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(11) **EP 1 571 237 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
07.09.2005 Bulletin 2005/36

(51) Int Cl.7: **C23C 22/34**

(21) Application number: **03780727.8**

(86) International application number:
PCT/JP2003/015868

(22) Date of filing: **11.12.2003**

(87) International publication number:
WO 2004/055237 (01.07.2004 Gazette 2004/27)

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**
Designated Extension States:
AL LT LV MK

(30) Priority: **13.12.2002 JP 2002362640**

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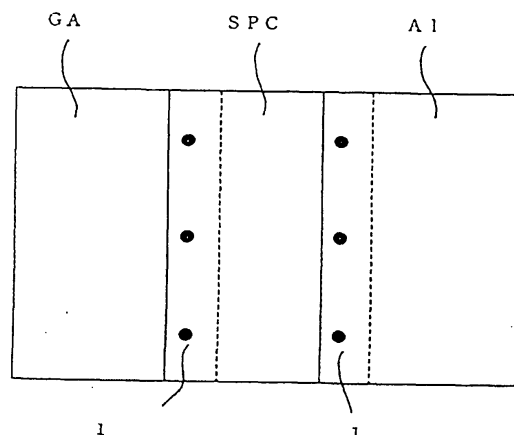
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(54) **TREATING FLUID FOR SURFACE TREATMENT OF METAL AND METHOD FOR SURFACE TREATMENT**

(57) Treating solution for surface treatment of metal to treat one metal material selected from the group consisting of ferriferous material, zinciferous material, aluminiferous material and magnesiferous material or to treat two or more metal materials selected from the group consisting of ferriferous material, zinciferous material, aluminiferous material and magnesiferous material at the same time, wherein the aqueous surface treating solution contains from 5 to 5000 ppm of at least one compound selected from the group consisting of zirconium compound and titanium compound by the metal element, and from 0.1 to 100 ppm of free fluorine ion, further the pH of the treating solution is from 2 to 6. To the treating solution, calcium compound, magnesium compound, strontium compound, nitric acid group, oxygen acid and/or salt of oxygen acid, polymer compound and surface active agent can be added.

Fig.1



EP 1 571 237 A1

Description

Technical Field

[0001] The present invention relates to the treating solution for surface treatment of metal which may deposit a surface treated film having excellent corrosion resistance after being coated on the surface of a metal material of a structural construction such as car body consisting of a single material or two to four materials selected from the group consisting of ferriferous material, zinciferous material, aluminiferous material and magnesiferous material independently or simultaneously.

Background Art

[0002] As the method to form on metal surface a surface treated film having excellent corrosion resistance after coated, a zinc phosphate treatment and a chromate treatment are currently used as ordinary methods. According to the zinc phosphate treatment, it is possible to deposit a film having excellent corrosion resistance on the surface of steel such as cold rolled steel plate, zinc plated steel plate and some of aluminum alloys. However, in the zinc phosphate treatment, the generation of sludge, which is the byproduct of the reaction can not be avoided, and depending on the kind of aluminum alloy, the sufficient corrosion resistance after coated can not be obtained. While, in the case of aluminum alloy, it is possible to obtain sufficient properties after coated by applying the chromate treatment. Concerning the recent environmental regulations, the chromate treatment which contains harmful hexavalent chrome in the treating solution is more likely to be avoided. As the method for metal surface treatment, which does not contain harmful component in the treating solution, various methods have been proposed as described below.

[0003] For example, in JP 2000-204485 A, a compound containing nitrogen atom having a lone electron-pair and a non-chrome coating agent for metal surface treatment containing said compound and zirconium compound are suggested. This method may obtain a surface treated film which is excellent in corrosion resistance and adhesiveness after being coated, and yet does not contain harmful hexavalent chrome by coating above mentioned coating agent. However, in the case of the method, the metal material which can be treated is limited to aluminum alloys only, and, it is difficult to be applied to a structural construction having complex structure such as car body, because the surface treated film is formed by coating and drying.

