc salt, nickel salt excluding a sodium salt since it does not produce a desired effect), as a source for fluoride ions. Also, a complex fluoride, which is a borofluoride and/or a silicofluoride, or the like can be used as a source for the complex fluoride ions. The chemical conversion promoter may be, for example, sodium nitrite, ammon nitrite, sodium m-benzenesulfonate, hydrogen peroxide, hydroxylamine or the like.

[0032] The treatment solution of the present invention may further contain nitrate ions and/or chlorate ions. The nitrate ions are preferably contained at a concentration of 1 to 10 g/liter, preferably 2 to 8 g/liter. The chlorate ions are contained at a concentration of 0.05 to 2 g/liter, preferably 0.2 to 1.5 g/liter. As a source for nitrate ions, it is possible to use sodium nitrate, ammon nitrate, zinc nitrate, manganese nitrate, nickel nitrate, or the like. As a source for chlorate ions, it is possible to use sodium chlorate, ammonium chlorate, or the like.

[0033] A treatment temperature by means of the chemical conversion treatment solution according to the present invention may be, for example, 30 to 70°C, preferably 35 to 50°C. If the temperature is too low, the chemical conversion property will be poor, requiring a long period of time for the treatment. If the temperature is too high, the balance of the treatment solution is likely to be destroyed due to decomposition of the chemical conversion promoter, precipitate generation of the treatment solution, or the like, so that it is difficult to obtain a good film.

[0034] The period of time for immersion may be not less than 15 seconds, preferably 30 to 120 seconds. If the period of time for immersion is too short, a film having a desired crystal cannot be sufficiently formed. Practically, if an article having a complex shape like an automobile body is to be treated, an immersion treatment may include dipping treatment which may be carried out for not less than 15 seconds, preferably 30 to 90 seconds, and then a spraying treatment is carried out for not less than 2 seconds, preferably 5 to 45 seconds. Here, in order to wash away an adhering sludge formed at the dipping treatment, the spraying treatment is carried out for as long a period of time as possible. Therefore, the immersion treatment according to the present invention includes an embodiment of such dipping treatment / spraying treatment.

[0035] The present invention also relates to a concentrated treatment agent that provides a treatment solution having the above-mentioned construction. It is sufficient that this concentrated treatment solution contains a source for supplying zinc ions, a source for supplying phosphate ions, a source for supplying nickel ions, a source for supplying manganese ions, a source for supplying fluoride ions, and a source for supplying copper ions at amounts that are sufficient to construct the treatment solution having the above composition by diluting the treatment solution to 1 to 4 weight/volume %. However, in this solution, a sodium-based compound must not be contained. This is because, if manganese ions and/or fluoride ions are present together with sodium ions, a precipitate is formed, raising a problem in preparing the treatment solution. Therefore, if a sodium compound is to be used, it is necessary to add it as a separate solution into the treatment bath.

[0036] According to the present invention as constructed above, it is possible to form by a low-temperature process a film that shows a sufficient effect as well as close adhesion and anti-corrosion property as a substrate for cationic electrodeposition coating on a metal surface having a zinc-based surface as well as an iron-based surface or both.

[0037] The AC impedance of the chemical conversion treated metal surface can be measured as follows on the basis of a principle described in "Basic Electrochemistry" by Shinobu Sotojima [p. 373, published by Asakura Shoten Co., Ltd., July 10, 1967] and "Electrochemistry Measurement Method" by Akira Fujishima, Masuo Aizawa, and Tooru Inoue [pp. 219-222, published by Gihodo Shuppan Co., Ltd., November 15, 1984].

[0038] A metal plate to be measured was placed in a cell filled with a corrosive solution, and an impedance was measured by sweeping a frequency to calculate a corrosion resistance value by an equivalent circuit analysis shown in Fig. 2.

[Impedance measurement condition]

[0039]

Frequency range : 100 kHz to 50 mHz
Applied voltage : 10 mV relative to an immersion potential
Corrosive solution : 5 wt% saline solution
Area of measurement : 1 cm^2
Measurement starting time : 30 minutes after the immersion
Equivalent circuit : The one shown in Fig. 2 was used.
Measurement devices : The measurement devices incorporated in the measuring apparatus were as follows.

