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(19) **United States**(12) **Patent Application Publication****Ando et al.**(10) **Pub. No.: US 2006/0113005 A1**(43) **Pub. Date: Jun. 1, 2006**(54) **METHOD FOR SURFACE TREATMENT OF ALUMINUM ALLOY****Publication Classification**(75) Inventors: **Katsutoshi Ando**, Saitama (JP);
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ABSTRACT(73) Assignees: **HONDA MOTOR CO., LTD; NIPPON PAINT CO., LTD.**(21) Appl. No.: **11/288,798**(22) Filed: **Nov. 29, 2005**(30) **Foreign Application Priority Data**

Nov. 30, 2004 (JP) 2004-347244

A method for surface treatment of aluminum alloy to form a uniform and dense zinc phosphate coating, which has excellent corrosion resistance properties on the surface of the aluminum alloy. The method includes steps of surface adjusting the surface of the aluminum alloy by a surface adjustor containing a predetermined volume of zinc phosphate particles, copolymer containing carboxylic acid group, and natural hectorite and/or synthetic hectorite respectively, and chemical conversion treating the surface of the resultant aluminum alloy by a zinc phosphate treating agent containing a predetermined volume of chelating agent that can chelate bond with iron ion.

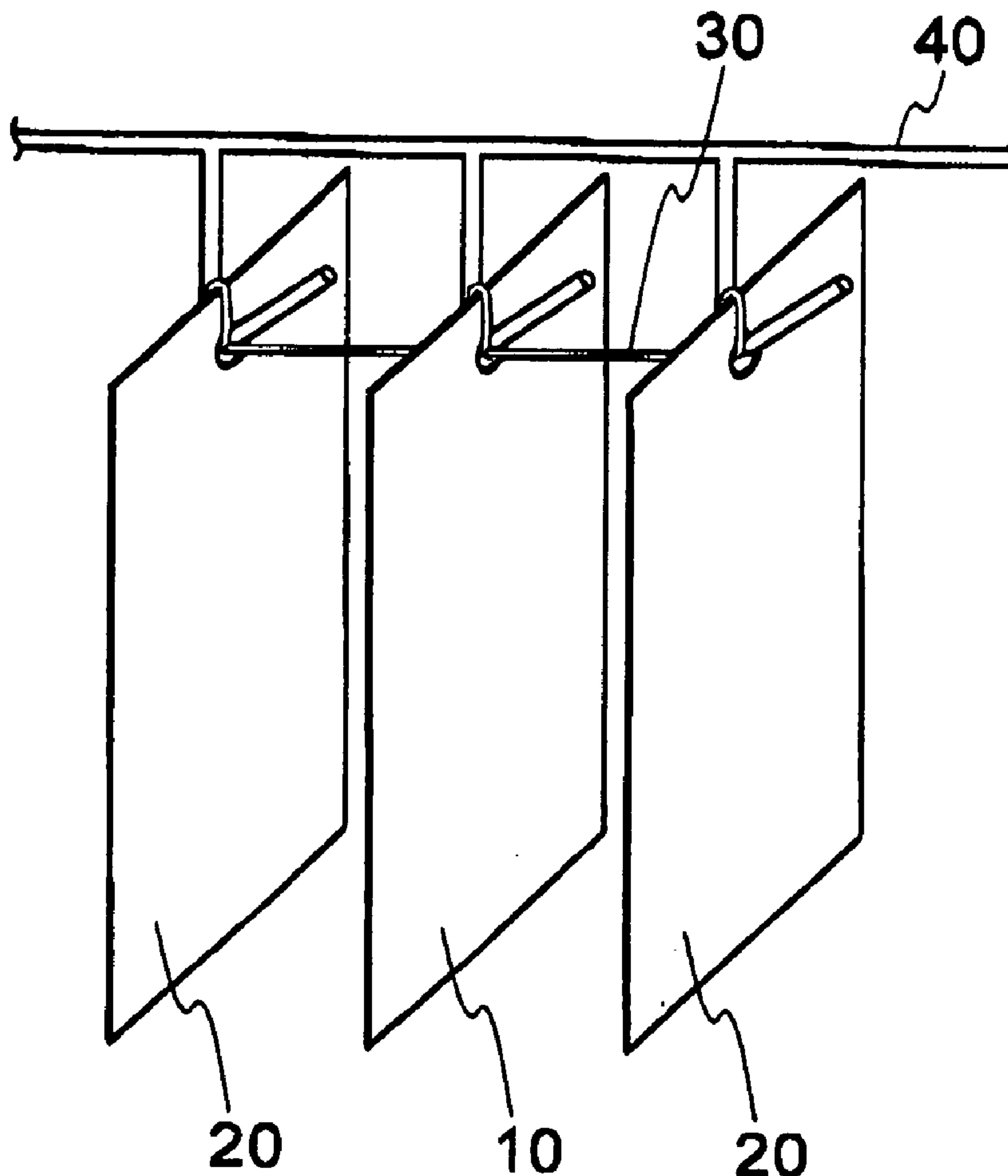
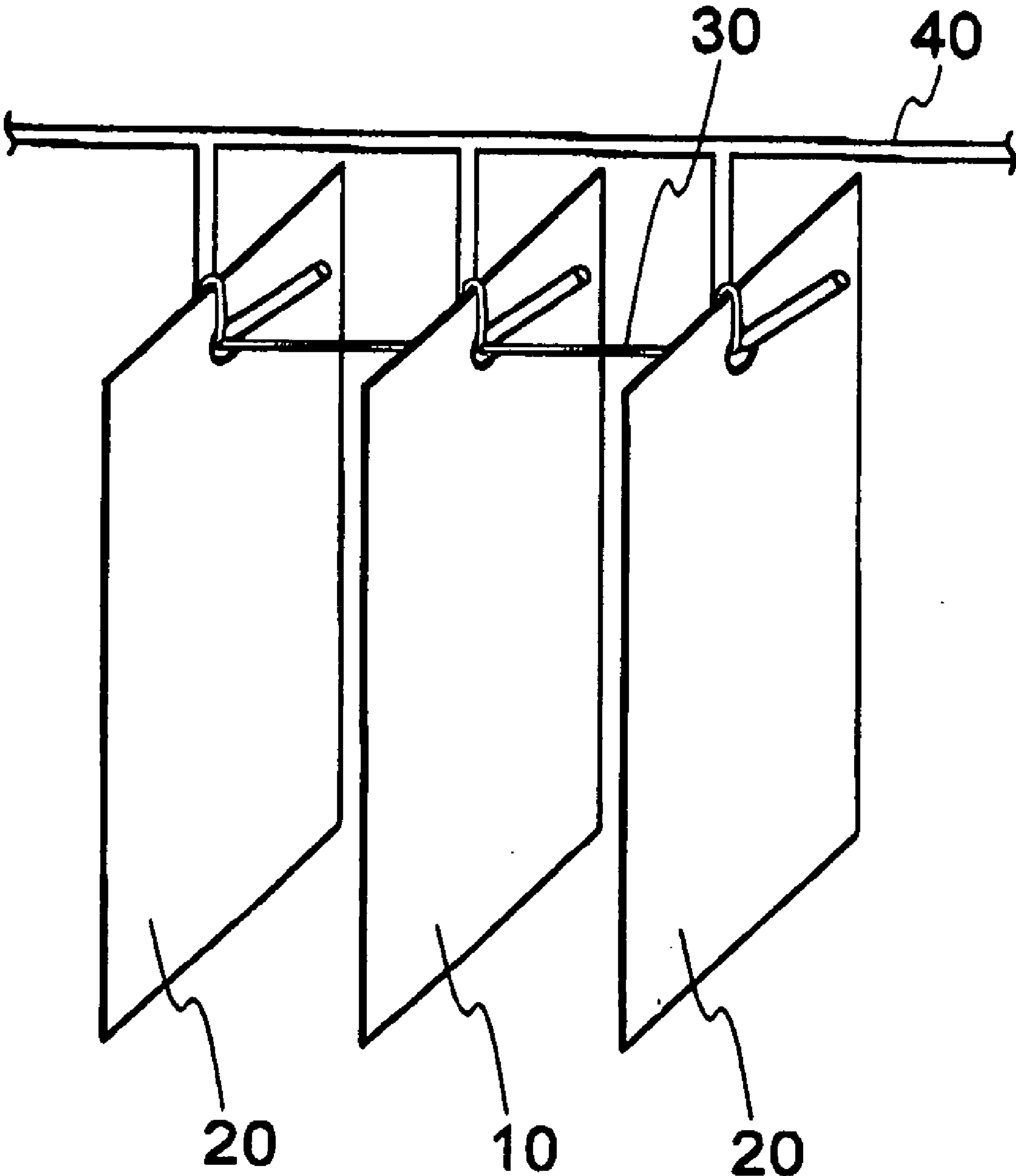