[0004] Further, as the method to deposit a metal surface treated film having excellent adhesiveness and corrosion resistance after coated due to the chemical reaction, various methods such as those disclosed in JP 56-136978 A, JP 8-176841 A, JP 9-25436 A and JP 9-31404 A have been suggested. However, in any of these methods, the metal material which can be treated is limited to the aluminum alloy only, originally having excellent corrosion resistance; these methods may not deposit a surface treated film on the surface of ferriferous material or zinciferous material.

[0005] Furthermore, proposed is a method to form a metal surface treated film having excellent corrosion resistance and adhesion after coated, by using a surface treating agent composed of metal acetylacetonate and water soluble inorganic titanium compound or water soluble inorganic zirconium compound (see JP 2000-199077). By this method, metal materials to be treated may include magnesium, magnesium alloy, zinc and zinc plated alloy other than aluminum alloy. However, by this method, it is difficult to form a surface treated film on a surface of ferriferous material such as cold rolled steel, and is not possible to treat ferriferous material at the same time.

[0006] Still further, a method for metal surface treatment by chrome free coating acid composition by coating aqueous solution containing component which can be a film having excellent corrosion resistance over the surface of metal, then baking and drying without rinsing with water so as the film to be fixed (see JP 5-195244 A). This method does not involve any chemical reaction to form a film, so this method may form a film on the surface of metal such as zinc plated steel plate, cold rolled steel plate or aluminum alloy. However, similarly to the invention disclosed in above mentioned JP 2000-204485 A, since the film is formed by coating and drying, it is difficult to form a uniform film on the surface of a structural construction having complex structure such as car body.

[0007] As mentioned above, according to the prior arts, it was impossible to perform surface treatment excellent in corrosion resistance and adhesion on car body and the like composed of two to four metal materials of ferriferous material such as cold rolled steel plate, zinciferous material such as zinc plated steel plate, aluminiferous material and magnesiferous material simultaneously with a treating solution containing no harmful component to the environment and not generating waste sludge.

Disclosure of the Invention

[0008] The object of the present invention is to provide a treating solution for surface treatment of metal to form a surface treated film having excellent corrosion resistance after coated on the surface of ferriferous material, zinciferous material, aluminiferous material and magnesiferous material, which does not contain harmful component to the envi-

ronment and does not generate sludge to be wasted, which was not accomplished by the prior arts. Further, the object of the present invention is to provide a treating solution for metal surface treatment to form a surface treated film of a uniform component having excellent corrosion resistance after coated on the surface of a metal material composing a structural construction such as car body consisting of two to four materials selecting from the group consisting of ferri-
 5 ferrous material, zinciferous material, aluminiferous material and magnesiferous material by same component simultaneously under a uniform condition. And another object of the present invention is to provide a method for treatment using the treating solution.

[0009] The inventors of the present invention have conducted intensive study to dissolve the above mentioned problem and have accomplished a treating solution for surface treatment of metal and a method for surface treatment which
 10 were not provided by the prior art.

[0010] That is, the present invention is the treating solution for surface treatment of metal, which is aqueous surface treating solution to treat independently each metal material or simultaneously two or more metal materials selected from the group consisting of ferri-
 15 ferrous material, zinciferous material, aluminiferous material and magnesiferous material, the treating solution containing 5 to 5000 ppm of at least one compound selected from the group consisting of zirconium compound and titanium compound calculated as metal element, and 0.1 to 100 ppm of free fluorine ion, and having pH 2 to 6.

[0011] The treating solution for surface treatment of metal may further contain at least one compound selected from the group consisting of calcium compound, magnesium compound and strontium compound, wherein concentration of the compound calculated as metal element is 5 to 100 ppm in the case of the calcium compound, 10 to 5000 ppm
 20 in the case of the magnesium and 10 to 5000 ppm in the case of the strontium compound. It is desirable that the treating solution for surface treatment of metal further contains 1000 to 50000 ppm of nitrate group. And, it is desirable that the treating solution for surface treatment of metal further contains at least one oxygen acid and/or salt of oxygen acid selected from the group consisting of HClO_3 , HBrO_3 , HNO_2 , HNO_3 , HMnO_4 , HVO_3 , H_2O_2 , H_2WO_4 , H_2MoO_4 and salts thereof. The treating solution for surface treatment of metal may further contain at least one polymer compound selected
 25 from the group consisting of water soluble polymer compounds and water dispersible polymer compounds, and may further contain at least one surface active agent selected from the group consisting of nonionic surface active agents, anionic surface active agents and cationic surface active agents.