1) Potentiostat : HA-501G (manufactured by Hokuto Denko Co., Ltd.)
2) Frequency characteristics analyzer : S-5720C (Block manufactured by NF Circuit Co., Ltd.)
3) AC impedance measurement software : HZ-1AC (manufactured by Hokuto Denko Co., Ltd.)

EXAMPLES

[0040] The present invention will be more specifically explained with reference to the examples shown below.

Examples 1 to 3

(I) Chemical conversion treatment of a substrate metal

[0041] A metal plate SPCC-SD (G3141) of 7 cm × 15 cm, which had been degreased, washed with water, and surface-adjusted, as shown in Fig. 1 was immersed in a chemical conversiontreatment solution of 42°C having a composition shown in Table 1 to carry out a chemical conversion treatment. A period of time for immersion is also shown in Table 1.

[0042] In Table 1, a standard phosphate chemical conversion treatment solution refers to a solution containing the following components in one liter of the treatment solution.

[Standard phosphate chemical conversion treatment solution]

[0043]

Zinc ions	1.0 g/liter
Phosphate ions	15.0 g/liter
Nickel ions	1.0 g/liter
Manganese ions	0.6 g/liter
Nitrate ions	6.0 g/liter
Nitrite ions	0.14 g/liter
Silicon fluoride ions	1.0 g/liter
Total acid	21.0 points
Free acid	0.7 point

[0044] The metal plate which had been chemical conversion treated was further washed with water, washed with purified water, and dried, as shown in Fig. 1, to obtain a chemical conversion treated metal plate.

[0045] The steps before and after the chemical conversion treatment shown in Fig. 1 will be hereafter explained.

(a) Degreasing

[0046] A metal plate was immersed in a mixture of alkaline degreasing agents A and B "Surfcleaner SD 250" (manufactured by Nippon Paint Co., Ltd.) (concentration in water is adjusted so that A is contained at 1.5 wt% and B at 0.7 wt%) at 42°C for two minutes.

(b) Washing with water

[0047] A tap water is used to wash the metal plate at room temperature for 15 seconds.

(c) Surface-adjustment

[0048] The metal plate is subjected to immersion treatment at room temperature for 15 seconds in a surface-adjusting agent "Surffine 5N-10" (manufactured by Nippon Paint Co., Ltd., at a concentration of 0.1 wt%).

(d) Washing with water

[0049] A tap water is used to wash the metal plate at room temperature for 15 seconds.

(e) Washing with purified water

[0050] Ion-exchanged water is used for immersion treatment of the metal plate at room temperature for 15 seconds.

(f) Drying

[0051] The metal plate is dried for 10 minutes by hot wind of 100°C.

(II) Measurement of AC impedance of chemical conversion treated metal plate

[0052] The AC impedance of the chemical conversion treated metal plate was measured by the above-mentioned method.

(III) Cationic electrodeposition coating on the chemical conversion treated metal plate

Synthesis Example 1 : Synthesis of base resin

[0053] A flask equipped with a stirring rod, a cooler, a nitrogen-introducing tube, a thermometer, and a dropping funnel was prepared. Into this flask were added 92 g of 2,4-/2,6-tolylene diisocyanate (weight ratio 8/2), 95 g of methyl isobutyl ketone, and 0.5 g of dibutyltin dilaurate, and further 21 g of methanol was dropwise added to the mixture with stirring. The reaction was started at room temperature and the temperature was raised to 60°C by generated heat. Then, after the reaction was continued for 30 minutes, 57 g of ethylene glycol mono-2-ethylhexyl ether was dropwise added with the dropping funnel, and further 42 g of 5-mol adduct of bisphenol A-propylene oxide was added. The reaction was carried out mainly at a temperature range of 60°C to 65°C and continued while measuring the IR spectrum until the isocyanate group disappeared. Next, 365 g of an epoxy resin having an epoxy equivalent of 188 and synthesized from bisphenol A and epichlorohydrin was added, and the temperature was raised to 125°C. Thereafter, 1.0 g of benzyldimethylamine was added to carry out a reaction at 130°C until the epoxy equivalent became 410. Subsequently, 87 g of bisphenol A was added into a reaction vessel to carry out a reaction at 120°C, whereby the epoxy equivalent became 1190. Then, the reaction product was cooled, and 11 g of diethanolamine, 24 g of N-methylethanolamine, and 25 g of ketiminated compound of aminoethylethanolamine (79 wt% methyl isobutyl ketone solution) were added to carry out a reaction at 110°C. for two hours. Thereafter, the resultant was diluted with methyl isobutyl ketone until the non-volatile component occupied 80% to obtain a base resin containing an oxazolidone ring.