Fig. 1



METHOD FOR SURFACE TREATMENT OF ALUMINUM ALLOY

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is based upon and claims the benefit of priority from Japanese Patent application No. 2004-347244 filed on Nov. 30, 2004, the contents of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to a method for surface treatment of aluminum alloy. More particularly, it relates to a method for surface treatment of aluminum alloy that can form a zinc phosphate coating that is uniform, dense and excellent in corrosion resistance.

[0004] 2. Related Art

[0005] In the field of vehicle bodies and automobile parts, building materials, and furniture, etc., metallic materials such as steel plates, galvanized steel plates and aluminum alloys have been used. These metallic materials are, after molding, painted to be final products. Paint is applied to improve the appearance of these metallic materials, and has its principal object, to prevent corrosion of the material. The material is then sent to surface treatment processes such as degreasing, surface control, and chemical conversion treatment in sequence.

[0006] In order to perform the following chemical conversion treatment step, the surface must be adjusted to form a uniform and highly dense chemical conversion treatment coating rapidly over the surface of the metallic material. Specifically, a surface control agent is brought into contact with the surface of the material in order to have the particles of the surface control agent adsorbed on the surface of the material, therefore promoting the formation of the chemical conversion treatment coating.

[0007] In vehicle body and other vehicle parts, aluminum alloy is employed in part, and a member of the aluminum alloy is in contact with a cold rolled steel plate (hereinafter, referred to as a SPC) or an alloyed hot-dip zinc-coated steel plate (hereinafter, referred to as a GA). In these members wherein aluminum is a base metal, there may be a case wherein aluminum is excessively dissolved in the chemical conversion treatment agent to disturb a proper formation of the chemical conversion coating.

[0008] To avoid this problem, a vehicle body can be assembled with an insulating material sandwiched between the aluminum alloy and SPC or aluminum alloy and GA. With this configuration, the excess dissolution of aluminum in the chemical conversion treatment agent is inhibited in the chemical conversion treatment agent so that the formation of excellent chemical conversion coating on the aluminum alloy can be attained.

[0009] Use of insulating materials, however, disturbs current flow of the aluminum alloy during the next electro-deposition coating step, leading to failure of a proper coating. For this reason, an additional connection to the aluminum alloy via an electric cable, etc., is needed in the electro-deposition coating step. Moreover, retightening is

further required as the insulating material contracts during a baking step after the electro-deposition coating step. In short, the case in which insulating material requires more processes than usual operations and production lines specific to these additional steps.

[0010] A larger content of copper in aluminum alloy reduces its corrosion resistance property, in particular, filiform rust resistance and water adherence resistance properties. Degradation of these properties is caused by a large potential difference existing between the aluminum and copper that lead to a considerable amount of dissolution of aluminum under the corrosive environment. In order to assure excellent corrosion resistance property, contents of copper in the aluminum alloy need to be reduced; however, this solution poses a problem as it leads to a cost increase.

[0011] It is therefore an urgent necessity for those with ordinary skill in the art to develop a surface treatment method that enables to form a uniform and highly dense chemical conversion treatment coating with excellent corrosion resistance property on the surface of aluminum alloy. Research toward an improvement of chemical conversion treatment agent has been carried out in order to attain the method and is disclosed in the Japanese Patent No. 3366826 (hereinafter Patent Document 1). The patent document 1 proposed a water solution which mainly contains 0.1 g/l to 2.0 g/l of zinc ion, 0.1 g/l to 4.0 g/l of nickel ion, 0.1 g/l to 3.0 g/l of manganese ion, 5 g/l to 40 g/l of phosphate ion, 0.1 g/l to 15 g/l of nitrate ion, 0.01 g/l to 0.5 μ l of nitrite ion, and as a fluoride, 0.5 g/l to 1.0 g/l of fluoride in a complex fluoride, 0.3 g/l to 0.5 g/l of fluoride in a simple fluoride, and further proposes zinc phosphate treating agent that contains 0.025 g/l to 0.45 g/l of iron (Fe) in a chelating agent that can chelate bond with iron ion. According to the zinc phosphate treating agent, a uniform and highly dense zinc phosphate coating with excellent corrosion resistance property can be formed on the surface of an aluminum alloy having a copper content of 0.1% by weight or less, or on the surface treated by grinding thereof.