[0012] And, the present invention is the method for surface treatment of metal comprising, contacting independently each metal material or simultaneously two or more metal materials selected from the group consisting of ferri-
 30 ferrous material, zinciferous material, aluminiferous material and magnesiferous material with the treating solution for surface treatment. In the method for surface treatment, after contacting with the treating solution for surface treatment, it is possible to further contact the metal material or the two or more metal materials with acidic aqueous solution of compound containing at least one element selected from the group consisting of cobalt, nickel, tin, copper, titanium and zirconium, with or without washing by water, or it is possible to further contact the metal material or the two or more
 35 metal materials with treating solution containing at least one polymer compound selected from water soluble polymer compounds and water dispersible polymer compounds.

[0013] Moreover, the present invention is the method for surface treatment of metal comprising, electrolytic treating in the treating solution for surface treatment, wherein independently each metal material or simultaneously two or more metal materials selected from the group consisting of ferri-
 40 ferrous material, zinciferous material, aluminiferous material and magnesiferous material are a cathode. In the method for surface treatment, after electrolytic treating in the treating solution for surface treatment, it is possible to further contact the metal material or the two or more metal materials with acidic aqueous solution of compound containing at least one element selected from the group consisting of cobalt, nickel, tin, copper, titanium and zirconium, with or without washing by water, or it is possible to further contact the metal material or the two or more metal materials with treating solution containing at least one polymer compound selected
 45 from water soluble polymer compounds and water dispersible polymer compounds, with or without washing by water.

[0014] And, the present invention is the method for surface treatment of metal comprising, contacting independently each metal material or simultaneously two or more metal materials selected from the group consisting of ferri-
 50 ferrous material, zinciferous material, aluminiferous material and magnesiferous material whose surfaces are not degreased and cleaned, with the treating solution for surface treatment containing at least one surface active agent selected from the group consisting of the above described nonionic surface active agents, anionic surface active agents and cationic surface active agents.

[0015] Furthermore, the present invention is the metal material having a surface treated film containing at least one metal element selected from the group consisting of titanium and zirconium formed on a surface of iron metal material by the method for surface treatment, wherein an adhesion amount of the surface treated film calculated as the metal
 55 element is 30 mg/m^2 or more; in the case where formed on a surface of zinc metal material, an adhesion amount of the surface treated film calculated as the metal element is 20 mg/m^2 or more; in the case where formed on a surface of aluminum metal material, an adhesion amount of the surface treated film calculated as the metal element is 10 mg/m^2 or more; and in the case where formed on a surface of magnesium metal material, an adhesion amount of the

surface treated film calculated as the metal element is 10mg/m² or more.

Brief Description of Drawings

[0016]

Fig.1 is a plane view of the test plate used in the Examples and Comparative Examples.

Fig.2 is an elevation view of the test plate.

Best Mode for Carrying out the Invention

[0017] The present invention relates to the art characterizing to deposit a surface treated film having excellent corrosion resistance after coated, by surface treatment on independently each metal material or simultaneously two or more metal materials selected from the group consisting of ferriferous material, zinciferous material, aluminiferous material and magnesiferous material. In the present invention, ferriferous material is an iron metal such as cold rolled steel plate, hot rolled steel plate, cast iron or sintered steel. Zinciferous material is a die casting zinc or a zinc containing plating. This zinc containing plating means a metal plating with zinc or zinc alloy composed of zinc and other metals (for example, at least one metal selected from the group consisting of nickel, iron, aluminum, manganese, chromium, magnesium, cobalt, lead or antimony) and inevitable impurities, and the methods for such plating includes hot galvanizing, electric plating and vapor deposition plating, and are not limited to these methods. Further, the aluminiferous material is an aluminum alloy board such as JIS 5000 series aluminum alloy or JIS 6000 series aluminum alloy, or an aluminum alloy die cast represented by ADC-12. Still more, the magnesiferous material is a metal board or a die cast made of magnesium alloy.