Synthesis Example 2 : Synthesis of blocked isocyanate

[0054] A flask equipped with a stirring rod, a cooler, a nitrogen-introducing tube, a thermometer, and a dropping funnel was prepared. Into this flask were added 199 g of trimer of hexamethylene diisocyanate (Coronate HX : manufactured by Nippon Polyurethane Co., Ltd.) and 11.3 g of ε-caprolactam. Then, the temperature of the contents in the flask was raised to 80°C to uniformly dissolve the mixture, to which were added 32 g of methyl isobutyl ketone, 0.05 g of dibutyltin ldiaurate, and 0.05 g of 1,8-diazabicyclo(5,4,0)-7-undecene. While this mixture is stirred by bubbling nitrogen, 78.3 g of methyl ethyl ketoxime was dropwise added in one hour from the dropping funnel, while paying attention to generation of heat. The reaction was continued until the isocyanate group disappeared in the IR spectrum to obtain a blocked isocyanate cross-linking agent.

Synthesis Example 3 : Preparation of pigment-dispersing resin

[0055] A flask equipped with a stirring rod, a cooler, a nitrogen-introducing tube, a thermometer, and a dropping funnel was prepared. Into this flask was added 222.0 g of isophorone diisocyanate and, after dilution with 39.1 g of methyl isobutyl ketone, 0.2 g of dibutyltin dilaurate was added. After the temperature was raised to 50°C, 131.5 g of 2-ethylhexanol was dropwise added from the dropping funnel in two hours while the mixture is being stirred by bubbling nitrogen. By suitably cooling the mixture, the temperature was maintained at 50°C during the reaction. As a result, 2-ethylhexanol half-blocked isophorone diisocyanate was obtained (with solid components contained at 90%).

[0056] A flask equipped with a stirring rod, a cooler, a nitrogen-introducing tube, a thermometer, and a dropping funnel was prepared. Into this flask were added 376.0 g of Epon 828 (epoxy resin manufactured by Shell Chemical Co., Ltd.) and 114.0 g of bisphenol A, and the temperature was raised to 130°C under a nitrogen atmosphere. Then, 0.75 g of dimethylbenzylamine was added to carry out a reaction at an exothermic reaction 170°C for one hour to obtain a bisphenol A-type epoxy resin having an epoxy equivalent of 490 g. Then, after the resultant was cooled to 140°C, 198.4 g of the above 2-ethylhexanol half-blocked isophorone diisocyanate was added to carry out a reaction at 140°C for one hour. Thereafter, 161.8 g of ethylene glycol monobutyl ether was added, and the reaction mixture was cooled to 100°C. To this mixture were added 366.0 g of thiodiethanol, 134.0 g of dimethylolpropionic acid, and 144.0 g of deionized water to carry out a reaction at 70°C to 75°C until an acid value of 0.241 was obtained. Thereafter, the resultant was diluted with 353.3 g of ethylene glycol monobutyl ether to obtain a pigment-dispersing resin with a sulfonium ratio of 82 % (with solid components contained at 50 %).

Synthesis Example 4 : Preparation of pigment-dispersed paste

[0057] To the pigment-dispersing resin obtained in Synthesis Example 3 were dispersed carbon black, kaolin, and titanium dioxide at the following blending ratio, and the dispersion was crushed and adjusted by a sand mill to obtain a pigment-dispersed paste.