SUMMARY OF THE INVENTION

[0012] In order to solve the aforementioned problems, the present invention offers an improvement in both a surface adjustor and a chemical conversion treatment agent. It is an object of the present invention to provide a method for surface treatment of an aluminum alloy that can form a uniform and highly dense zinc phosphate coating with excellent corrosion resistance properties on the surface of the aluminum alloy.

[0013] The present inventors have diligently studied to solve the aforementioned problems. As a result, they finally achieved a formation of a uniform and highly dense zinc phosphate coating with excellent corrosion resistance property on the surface of the aluminum alloy. The method includes steps of surface adjusting the surface of the aluminum alloy by way of a surface adjustor that contains a determined amount of zinc phosphate particles, copolymer containing carboxylic acid group, and natural hectorite and/or synthetic hectorite, respectively, and then of chemical treating of chelating agent that can chelate bond with iron ion. More specific description will be given below.

[0014] A first aspect of the present invention is a method for surface treatment of aluminum alloy which includes

steps of degreasing and rinsing a surface of aluminum alloy, surface adjusting the surface of the degreased and rinsed aluminum alloy with a surface adjustor, chemical conversion treating of the surface of the surface adjusted aluminum alloy with a zinc phosphate chemical conversion treatment agent, the surface adjustor having a pH of not less than 7 and not more than 12 and containing not less than 50 ppm and not more than 2000 ppm of zinc phosphate particles having not more than three micrometers of D_{50} , not less than 2 ppm and not more than 200 ppm of a copolymer containing carboxylic acid group that copolymerizes a monomeric composition containing less than 50% by weight of acrylic acid and more than 50% by weight of 2-acrylamide-2-methylpropanesulfonic acid, and not less than 3 ppm and not more than 200 ppm of natural hectorite and/or synthetic hectorite, the zinc phosphate chemical conversion treatment agent comprising an acid aqueous solution containing more than 0.1 g/l and less than 2.0 g/l of zinc ion, more than 0.1 g/l and less than 4.0 g/l of nickel ion, more than 0.1 g/l and less than 3.0 g/l of manganese ion, 5 g/l and less than 40 g/l of phosphate ion, more than 0.5 g/l and less than 1.0 g/l of fluoride in a complex fluoride, more than 0.3/l and less than 0.5 g/l of fluoride in a simple fluoride, and more than 0.025 g/l and less than 0.45 g/l of iron (Fe) in a chelating agent that can chelate bond with iron ion.

[0015] A second aspect of the present invention is a method for surface treatment of aluminum alloy as in the first aspect of the present invention in which the content of copper in the aluminum alloy is not more than 0.2% by weight.

[0016] According to the present invention, a method for surface treatment of aluminum alloy can be provided that can form a uniform and highly dense zinc phosphate coating with excellent corrosion resistance properties on the surface of the aluminum alloy.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] **FIG. 1** shows an object material for treatment in which aluminum alloy and SPC are contacted and conducted.

DETAILED DESCRIPTION OF THE INVENTION

[0018] Hereinafter, embodiments of the present invention will be described in detail.

Surface Adjustor

[0019] The surface adjustor employed in the present invention contains a determined amount of zinc phosphate particles, copolymer containing carboxylic acid group, and natural hectorite and/or synthetic hectorite, respectively. More specifically, the surface adjustor has a pH of not less than 7 and not more than 12, and contains not less than 50 ppm and not more than 2000 ppm of zinc phosphate particles having not more than 3 micrometers of D_{50} , not less than 2 ppm and not more than 200 ppm of a copolymer containing carboxylic acid group that copolymerizes a monomeric composition containing less than 50% by weight of acrylic acid and more than 50% by weight of 2-acrylamide-2-methylpropanesulfonic acid, and not less than 3 ppm and not more than 200 ppm of natural hectorite and/or synthetic hectorite. Conventionally known surface adjustor containing

bivalent or trivalent phosphate particles cannot form a sufficient amount of chemical conversion coating on the surface of aluminum alloy. On the other hand, the surface adjustor employed in the present invention can form a sufficient amount of chemical conversion coating on the surface of aluminum alloy. Therefore a method for surface treatment according to the present invention can provide a sufficient amount of corrosion resistance property to the aluminum alloy.

[0020] The zinc phosphate particle contained in the surface adjustor employed in the present invention is not more than 3 micrometers of D_{50} , which is smaller than a zinc phosphate particle employed in the conventional surface adjustor. Because of this particle size, sedimentation of zinc phosphate particle in the surface adjustor can be inhibited and thus assures excellent stability. Moreover, larger amounts of surface adjustor particles can be adsorbed on the surface of the aluminum alloy and thus promote formation of chemical conversion coating. In this connection, it is not preferred that the zinc phosphate particle is not more than 0.01 micrometers of D_{50} because due to excessive dispersion it may lead to coagulation of zinc phosphate particles, but it is preferred that the zinc phosphate particle be not less than 0.05 micrometers and not more than 1 micrometers of D_{50} .

[0021] The term " D_{50} " employed herein is called a "volume 50% median diameter" and means a particle diameter at a point where accumulative curve exhibits 50% wherein the curve is determined as the entire volume of the zinc phosphate particle is assumed as 100% based upon the particle size distribution in the dispersion. The D_{50} can be measured by using for example a particle size measuring device such as a laser Doppler type particle size analyzer ("Microtrac UPA150" manufactured by Nikkiso Co., Ltd).