[0018] The present invention can be applied to the structural construction which contains one metal material mentioned above alone in the composing parts or to the structural construction which contains two to four metal materials mentioned above in the composing parts. And, in the case to apply the present invention to the structural construction which contains two to four metal materials mentioned above, it is possible to treat the surfaces of two to four metal materials at the same time. In the case to treat the surfaces of two to four metal materials at the same time, the different metals can be in the condition not contacting each other or in the condition being joined and contacted by means of joining method such as welding, adhesion or riveting.

[0019] The treating solution for surface treatment of metal of the present invention contains 5 to 5000 ppm of at least one compound selected from the group consisting of zirconium compound and titanium compound calculated as the metal element, and 0.1 to 100 ppm of free fluorine ion, further having pH of 2 to 6. Here, as the zirconium compound used in the present invention, ZrCl₄, ZrOCl₂, Zr(SO₄)₂, ZrOSO₄, Zr(NO₃)₄, ZrO(NO₃)₂, H₂ZrF₆, salt of H₂ZrF₆, ZrO₂, ZrOBr₂ and ZrF₄ can be mentioned. And as the titanium compound, TiCl₄, Ti(SO₄)₂, TiOSO₄, Ti(NO₃)₄, TiO(NO₃)₂, TiO₂OC₂O₄, H₂TiF₆, salt of H₂TiF₆, TiO₂ and TiF₄ can be mentioned. In the present invention, zirconium compound is desirably used.

[0020] The desirable concentration of at least one compound selected from the group consisting of zirconium compound and titanium compound is 5 to 5000 ppm calculated as the metal element (that is, as zirconium and/or titanium), and the more desirable concentration is 10 to 3000 ppm. The film obtained by using the treating solution for surface treatment of metal and the method for surface treatment of the present invention is oxide or hydroxide of zirconium or titanium. Therefore, when the concentration of the compound selected from the group consisting of zirconium compound and titanium compound calculated as zirconium and/or titanium is smaller than 5 ppm, it is difficult to obtain sufficient adhesion amount to attain corrosion resistance in a practical period of time for treating, because the concentration of main component of film is too low. On the contrary, when the concentration is larger than 5000 ppm, the sufficient adhesion amount can be obtained, but it is not effective to improve the corrosion resistance and is disadvantageous from the economical view point.

[0021] The zirconium compound and the titanium compound can be easily dissolved in the acidic solution, but are not stable in the alkaline solution, and easily deposit as the oxide or the hydroxide of zirconium or titanium. The desirable pH of the treating solution for surface treatment of metal of the present invention is pH 2 to 6, more desirably pH 3 to 6. When the metal material to be treated is in contact with the treating solution for surface treatment of metal of the present invention in the pH range, the dissolving reaction of the metal material to be treated occurs. And by the dissolving of the metal material to be treated, the pH becomes higher at the surface of the metal material to be treated, and the oxide or the hydroxide of zirconium or titanium deposits as a film on the surface of the metal material to be treated.

[0022] The treating solution for surface treatment of metal of the present invention has free fluorine ion existing therein. To allow free fluorine ion to exist, the fluorine compound is added into the treating solution for surface treatment of metal. As the supplying source of the free fluorine ion, hydrofluoric acid, H₂ZrF₆ and salt of H₂ZrF₆, H₂TiF₆, salt of

H_2TiF_6 , H_2SiF_6 , salt of H_2SiF_6 , HBF_4 and salt of HBF_4 , NaHF_2 , KHF_2 , NH_4HF_2 , NaF , KF and NH_4F can be mentioned. The free fluorine ion has an effect to improve the stability of the zirconium compound and the titanium compound in the treating solution for surface treatment of metal. Further, the free fluorine ion has the function to promote the dissolving reaction of any of ferrous material, zinciferous material, aluminiferous material and magnesiferous material which are the metal materials to be surface treated in the present invention. Therefore, by allowing free fluorine ion to exist therein by adding fluorine compound, the stability of the treating solution for surface treatment of metal of the present invention is improved, and further the reactivity to the metal material to be treated can be improved.