Component	parts by weight
Pigment-dispersing resin (solid components 50%)	60
Carbon black	2
Kaolin	15
Titanium dioxide	53
Deionized water	40

[0058] The base resin (350 g) (solid component) obtained in Synthesis Example 1 and the cross-linking agent (150 g) (solid component) obtained in Synthesis Example 2 were mixed, and ethylene glycol mono-2-ethylhexyl ether was added at 3 % (15 g) with respect to the solid components. Then, glacial acetic acid was added for neutralization so that the neutralization degree was 40.5 %, followed by slow dilution with ion-exchanged water. Then, methyl isobutyl ketone was removed under a reduced pressure so that the solid components occupied 36.0 %.

[0059] To 2,000 g of the emulsion thus obtained were added and mixed 460.0 g of pigment-dispersed paste obtained in Synthesis Example 4, 2,252.0 g of ion-exchanged water, and 1.0 wt% of dibutyltin oxide relative to the resin solid components to prepare an electrodeposition coating material containing solid components at 20.0 wt%.

[0060] A lead-containing electrodeposition coating material was prepared by adding lead acetate in the above-mentioned lead-free electrodeposition coating bath at 1,000 ppm as lead ions.

[0061] The above-mentioned surface-treated cold-rolled steel plate was immersed as a cathode in these electrodeposition coating baths and, after the electrodeposition was carried out so that the dried film thickness would be 20 μm, the coating film was cured at 160°C × 10 minutes for evaluation of the coating film.

(IV) Durability evaluation of electrodeposition coating film

[0062] The durability of the obtained electrodeposition coated plate was measured by the following two methods

(1) CCT test (cycle corrosion test)

[0063] After a cross cut (cut in a cross shape) was made on the plate, a cycle corrosion test (CCT) was carried out for 100 cycles. After the 100 cycles, the plate was taken out to evaluate the outer appearance by eye inspection.

[0064] Here, in one cycle of CCT, the following environment conditions are applied.

Salt water spraying test (SST : 5% NaCl × 35°C) for two hours

→ High-temperature high-humidity condition (98% RH × 40°C) for two hours

→ Drying condition (60°C) for four hours

(2) SDT test (Salt water dipping test)

[0065] A cut was made in a longitudinal direction on the test piece and, after immersion in 5% aqueous solution of table salt at 40°C for 240 hours, the cut portion was tape-peeled to evaluate the peeling width.

[0066] The composition of the chemical conversion treatment solution, the treatment time, and the results of measurement of the corrosion resistance value and the anti-corrosion property are shown in Table 1.

[0067] The standard for judgement of the evaluation results of the CCT test and the SDT test in Table 1 was as follows.

CCT : ○ both side maximum rust or blister width of 0 to 3 mm
X both side maximum rust or blister width of 3 mm or more

SDT : ○ with no peeling
△ peeling width of 0 to 1 mm
X peeling width of 1 mm or more

Comparative Example 1

[0068] The chemical conversion treatment and the cationic electrodeposition coating were carried out in the same manner as in Example 1 except that the standard phosphate chemical conversion treatment solution was used, without any change, as the chemical conversion treatment solution to evaluate the AC impedance of the chemical conversion treated metal plate and the anti-corrosion property of the electrodeposition coating film. The results are shown in Table 1.

Comparative Example 2

[0069] The chemical conversion treatment and the cationic electrodeposition coating were carried out in the same manner as in Example 1 except that the standard phosphate chemical conversion treatment solution with nickel ions removed and copper ions added instead at 10 ppm was used as the chemical conversion treatment solution to evaluate the AC impedance of the chemical conversion treated metal plate and the anti-corrosion property of the electrodeposition coating film. The results are shown in Table 1.