[0022] The zinc phosphate particle can be obtained by using zinc phosphate that is generally employed as a raw material. Zinc phosphate includes tetrahydrate, dihydrate, monohydrate, and anhydrate. The surface adjustor according to the present invention can use any zinc phosphate described above. Typically, a white colored tetrahydrate powder which is readily available in general can be used without being treated. Alternatively, these zinc phosphates can be surface treated in various manners, for example, surface treated with silane coupling agent, rosin, silicone compound, or metallic alkoxide such as silicone alkoxide or aluminum alkoxide. In addition, zinc phosphate are not particularly limited in shape but can be any shape such as a plate or a scale. These zinc phosphates are miniaturized by conventionally known dispersion method using a bead mill, a high-pressure homogenizer, or a supersonic disperser to obtain a zinc phosphate having not more than 3 micrometers of D_{50} .

[0023] The content of zinc phosphate particles are not less than 50 ppm and not more than 2000 ppm, preferably, not less than 60 ppm and not more than 1500 ppm. In the case in which not more than 50 ppm of zinc phosphate particle is contained, only a small amount of surface adjusting particles are absorbed, leading to a failure of formation of the chemical conversion coating. Also in the case in which more than 2000 ppm of particles are contained, it is not economical as the surface adjusting effect corresponding to the increase in volume will not be provided.

[0024] The surface adjustor employed in the present invention contains a copolymer containing a carboxylic acid

group having monomeric compounds copolymerized. The monomeric compounds contain less than 50% by weight of acrylic acid and more than 50% by weight of 2-acrylamide-2-methylpropanesulfonic acid. The copolymer containing a carboxylic acid group acts as a dispersion agent and at the same time have an effect of promoting a formation of chemical conversion coating. With this property, uniform and dense chemical conversion coating can be formed and excellent corrosion resistance property can be provided with aluminum alloy at the next chemical conversion step.

[0025] The copolymer containing a carboxylic acid group can be obtained easily according to conventionally known methods of copolymerization of monomeric compound under catalysis of, for example, peroxide. The monomeric compound contains not more than 50% by weight of acrylic acid and more than 50% by weight of 2-acrylamide-2-methylpropanesulfonic acid. When the contents of acrylic acid are more than 50% by weight or the contents of 2-acrylamide-2-methylpropanesulfonic acid are less than 50% by weight, excellent chemical conversion coating cannot be formed on the surface of the aluminum alloy. It is preferable that the lower limit of acrylic acid content be 20% by weight, and more preferably 25% by weight.

[0026] It is preferable that the higher limit of acrylic acid content be 45% by weight, and more preferably 40% by weight. It is preferable that the lower limit of the content of 2-acrylamide-2-methylpropanesulfonic acid be 55% by weight, and more preferably 60% by weight. It is also preferable that the higher limit of the content of 2-acrylamide-2-methylpropanesulfonic acid be 80% by weight, and more preferably 75% by weight.

[0027] The aforementioned monomeric compound may contain other monomeric substances within a range that will not impair the effect of the present invention. The other monomeric substances cited herein include acrylic acid methyl, acrylic acid ethyl, acrylic acid propyl, acrylic acid butyl, acrylic acid pentyl, methacrylic acid methyl, methacrylic acid ethyl, a methacrylic acid propyl, methacrylic acid butyl, methacrylic acid pentyl, acrylic acid hydroxy methyl, acrylic acid hydroxyethyl, an acrylic acid hydroxypropyl, acrylic acid hydroxybutyl, acrylic acid hydroxypentyl, methacrylic acid hydroxymethyl, methacrylic acid hydroxyethyl, a methacrylic acid hydroxypropyl, methacrylic acid hydroxybutyl, methacrylic acid hydroxypentyl, acetic acid vinyl, etc. These monomeric substances can be independently mixed or two or more substances may be mixed together in the above mentioned monomeric compound.

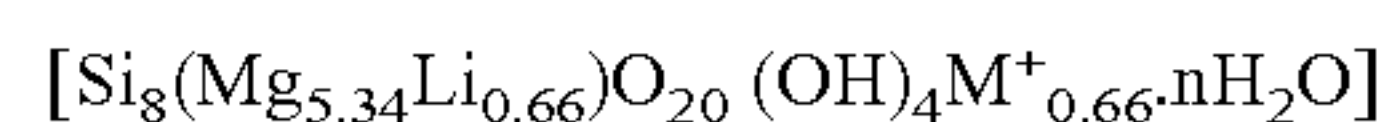
[0028] The content of copolymer containing a carboxylic acid group is not less than 2 ppm and not more than 200 ppm, more preferably, not less than 4 ppm and not more than 100 ppm. In the case where not more than 2 ppm of copolymer containing a carboxylic acid group are contained, the diameter of zinc phosphate particles become larger due to lack of dispersion properties, causing reduction of stability of surface adjustor and sedimentation thereof. Also, in the case in which more than 200 ppm of copolymer containing a carboxylic acid group are contained, it is not economical as the surface adjusting effect corresponding to the increase in volume will not be provided.

[0029] Moreover, the surface adjustor employed in the present invention contains natural hectorite and/or synthetic

hectorite. The natural hectorite and synthetic hectorite respectively can be employed separately, or two or more types of hectorite can be employed together. The natural hectorite and/or synthetic hectorite is/are contained in the surface adjustor so that the adjustor can provide more excellent dispersion stability and can avoid sedimentation of the zinc phosphate particles.

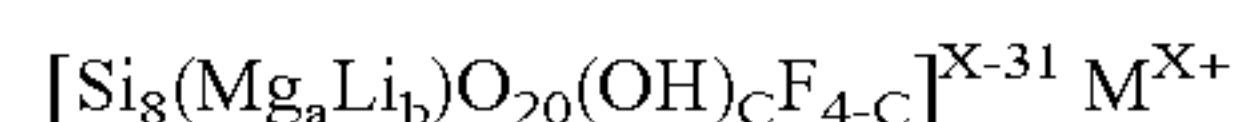
[0030] The natural hectorite is a trioctahedral type clay mineral belonging to the montmorillonite group represented in formula 1. The commercially available natural hectorite includes, for example, BENTON EW, and BENTON AD; manufactured by ELEMENTIS Co., Ltd.).