[0023] The inventors of the present invention have previously suggested a composition for surface treatment and treating solution for surface treatment of metal containing at least one of iron and zinc in WO02/103080 as follows. That is, the composition for surface treatment and treating solution for surface treatment of metal use titanium compound or zirconium compound and fluorine containing compound, wherein the ratio A/B is set within the specific range from 0.06 to 0.18, where A refers to the total mole weight of metal elements in the composition for surface treatment and treating solution for surface treatment of metal and B refers to the mole weight which when total fluorine atom in fluorine containing compound is calculated as HF. According to the present invention, it is possible to perform surface treatment on independently one metal material or simultaneously two or more metal materials selected from the group consisting of ferrous material, zinciferous material, aluminiferous material and magnesiferous material, even if out of above mentioned specific range of the ratio, by regulating the concentration of metal element in the titanium compound and zirconium compound, pH and the concentration of free fluorine ion.

[0024] It was impossible in the prior arts to perform the surface treatment on two or more metal materials mentioned above at the same time, because the respective reactivity of ferrous material, zinciferous material, aluminiferous material and magnesiferous material are different. In the present invention, it is possible to perform the surface treatment independently on each metal material or simultaneously on each metal material or two or more metal materials selected from the group consisting of ferrous material, zinciferous material, aluminiferous material and magnesiferous material, because the stability of the treating solution for surface treatment of metal and the reactivity can be balanced arbitrarily by regulating the concentration of free fluorine ion.

[0025] In the present invention, the concentration of free fluorine ion means the concentration of fluorine ion measured by an ion electrode which is on the market. The concentration of free fluorine ion in the treating solution for surface treatment of metal of the present invention is desirably 0.1 to 100 ppm, and more desirably 2 to 70 ppm. In the case where the concentration of free fluorine ion is higher than 100 ppm, the dissolving reaction of the metal material to be treated is promoted. However, since zirconium compound and titanium compound in the treating solution for surface treatment of metal are very stable, even if the pH of the surface of metal material to be treated increases, it becomes difficult to deposit as a film. And, in the case where the concentration of free fluorine ion is lower than 0.1 ppm, the effect for the improvement of the stability of the treating solution for surface treatment of metal and the reactivity thereof is small, and thus, it is no longer advantageous for the treating solution to contain free fluorine ion.

[0026] Other than the effect for improvement of the stability and reactivation of the treating solution for surface treatment of metal, the free fluorine ion of the present invention has a role to keep the eluted component by dissolution of the metal material to be treated stable in the treating solution for surface treatment of metal. In the case of a zinc phosphate treatment of the prior arts, sludge generates, because, for example, iron ion eluted from iron metal material reacts with phosphoric acid and forms iron phosphate which is an insoluble salt. The treating solution for surface treatment of metal of the present invention may also contain phosphoric acid group, but, if the concentration of phosphoric acid group exceeds 1.0g/L, sludge can be generated. And, in the case where the treating amount of the metal material to be treated is remarkably large with respect to the volume of the bath for treatment, one or more compounds selected from the group, for example, consisting of inorganic acid such as sulfuric acid or hydrochloric; organic acid such as acetic acid, oxalic acid, tartaric acid, citric acid, succinic acid, gluconic acid or phthalic acid; and chelating agent which can chelate eluted component, may be added in the treating solution to thereby solubilize the eluted component.