Table 1

Examples	Treatment solution composition	Treatment time (sec)	AC impedance of metal plate after the treatment with acidic phosphate (Ω cm^2)	Durability of coating film after the electrodeposition coating			
				CCT		SDT	
				Pb present	Pb absent	Pb present	Pb absent [1]
1	Standard chemical conversion treatment solution + Cu at 5 ppm	120	2800	○	○	○	○
2	Standard chemical conversion treatment solution + Cu at 10 pp	120	2900	○	○	○	○
3	Standard chemical conversion treatment solution + Cu at 20 pp	120	3000	○	○	○	○
Comparative Example 1	Standard chemical conversion treatment solution only	120	1250	○	×	○	×
Comparative Example 2	Standard chemical conversion treatment solution with Ni removed and Cu added at 10 ppm	120	2350	○	×	△	×

[1] Presence or absence of lead in the cationic electrodeposition coating bath

[0070] The chemical conversion treated metal obtained according to the method of the present invention has a film having a high corrosion resistance value on its surface. By using the metal plate having the film with this corrosion resistance value, it is possible to form a coating film having an excellent anti-corrosion property even if the cationic electrodeposition coating process is carried out in an electrodeposition coating bath containing no lead or with a low lead content. Also, according to the chemical conversion treating method of the present invention, a chrome rinsing process generally conducted at the last stage of the chemical conversion treatment process is no longer necessary, thereby further reducing the use of a heavy metal.

[0071] As this invention may be embodied in several forms without departing from the spirit of essential characteristics thereof, the present embodiment is therefore illustrative and not restrictive, since the scope of the invention is defined by the appended claims rather than by the description preceding them, and all changes that fall within metes and bounds of the claims, or equivalence of such metes and bounds thereof are therefore intended to be embraced by the claims.

Claims

1. A method of chemical conversion treating a substrate metal useful for cationic electrodeposition coating with an electrodeposition coating bath containing lead at a concentration of not more than 300 ppm, which comprises the step of forming a zinc phosphate film on the metal surface so that a corrosion resistance value according to an AC impedance method is not less than 2,500 Ω cm^2.

2. The method according to claim 1, wherein the electrodeposition coating bath contains the lead at a concentration of not more than 100 ppm.

3. The method according to claim 1, wherein the cationic electrodeposition coating bath contains substantially no lead.

4. The method according to any one of claims 1 to 3, wherein the metal surface is subjected to an immersion-treatment with a chemical conversion treatment solution containing 0.5 to 1.5 g of zinc ions, 5 to 30 g of phosphate ions, 0.1 to 4 g of nickel ions, 0.6 to 3 g of manganese ions, 0.05 g or more of fluoride ions, 5 to 20 ppm of copper ions, and a chemical conversion promoter as major components in one liter of the chemical conversion treatment solution.

5. The method according to claim 4, wherein the fluoride ions are complex fluoride ions.

6. The method according to claim 5, wherein a complex fluoride of borofluoride and/or silicofluoride is used as a source of the complex fluoride ions.

7. The method according to claim 4, wherein the chemical conversion promoter is one kind selected from the group consisting of 0.01 to 0.2 g/liter of nitrite ions, 0.05 to 2 g/liter of m-nitrobenzenesulfonate ions, 0.5 to 5 g/liter of hydrogen peroxide, and 0.1 to 5 g/liter of hydroxylamine, each representing a concentration in the chemical conversion treatment solution.

8. The method according to claim 4, wherein the chemical conversion treatment solution further contains 1 to 10 g of nitrate ions and/or 0.05 to 2 g of chlorate ions in one liter of the chemical conversion treatment solution.

9. The method according to any one of claims 1 to 8, wherein a treatment temperature is 30 to 70°C.

10. The method according to any one of claims 1 to 9, wherein the immersion treatment comprises a combination of dipping treatment of not less than 15 seconds and a subsequent spraying treatment of not less than 2 seconds.

11. The method according to any one of claims 1 to 10, wherein the surface of the substrate metal includes an iron-based surface and a zinc-based surface.

12. The concentrated treatment agent for preparing the chemical conversion treatment solution according to claim 4 or 8 by dilution with water.