Formula 1



[0031] The synthetic hectorite, represented in formula 2, has a three crystalline layer structure, and is similar to a hectorite that belongs to an unlimited layer expansion type trioctahedral having an expansion lattice. The commercially available synthetic hectorite includes, for example, B, S, RD, RDS, XLG, XLS, etc., manufactured by Laporte Industries Ltd. These hectorites are white colored powders and can easily form sol or gel when water is added. As other commercially available synthetic hectorite, LUCENTITE SWN manufactured by Co-op Chemical Co Ltd can be included.

Formula 2



[0032] In formula 2, $0 < a \leq 6$, $0 < b \leq 6$, $4 < a+b < 8$, $0 \leq c < 4$, $x=12-2a-b$, and M is almost Na. Synthetic hectorite contains magnesium, silicone, and sodium as a principal component and a small quantity of lithium and fluoride.

[0033] The content of natural hectorite and/or synthetic hectorite is not less than 3 ppm and not more than 200 ppm, more preferably, not less than 20 ppm and not more than 100 ppm. In the case in which less than 3 ppm of natural hectorite and/or synthetic hectorite is contained, sedimentation of phosphate zinc particles may not be effectively avoided. Also, in the case in which more than 200 ppm of hectorite is contained, it is not economical as the surface adjusting effect corresponding to the increase in volume will not be provided.

[0034] The pH of surface adjustor employed in the present invention is not less than 7 and not more than 12. When the pH is less than 7, phosphate zinc particles cannot be easily dissolved and can become unstable. On the other hand, when the pH is more than 12, the pH of the chemical conversion agent increases and may cause improper chemical conversion.

[0035] The surface adjustor employed in the present invention may further be mixed with other dispersion agents, dispersing medium, or viscosity improver agents within a range that will not impair the effects provided according to the present invention. When a surface adjustor prepared as such is used in order to surface adjust the aluminum alloy, the surface adjustor is brought into contact with the surface of aluminum alloy. Their contacting method is not particularly limited, and conventionally known methods such as dipping or spraying can be used.

Zinc Phosphate Chemical Conversion Treatment Agent

[0036] The zinc phosphate chemical conversion treatment agent employed in the present invention may include an acid aqueous solution containing not less than 0.1 g/l and not more than 2.0 g/l of zinc ion, not less than 0.1 g/l and not more than 4.0 g/l of nickel ion, not less than 0.1 g/l and not more than 3.0 g/l of manganese ion, not less than 5 g/l and not more than 40 g/l of phosphate ion, not less than 0.5 g/l and not more than 1.0 g/l of fluoride in a complex fluoride, not less than 0.3 g/l and not more than 0.5 g/l of fluoride in a simple fluoride, and not less than 0.025 g/l and not more than 0.45 g/l of iron (Fe) in a chelating agent that can chelate bond with iron ion.

[0037] In the zinc phosphate chemical conversion treatment, it is known that a uniform and dense zinc phosphate coating can be formed on an iron based surface or a zinc based surface by having bivalent or trivalent iron ion contained in the chemical conversion treatment agent. The zinc phosphate chemical conversion treatment agents employed in the present invention have a chelating agent that can chelate bond with iron ion. The chelating agent chelates an eluted iron ion from the iron based surface. Because of this, a constant amount of iron ion can be stably held during the chemical conversion treatment. The effect of the above mentioned iron ion can appear in the formation of the zinc phosphate coating on the aluminum based surface.

[0038] Preferably, the concentration of zinc ions is not less than 0.1 g/l and not more than 2.0 g/l, and more preferably not less than 0.3 g/l and not more than 1.5 g/l. In the case in which the concentration of zinc ion is less than 0.1 g/l, a uniform zinc phosphate coating cannot be formed on an aluminum based surface, and it causes lack of hiding. In addition, formation of blue colored coatings is observed partially where improper coating is applied. In the case in which concentration of zinc ion is more than 2.0 g/l, zinc phosphate coating can be uniformly formed; however, it is easily dissolved in alkalis. It is particularly unfavorable for the coating as it is exposed to an alkaline atmosphere during the next cationic electro-deposition coating.

[0039] The concentration of nickel ion is not less than 0.1 g/l and not more than 4.0 g/l, and more preferably not less than 0.1 g/l and not more than 2.0 g/l. In the case in which the concentration of nickel ion is less than 0.1 g/l, the corrosion resistance properties of iron are degraded, and when the concentration of nickel ion is more than 4.0 g/l, the corrosion resistance properties of aluminum are degraded.

[0040] The concentration of manganese ion is not less than 0.1 g/l and not more than 3.0 g/l, and more preferably not less than 0.6 g/l and not more than 3.0 g/l. In the case in which the concentration of manganese ion is less than 0.1 g/l, adhesion properties between the zinc based surface and the coating as well as resistance properties to hot salt water will not be sufficiently enhanced. Moreover, when the concentration of manganese ion is more than 3.0 g/l, it is economically disadvantageous as the expected effects corresponding to the increase in volume will not be provided.

[0041] The concentration of phosphate ion is not less than 5 g/l and not more than 40 g/l, and more preferably not less than 10 g/l and not more than 30 g/l. When the concentration of phosphate ion is less than 5 g/l, it often forms a non uniform zinc phosphate coating, and when the concentration

of phosphate ion is more than 40 g/l, it is economically disadvantageous as the expected effects corresponding to the increase in volume will not be provided.

[0042] As for fluoride, the concentration of complex fluoride is not less than 0.5 g/l and not more than 1.0 g/l of fluoride in a complex fluoride. In the case in which the concentration of complex fluoride is less than 0.5 g/l of fluoride in a complex fluoride, uniform zinc phosphate coating cannot be formed on the aluminum based surface and thus fails to obtain excellent corrosion resistance properties. Moreover, when the concentration of complex fluoride is more than 1.0 g/l of fluoride in a complex fluoride, the iron based surface is excessively etched to reduce the amount of zinc phosphate coating and thus also fails to obtain excellent corrosion resistance properties.

[0043] On the other hand, the concentration of simple fluoride is not less than 0.3 g/l and not more than 0.5 g/l of fluoride in a simple fluoride. In the case in which the concentration of simple fluoride is less than 0.3 g/l of fluoride in a simple fluoride, uniform zinc phosphate coating cannot be formed on the aluminum based surface and thus fails to obtain excellent filiform rust resistance properties. Moreover, when the concentration of simple fluoride is more than 0.5 g/l of fluoride in a simple fluoride, the etching volume on the aluminum based surface is increased to promote the formation of by-products having Al, F, and Na as principal components on the aluminum based surface and thus fails to obtain excellent resistance properties to filiform rust and to water adhesion.