[0027] The treating solution for surface treatment of metal in the present invention may contain at least one compound selected from the group consisting of calcium compound, magnesium compound and strontium compound. The present invention realizes to perform surface treatment on each metal material independently or two to four materials simultaneously selected from the group consisting of ferrous material, zinciferous material, aluminiferous material and magnesiferous material by regulating the concentration of free fluorine ion in the aqueous solution containing zirconium compound and titanium compound of specific concentration within the specified range. Here, the metal elements (calcium, magnesium or strontium) contained in above mentioned calcium compound, magnesium compound or strontium compound have a function to maintain the concentration of free fluorine ion in aqueous solution to a certain value by generating salt of fluorine and fluorinated compound in the aqueous solution. Due to the function, when the surface of various kinds of metal materials are treated at the same time, the optimum deposit amount of film can be obtained on each metal material to be treated, because certain concentration of free fluorine ion can be maintained regardless of the ratio among the materials used.

[0028] As the example of calcium compound, magnesium compound or strontium compound which can be used in the present invention, for example, oxide, hydroxide, chloride, sulfate, nitrate and carbonate of these metal elements can be mentioned. Further, besides calcium compound, magnesium compound and strontium compound, the compound which has a function to maintain the concentration of free fluorine ion constant can be used regardless of whether

[0029] The concentration of the magnesium compound or the strontium compound which can be used in the present invention is desirably 10 to 5000 ppm as the metal element, and more desirably is 100 to 3000 ppm. In the case of calcium compound, the desirable concentration as calcium is 5 to 100 ppm and more desirable concentration is 5 to 50 ppm, because the solubility of calcium is remarkably small. When the concentration of these compounds is higher than the upper limit, the stability of the treating solution for surface treatment of metal may decrease, and the continuous treatment is interrupted. And, when the concentration of these compounds is lower than the lower limit, the deposit amount of film particularly on ferrous material decreases.

[0030] In the treating solution for surface treatment of metal of the present invention, desirably 1000 to 50000 ppm, more desirably 1000 to 30000 ppm of nitric acid group may be added. Nitric acid group acts as an oxidizing agent, and has a function to promote film depositing reaction of the present invention and a function to improve the solubility of above mentioned calcium compound, magnesium compound or strontium compound in the treating solution for surface treatment of metal. Therefore, even if the concentration of nitric acid group is lower than 1000 ppm, the film having excellent corrosion resistance can be deposited. However, in the case where the concentration of above mentioned calcium compound, magnesium compound or strontium compound is high, the stability of the treating solution for surface treatment of metal may decrease. The concentration of nitric acid group of 50000 ppm is sufficient, and it is disadvantageous to add more nitric acid group from the economical view point.

[0031] Further, in the treating solution for surface treatment of metal of the present invention, at least one oxygen acid and/or salt of oxygen acid selected from the group consisting of HClO_3 , HBrO_3 , HNO_3 , HNO_2 , HMnO_4 , HVO_3 , H_2O_2 , H_2WO_4 , H_2MoO_4 . Oxygen acid or salt thereof acts as oxidizing agent to the materials to be treated, and promotes the film forming reaction in the present invention. The concentration of these oxygen acid or salts thereof to be added is not restricted, but adding an amount to 10 to 5000 ppm exhibits sufficient effect as the oxidizing agent.

[0032] Still further, in the treating solution for surface treatment of metal of the present invention, at least one polymer compound selected from the group consisting of water soluble polymer compounds and water dispersible polymer compounds may be added. The metal element whose surface is treated by using the treating solution for surface treatment of metal of the present invention has an enough corrosion resistance, but, if additional function such as lubricity is required, it is possible to improve the physical property of the film by adding preferably selected polymer according to the desired function. As the examples of above mentioned water soluble polymer compounds and water dispersible polymer compounds, polymer compounds which are generally used for the surface treatment of metal such as polyvinyl alcohol, poly(meth)acrylic acid, copolymer of acrylic acid and methacrylic acid, copolymer of ethylene with acrylic monomer such as (meth)acrylic acid or (meth)acrylate, copolymer of ethylene and vinyl acetate, polyurethane, amino-modified phenol resin, polyester resin and epoxy resin can be used.