Fig. 1

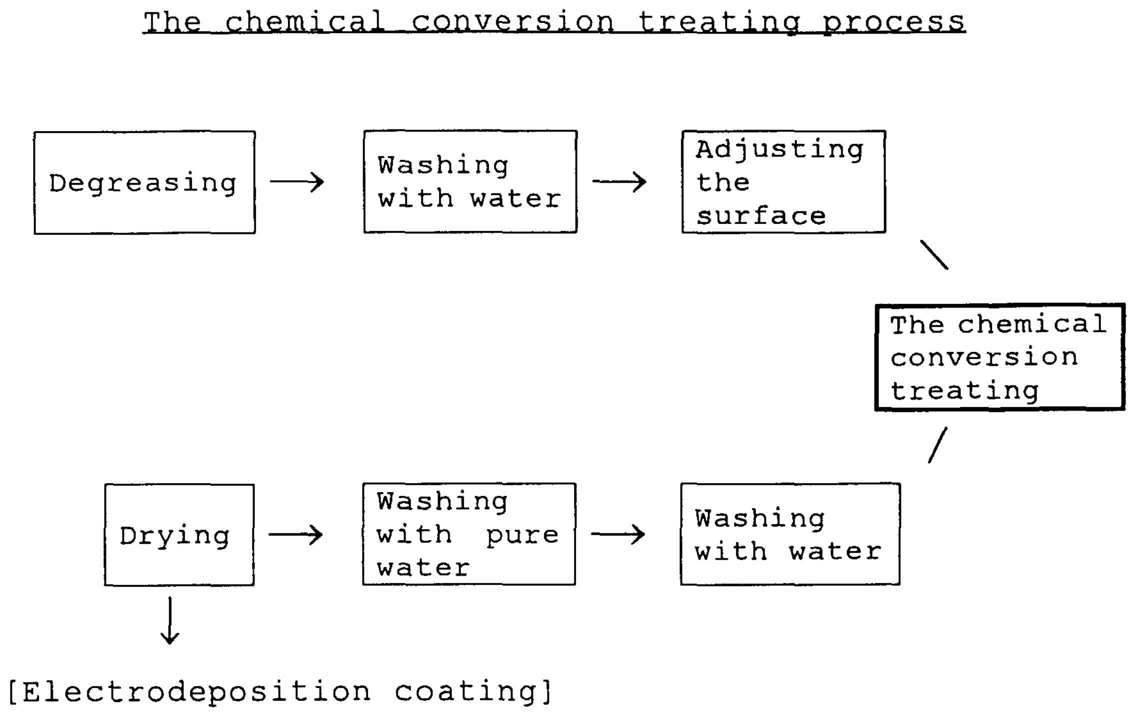
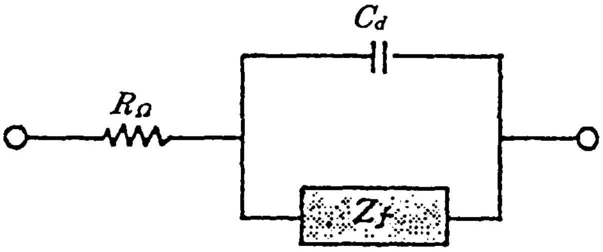

The chemical conversion treating process
Degreasing
Washing with water
Adjusting the surface
The chemical conversion treating
Washing with water
Washing with pure water
Drying
[Electrodeposition coating]

Fig. 2



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EUROPEAN SEARCH REPORT

Application Number
EP 99 10 0326

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	PATENT ABSTRACTS OF JAPAN vol. 096, no. 009, 30 September 1996 -& JP 08 134661 A (NIPPON PAINT CO LTD), 28 May 1996 * Table on page 7 of the original application * * abstract *	1-9,12	C23C22/36 C25D13/20
Y	---	10,11	
Y	EP 0 454 361 A (NIPPON PAINT CO LTD) 30 October 1991 * page 1, line 9-11; claim 1 * ---	10,11	
A	DE 43 30 002 C (HERBERTS GMBH) 23 March 1995 * page 4, line 52-55; claims 1,4 * ---	1-3	
A	DE 44 34 593 A (HERBERTS GMBH) 4 April 1996 * page 4, line 1-6; claims 1-3 * ---	1-3	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)**
A	EP 0 019 430 A (AMCHEM PROD) 26 November 1980 * page 2, line 1-11 * ---	1	C23C C25D
A	EP 0 287 133 A (METALLGESELLSCHAFT AG) 19 October 1988 * claim 13 * ---	10	
A	EP 0 401 616 A (HENKEL KGAA) 12 December 1990 ---		
A	FR 2 203 893 A (FOSFA COL SAS DI A DAL PANE ET) 17 May 1974 * examples III,,IV * --- -/--	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 April 1999	Torfs, F