[0044] A source of supply for zinc ion includes, for example, zinc oxide, carbonic acid zinc, nitric acid zinc, etc. A source of supply for nickel ion includes, for example, carbonic acid nickel, nitric-acid nickel, nickel chloride, phosphate nickel, nickel hydroxide, etc. A source of supply for manganese ion includes, for example, manganese carbonate, manganese nitrate, manganese chloride, manganese phosphate, etc. Moreover, a source of supply for phosphate ion includes, for example, phosphate, zinc phosphate, manganese phosphate, etc.

[0045] Furthermore, complex fluoride includes, for example, SiF_6 , BF_4 , etc., and a source of supply for SiF_6 includes, for example, hydrofluosilicic acid, hydrofluosilicic acid nickel, hydrofluosilicic acid zinc, hydrofluosilicic acid manganese, hydrofluosilicic acid iron, hydrofluosilicic acid magnesium, hydrofluosilicic acid calcium, etc. As for a source of supply for BF_4 , for example, boric hydrofluoric acid, boric hydrofluoric acid nickel, boric hydrofluoric acid zinc, boric hydrofluoric acid manganese, boric hydrofluoric acid iron, boric hydrofluoric acid magnesium, boric hydrofluoric acid calcium, etc., may be mentioned.

[0046] As for other fluoride, simple fluorides that supply free fluorine ions include, for example, hydrofluoric acid, potassium fluoride, sodium fluoride, ammonium fluoride, acidic potassium fluoride, acidic sodium fluoride, ammonium fluoride, acidic ammonium fluoride, etc. Aluminum ion eluted from aluminum alloy binds to free fluorine ion in the chemical conversion agent to form complex ions and promote the formation of zinc phosphate coating.

[0047] The chemical conversion agent of zinc phosphate according to the present invention includes not less than 0.025 g/l and not more than 45 g/l of iron (Fe) in a chelating

agent that can chelate (bind to) iron ion. As such, an addition of a chelating agent that can chelate bond with iron ion into chemical conversion agent of zinc phosphate makes possible holding iron ions that eluded from the iron based surface in the chemical conversion agent, and thus form a uniform and dense zinc phosphate coating with high coatability. Specific chelating agents include, for example, citrate acid, tartaric acid, EDTA, gluconic acid, succinic acid, digallic acid, malic acid, and their compounds or derivatives.

[0048] In the case in which the content of iron in a chelating agent is less than 0.025 g/l, the coatability of zinc phosphate coating on the aluminum based surface is degraded and fails to form a uniform and dense zinc phosphate coating with high coatability. On the other hand, when the content of iron in a chelating agent is more than 0.45 g/l, the amount of zinc phosphate coating is reduced and thus fails to obtain excellent property of resistance to filiform rust.

[0049] The pH of chemical conversion agent of zinc phosphate is not less than 2.0 and not more than 5.0, and more preferably, not less than 3.0 and not more than 4.0. The pH can be adjusted by NaOH, ammonia aqueous solution, nitric acid, etc. Aluminum alloy is chemical conversion treated by having a chemical conversion agent of zinc phosphate brought into contact with aluminum alloy. The temperature of the contact is preferably not less than 40 degrees C. and not more than 60 degrees C., and more preferably, not less than 42 degrees C. and not more than 48 degrees C. Examples of the method of the contact are spraying and dipping. The time for spraying process and dipping is not less than 1 minute and not more than 10 minutes, and more preferably, not less than 1.5 minutes and not more than 3 minutes. Other methods for contacting zinc phosphate with aluminum alloy may be conducted by flow coating and roll coating. The chemical conversion treated aluminum alloy is then advanced to rinse and drying processes. The temperature for drying is not less than 80 degrees C. and not more than 120 degrees C.

Aluminum Alloy

[0050] The content of copper in aluminum alloy according to the present invention is not more than 0.2% by weight. In the case in which the content of copper in aluminum alloy is large, because the corrosion resistance is reduced, the content of copper needs to be not more than 0.1% by weight, for example, in the Patent Document 1. On the other hand, a surface treatment method according to the present invention can provide excellent corrosion resistance properties even when the content of copper is 0.2% by weight.

EXAMPLES

[0051] The present invention will be further described in detail based on examples; however, the invention is not limited to these examples.

Examples 1 to 7 and Comparative Examples 1 to 5

Target Material for Treatment

[0052] In any of examples 1 to 7 and comparative examples 1 to 5, a similar aluminum alloy is used as a target material for treatment. Specifically, aluminum alloys containing copper of not more than 0.01% by weight, of 0.1% by weight, and of 0.2% by weight were used. The size of the

aluminum alloys were 70 mm×150 mm and widths were 0.8 mm. These aluminum alloys were ground on the entire surface by sand paper No. 180 using a Double Action Sander (905B4D manufactured by Compact Tool Co., Ltd.). Also, as a target material for treatment, aluminum alloys having the entire surface ground were brought into contact with and conduction into a SPC having a similar size and a thickness as with the aluminum alloys, i.e., the target materials for treatment was three types of aluminum alloys having different content of copper. On one hand of these aluminum alloys were contacted with and conducted into SPC, and on the other hand of these aluminum alloys were neither contacted with nor conducted into SPC.

[0053] FIG. 1 shows a target material for treatment in which aluminum alloy and SPC are in contact together and in conduction with each other. The target materials for treatment are prepared according to the following steps. First, SPC 20 is disposed with an interval of approximately 20 mm at both ends of the aluminum alloy 10 and hung by a hanger 40. Holes are made on the upper portion of the aluminum alloys 10 and SPC 20. An aluminum wire 30 connects the aluminum alloy 10 and SPC 20 by connecting one hole with another.