[0033] The method for surface treatment of the present invention can be illustrated as follows. Namely, the surface is merely treated by degreasing treatment according to an ordinary method, and the cleaned metal material to be treated is brought into contact with the treating solution for surface treatment of metal. Accordingly, the film composed of oxide and/or hydroxide of a metal element selected from the group consisting of zirconium and titanium is deposited and the surface treated film layer having good adhesiveness and corrosion resistance is formed. As the substantial method for this contacting process, any kind of treatment, e.g., spraying treatment, immersion treatment or pouring treatment can be used, and the properties of the product will not be influenced by the treating method. From the chemical view point, it is difficult to obtain the hydroxide of above mentioned metal as a pure hydroxide, and in general, the oxide of above mentioned metal to which hydrated water is attached is considered as hydroxide. Therefore, the hydroxide of the metal finally becomes the oxide by heating. The structure of the surface treated layer of the present invention is considered to be a state where oxide and hydroxide are mixed when dried at an ordinary temperature or at a low temperature after surface treatment. And, when dried at a high temperature after surface treatment, the structure of the surface treated layer is considered to be a state of oxide alone or oxide rich.

[0034] In the present invention, the condition to use the treating solution for surface treatment of metal is not restricted. The reactivity of the treating solution for surface treatment of metal of the present invention can be voluntarily regulated by changing the concentration of zirconium compound or titanium compound and the concentration of free fluorine ion in the treating solution for surface treatment of metal. Therefore, the treating temperature and treating period of time can be changed voluntarily in combination of the reactivity of the treating bath.

[0035] Further, to the treating solution for surface treatment of metal, at least one surface active agent selected from the group consisting of nonionic surface active agent, anionic surface active agent and cationic surface active agent can be added. In the case where the surface of a metal material is treated with this treating solution for surface treatment of metal, a good film can be formed without previous degreasing and cleaning treatment on the metal material to be

treated. That is, this treating solution for surface treatment of a metal can be used also as a surface treating agent and a degreasing agent.

[0036] Furthermore, for the treatment of the surface of metal using the treating solution for surface treatment of metal of the present invention, the method to carry out the electrolysis in the treating solution for surface treatment of metal having a metal material to be treated as a cathode. When the electrolysis treatment is carried out using the metal material to be treated as a cathode, the reduction occurs at the surface of the cathode and the pH goes up. Along with the elevation of the pH, the stability of zirconium compound and/or titanium compound at the surface of cathode is deteriorated, and the surface treated film is deposited as an oxide or a hydroxide containing water.

[0037] Still further, the effect of the present invention can be improved when, after contacting with treating solution for surface treatment of metal, or after being electrolyzed in the treating solution for surface treatment of metal with or without washed by water, the metal material is brought into contact with the acidic solution of the compound containing at least one element selected from the group consisting of cobalt, nickel, tin, copper, titanium and zirconium, or with the treating solution containing at least one polymer compound selected from the group consisting of water soluble polymer compound and water dispersible polymer.

[0038] The surface treated film layer obtained by the present invention is characterized in a thin film and exhibits excellent coating property, but depending on the surface condition of the metal material to be treated, sometimes tiny defects may be formed on the surface treated film layer. By bringing the layer in contact with the acidic solution of the compound containing at least one element selected from the group consisting of cobalt, nickel, tin, copper, titanium and zirconium or the treating solution containing at least one polymer compound selected from the group consisting of water soluble polymer compound and water dispersible polymer, the tiny defects are covered and the corrosion resistance can be further improved.

[0039] The compound containing at least one element selected from the group consisting of cobalt, nickel, tin, copper, titanium and zirconium is not restricted, and, it is possible to use oxide, hydroxide, fluoride, complex fluoride, chloride, nitrate, oxynitrate, sulfate, oxysulfate, carbonate, oxycarbonate, phosphate, oxyphosphate, oxalate, oxyoxalate, and organic metal compounds and the like. Further, desirably the pH of acidic solution containing the metal element is 2 to 6, and can be adjusted with acid such as phosphoric acid, nitric acid, sulfuric acid, hydrofluoric acid, hydrochloric acid and organic acid or alkali such as sodium hydroxide, potassium hydroxide, lithium hydroxide, salts of alkali metal, ammonium salt or amines.