CATEGORY OF CITED DOCUMENTS

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 99 10 0326

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 459 541 A (METALLGESELLSCHAFT AG ;PARKER STE CONTINENTALE (FR)) 4 December 1991 * claims 1,4,10 * ---	1	
A	WO 93 20259 A (HENKEL KGAA ;ROLAND WOLF ACHIM (DE); GOTTWALD KARL HEINZ (DE); HAM) 14 October 1993 * claims 1,3,4,6,10 * ---	1	
P,X	DE 197 35 314 A (BAYERISCHE MOTOREN WERKE AG) 26 March 1998 * column 4 * -----	1,4	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
	The present search report has been drawn up for all claims		

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 April 1999	Torfs, F

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 99 10 0326

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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19-04-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0454361 A	30-10-1991	JP 2065907 C	24-06-1996
		JP 4006281 A	10-01-1992
		JP 7100870 B	01-11-1995
		CA 2040813 A,C	25-10-1991
		DE 69108087 D	20-04-1995
		DE 69108087 T	16-11-1995
		US 5308413 A	03-05-1994
DE 4330002 C	23-03-1995	AT 166377 T	15-06-1998
		BR 9407384 A	29-10-1996
		CA 2170878 A	16-03-1995
		CN 1132519 A	02-10-1996
		CZ 9600631 A	14-08-1996
		DE 59406057 D	25-06-1998
		WO 9507319 A	16-03-1995
		EP 0739389 A	30-10-1996
		ES 2116615 T	16-07-1998
		JP 9502225 T	04-03-1997
		SI 739389 T	31-08-1998
		US 5702581 A	30-12-1997
		ZA 9406731 A	20-04-1995
DE 4434593 A	04-04-1996	AT 164870 T	15-04-1998
		DE 59501863 D	14-05-1998
		WO 9610057 A	04-04-1996
		EP 0783548 A	16-07-1997
		ES 2116108 T	01-07-1998
EP 0019430 A	26-11-1980	JP 1272481 C	11-07-1985
		JP 55152183 A	27-11-1980
		JP 58011515 B	03-03-1983
		AT 5487 T	15-12-1983
		AU 531740 B	01-09-1983
		AU 5828480 A	13-11-1980
		BR 8002887 A	23-12-1980
		CA 1136523 A	30-11-1982
		US 4311535 A	19-01-1982
EP 0287133 A	19-10-1988	DE 3712339 A	20-10-1988
		AU 1442788 A	13-10-1988
		CA 1332910 A	08-11-1994
		DE 3869455 A	30-04-1992
		GB 2204067 A,B	02-11-1988
		JP 2674075 B	05-11-1997
		JP 64000277 A	05-01-1989
		US 5236565 A	17-08-1993

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 99 10 0326

19-04-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0401616 A	12-12-1990	DE 3918136 A	06-12-1990
		CA 2058631 A	04-12-1990
		WO 9015167 A	13-12-1990
		EP 0477204 A	01-04-1992
		JP 4505479 T	24-09-1992
		PT 94242 A	08-02-1991
FR 2203893 A	17-05-1974	DE 2352659 A	02-05-1974
		ES 470637 A	11-10-1978
EP 0459541 A	04-12-1991	DE 4013483 A	31-10-1991
		CA 2039901 A	28-10-1991
		CZ 9101180 A	13-04-1994
		DE 59106926 D	04-01-1996
		ES 2081420 T	01-03-1996
		JP 4228579 A	18-08-1992
		MX 172859 B	17-01-1994
		PL 166676 B	30-06-1995
		RU 2051988 C	10-01-1996
		US 5268041 A	07-12-1993
WO 9320259 A	14-10-1993	DE 4210513 A	07-10-1993
		AT 138112 T	15-06-1996
		CA 2133455 A	14-10-1993
		DE 59206327 D	20-06-1996
		EP 0633950 A	18-01-1995
		ES 2086782 T	01-07-1996
		JP 7505445 T	15-06-1995
DE 19735314 A	26-03-1998	NONE	

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82