Treating Process

[0054] In any of Examples 1 to 7 and Comparative Examples 1 to 5, the process were made in sequence of (a) degreasing, (b) rinsing by water, (c) surface adjustment, (d) chemical conversion, (e) rinsing by water, (f) rinsing by pure water, (g) drying, and (h) electro-deposition coating. During a rinsing process in (b) and (e), tap water was sprayed on the target material for treatment for 15 seconds at room temperature, and during a rinsing process (f) by pure water, ion exchanged water was sprayed on the target material for treatment for 15 seconds at room temperature. During drying process (g), the target material for treatment was dried at 80 degrees C. for 5 minutes. For the process of (a) degreasing, (c) surface adjustment, (d) chemical and (h) electro-deposition coating, respectively, details will be described below.

Degreasing

[0055] In any of Examples 1 to 7 and Comparative Examples 1 to 5, a similar degreasing treatment was carried out for each of the above-mentioned target materials for treatment. Specifically, in a water solution containing 1.5% by weight of agent A and 0.9% by weight of agent B, these agents are alkaline degreasing agent ("Surf Cleaner SD 250") manufactured by Nippon Paint Co., Ltd., and the aforementioned target material for treatment was immersed and then degreased for two minutes at a temperature of 43 degrees C.

Surface Adjustment

[0056] In the Examples 1 to 7, a surface adjustor (hereinafter, referred to as surface adjustor 1 that contains zinc phosphate particles, copolymer containing carboxylic acid group, and natural hectorite and/or synthetic hectorite) was used to adjust the surface. Specifically, as an adjustment of surface adjustor 1, 0.3 part by mass of natural hectorite "BENTON EW" (manufactured by ELEMENTIS Co., Ltd.) was added into 87.7 part by mass of water, and stirred at 3000 rpm for 30 minutes by using a dispersing machine to obtain a pregel. The resultant pregel was added with 2 parts

by mass of commercially available “Aron A-6020” (a copolymer containing carboxylic acid group containing 40% by weight of acrylic acid and 60% by weight of 2-acrylamide-2-methylpropanesulfon manufactured by Toagosei Co., Ltd.) and 50 parts by mass of zinc phosphate particles. The pH was adjusted by caustic soda to obtain a surface adjustor (1500 ppm of concentration of zinc phosphate particles, 60 ppm of concentration of copolymer containing carboxylic acid group, and 45 ppm of concentration of natural hectorite). Then the target material for treatment was immersed into the resultant surface adjustor **1** for 30 seconds at room temperature to adjust the surface.

[0057] In Comparative Examples 1 to 5, not by using zinc phosphate based surface adjustor as shown in Examples, but by using titanium colloid based surface adjustor, surfaces were adjusted. Specifically, in order to conduct a surface treatment, the target material for treatment was immersed into a water solution (hereinafter, referred to as a surface adjustor **2**) having a pH of 9.0 and containing 0.1% by weight of a surface adjustor (“Surf Fine 5N-10” for initial make-up of electrolytic bath manufactured by Nippon Paint Co., Ltd.) for 30 seconds at room temperature. As for both surface adjustor **1** and surface adjustor **2**, dry solids contents are set almost equal.

[0058] As for Example 7 and Comparative Examples 5, degreasing and rinsing were conducted on the target materials for treatment and then the materials were immersed for 60 seconds at a temperature of 43 degrees C. into a chemical conversion agent that contains no zinc ions, nickel ions or manganese ions. In a case in which a surface adjustor **1** was used for surface adjustment, even though the chemical conversion in which aluminum material and SPC were brought into contact and conduct to each other, the reduction of zinc phosphate coating was rarely observed. In order to determine the threshold limit value that can hold the property at a side that has a small amount of coating, the aforementioned operations were conducted. The reason for immersing the target material for treatment into a chemical conversion agent containing no metal ion is that the amount of etching on the aluminum material needs to be equal to the amount of chemical conversion in which aluminum material and SPC were brought into contact and conduction to each other. More specifically, a treatment conducted within a short time using a proper chemical conversion agent in order to keep a small amount of coating can be performed with a small amount of coating; however, this leads to an amount of etching also becoming small. As this fails to attain similar conditions of the contact and conduction made between the aluminum material and the SPC, the target material for treatment were immersed into a chemical conversion agent containing no metal ion is used to control the amount of etching. The target amount of etching was 0.5 g/m².

Chemical Conversion Treatment

[0059] In any of Examples 1 to 7 and Comparative Examples 1 to 5, a similar chemical conversion treatment was carried out by immersing each of above mentioned target materials for two minutes at a temperature of 43 degrees C. Specifically, a chemical conversion treatment agent was used which includes more than 1.0 g/l of zinc ion, 1.0 g/l of nickel ion, 1.3 g/l of manganese ion, 20 g/l of phosphate ion, 0.5 g/l of fluoride in a complex fluoride e, 0.35 g/l of fluoride in a simple fluoride, and further including

0.025 g/l of iron (Fe) in a chelating agent that can chelate bond with iron ions. The overall acidity in the chemical conversion agent was adjusted to 22.2 pt and the free acidity in the agent was adjusted to 0.5 pt. As for the example 7 and comparative example 5, as described above, the time for chemical conversion treatment was made shorter, specifically 10 seconds in Example 7 and 20 seconds in Comparative example 5.

Electrodeposition Coating

[0060] In any of Examples 1 to 7 and Comparative Examples 1 to 5, a similar electro-deposition coating was carried out. Specifically, cationic electro-deposition coating was carried out using cationic electro-deposition coating (“Power Top V50 Gray” manufactured by Nippon Paint Co., Ltd.). As for the coating conditions, the coating thickness after baking and drying is set as 25 micrometers. After the electro-deposition coating, the material was baked for 25 minutes at a temperature of 170 degrees C., and cationic electro-deposition coating was formed on the surface of the chemical conversion treated aluminum alloy.

Intercoating

[0061] On the electro-deposition coating, an intercoating manufactured by Nippon Paint Co., Ltd. (Orga “P-5A N-2.0”) was spray coated and baked for 20 minutes at a temperature of 140 degrees C. The formed intercoating thickness after baking was 35 micrometers.

Overcoating

[0062] On the intercoating, overcoating manufactured by Nippon Paint Co., Ltd. (“superlac M-95HB YR-511P”) was spray coated and baked for 20 minutes at a temperature of 140 degrees C. The formed overcoating thickness was 15 micrometers.

Evaluation

Filiform Rust Resistance

[0063] On the coating of the three coated plates, crosscuts (length: 20 cm) were made by using a sharp cutter, and salt water was sprayed for 24 hours in conformance with JIS-Z2371. The resultant plates were exposed under a humid atmosphere having a relative humidity of 70 to 75% at a temperature of 40 degrees C. The exposure of the plate for 240 hours was deemed to be one cycle. After four cycles, blistering were visually checked from the crosscuts and evaluated according to the criteria shown below.

[0064] In Table 1, NB means almost no blisters were observed, MB means many blisters were observed.

Resistance to Water Adhesion

[0065] The test plate on which zinc phosphate coating and cationic electrodeposition coating was formed was immersed in hot water for 240 hours at a temperature of 40 degrees C., and then exposed to cool to room temperature. A cross-cut adhesion test was then performed in which degree of peeling was visually checked to evaluate the test plate according to the criteria shown below.

[0066] In Table 1, NP means almost no peeling was observed, LP means little peeling was observed, and EP means extensive peeling was observed.

Amount of Chemical Conversion Coating

[0067] The chemical conversion treated test plate was immersed into a water solution having 30% nitric acid for one minute at room temperature to dissolve the chemical conversion coating. The weight before/after the dissolution was measured and calculated to determine the amount of chemical conversion coating.

[0068] The results of evaluation of resistance properties against filiform rust and water adhesion carried out for Examples 1 to 7 and Comparative Examples 1 to 5 are shown in Table 1 and 2.

[0069] Here is a summary of evaluation results in Table 1 and 2. First, when aluminum alloy and SPC were contacted and conducted, excellent resistance property to corrosion could not be obtained in the Comparative Examples, whereas excellent resistance property to corrosion could be obtained when the copper content in the aluminum alloy was within a range of not more than 0.2% by weight in the Examples. Secondly, the copper content in the aluminum alloy was 0.2% by weight, excellent resistance property to

corrosion could not be obtained in the Comparative Examples, whereas excellent resistance property to corrosion could be obtained irrespective of whether aluminum alloy and SPC were contacted and conducted in the Examples. Thirdly, when the amount of coating of zinc phosphate was as low as 0.3 g/m², excellent resistance property to corrosion could not be obtained in the Comparative Examples, whereas excellent resistance property to corrosion could be obtained in the Examples. Therefore, it was recognized that a uniform and dense zinc phosphate coating with high coatability could be formed on the surface of aluminum alloy according to the present invention.

[0070] While preferred embodiments of the present invention have been described and illustrated above, it is to be understood that they are exemplary of the invention and are not to be considered to be limiting. Additions, omissions, substitutions, and other modifications can be made thereto without departing from the spirit or scope of the present invention. Accordingly, the invention is not to be considered to be limited by the foregoing description and is only limited by the scope of the appended claims.

TABLE 1

			Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Surface adjustor	1	Concentration (wt %)	0.3	0.3	0.3	0.3	0.3	0.3	0.3
		pH	9.0	9.0	9.0	9.0	9.0	9.0	9.0
	2	Concentration (wt %)	—	—	—	—	—	—	—
		pH	—	—	—	—	—	—	—
Cu Content(%) in aluminum alloy			Less than 0.01	Less than 0.01	0.1	0.1	0.2	0.2	Less than 0.01
Contact and conduction of aluminum and SPC			none	have	none	have	none	have	none
Weight(g/m ²) of chemical conversion coating on aluminum			1.8	1.5	1.9	1.6	2.0	1.6	0.3
Resistance to corrosion on aluminum material after electrodeposition coating	Resistance to filiform rust		NB	NB	NB	NB	NB	NB	NB
	Resistance to water adhesion		NP	NP	NP	NP	NP	NP	NP

[0071]

TABLE 2

			Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Surface adjustor	1	Concentration (wt %)	—	—	—	—	—
		pH	—	—	—	—	—
	2	Concentration (wt %)	0.1	0.1	0.1	0.1	0.1
		pH	9.0	9.0	9.0	9.0	9.0
Cu Content(%) in aluminum alloy			Less than 0.01	Less than 0.01	0.1	0.2	Less than 0.01
Contact and conduction of aluminum and SPC			none	have	none	none	none
Weight(g/m ²) of chemical conversion coating on aluminum			2.0	0.7	2.1	2.3	0.3
Resistance to corrosion on aluminum	Resistance to filiform rust		NB	MB	NB	MB	MB
	Resistance to		NP	LP	NP	LP	EP

TABLE 2-continued

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
material after electrodeposition coating	water adhesion					

What is claimed is:

1. A method for surface treatment of aluminum alloy comprising steps of:

degreasing and rinsing a surface of aluminum alloy; and

performing surface adjustment of the surface of aluminum alloy which is degreased and rinsed with a surface adjustor; and

performing chemical conversion treatment of the surface of the aluminum alloy which is surface-adjusted with a zinc phosphate chemical conversion treatment agent; and

wherein the surface adjustor has a pH of not less than 7 and not more than 12 and containing not less than 50 ppm and not more than 2000 ppm of zinc phosphate particles having a D₅₀ of not more than three micrometers, not less than 2 ppm and not more than 200 ppm of a copolymer containing carboxylic acid group that copolymerizes a monomeric composition containing less than 50% by weight of acrylic acid and more than 50% by weight of 2-acrylamide-2-methylpropane-

sulfonic acid, and not less than 3 ppm and not more than 200 ppm of natural hectorite and/or synthetic hectorite; and

the zinc phosphate chemical conversion treatment agent comprises an acid aqueous solution containing not less than 0.1 g/l and not more than 2.0 g/l of zinc ion, not less than 0.1 g/l and not more than 4.0 g/l of nickel ion, not less than 0.1 g/l and not more than 3.0 g/l of manganese ion, not less than 5 g/l and not more than 40 g/l of phosphate ion, not less than 0.5 g/l and not more than 1.0 g/l of fluoride in a complex fluoride, not less than 0.3 g/l and not more than 0.5 g/l of fluoride in a simple fluoride, and not less than 0.025 g/l and not more than 0.45 g/l of iron (Fe) chelating agent that can chelate bond with iron ion.

2. A method for surface treatment of aluminum alloy according to claim 1 wherein the content of copper in the aluminum alloy is not more than 0.2% by weight.

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