[0040] Further, as at least one polymer compound selected from above mentioned water soluble polymer compound or water dispersible polymer compound, for example, polyvinyl alcohol, poly(meth)acrylic acid, copolymer of acrylic acid and methacrylic acid, copolymer of ethylene with acrylic monomer such as (meth)acrylic acid or (meth)acrylate, copolymer of ethylene and vinyl acetate, polyurethane, amino-modified phenol resin, polyester resin or epoxy resin, tannin and tannic acid and salts thereof, and phytic acid can be used.

[0041] The present invention may remarkably improve the corrosion resistance of metal material by providing a surface treated film layer composed of oxide and/or hydroxide of metal elements selected from zirconium and/or titanium on the surface of metal material to be treated. The oxide and hydroxide of above mentioned metal elements have a physical property characterized not to be damaged by acid or alkali, and chemically stabilized. In the actual corrosive environment for metal, at the anode where the metal elution phenomenon occurs, the pH becomes lower, while, at the cathode where reduction occurs, the pH becomes higher. Therefore, the surface treated film of less resistant to acid and alkali may be dissolved under the corrosive environment and its effect would be lost. Since the main component of the surface treated film layer of the present invention is resistive to acid or alkali, the excellent effect can be maintained under the corrosive environment.

[0042] And since the oxide and hydroxide of above mentioned metal elements form a network structure mediated by metal and oxide, it becomes a very good barrier film. The corrosion of metal material, which can be varied depending on the environment for use, generally, is oxygen demanding type corrosion in the atmosphere in which water and oxygen exist, and the speed of corrosion is promoted by the presence of the components such as chloride. Having a barrier effect against water, an acid and a corrosion promoting component, the surface treated film layer of the present invention may exhibit excellent corrosion resistance.

[0043] For the purpose to enhance the corrosion resistance of iron metal material such as cold rolled steel plate, hot rolled steel plate, cast iron and sintered steel using above mentioned barrier effect, the adhesion amount over 30 mg/m² calculated as the metal element is necessary, desirably over 40 mg/m² and more desirably over 50 mg/m². And for the purpose to enhance the corrosion resistance of zinc metal material such as zinc, zinc plated steel plate and alloyed hot-dip zinc-coated steel plate, the adhesion amount over 20 mg/m² calculated as the metal element is necessary, desirably over 30 mg/m². Further, for the purpose to enhance the corrosion resistance of aluminiferous materials such as cast aluminum and aluminum alloy plate, the adhesion amount over than 10 mg/m² calculated as the metal element is necessary, desirably over 20 mg/m². For the purpose to enhance the corrosion resistance of magnesiferous materials such as magnesium alloy plate and cast magnesium, the adhesion amount over than 10 mg/m² calculated as the metal element is necessary, desirably over than 20 mg/m². Referring to the adhesion amount, there is no upper

limit. However, when the amount exceeds 1 g/m^2 , cracks easily generate on the surface treated film layer and it becomes difficult to form a uniform film. Therefore, in any case of iron metal material and zinc metal material and aluminiferous material, the desirable upper limit of adhesion amount is 1 g/m^2 , more desirably 800 mg/m^2 .

Examples

[0044] The effects of the treating solution for surface treatment of metal and the method for surface treatment of the present invention will be illustrated specifically in accordance with the Examples and Comparative Examples below. And a material to be treated, a degreasing agent and a coating used therein are arbitrarily selected from the materials which are on the market, and not intending to restrict the actual uses of the treating solution for surface treatment of metal and the method for surface treatment of the present invention.

[Test plate]

[0045] As the test plates, cold rolled steel plates, hot-dip zinc-coated steel plates, aluminum alloy plates and magnesium alloy plates are used in the Examples and Comparative Examples. The abbreviations and specifications of these test plates are shown below. For the evaluation of the appearance after surface treatment, the test plate prepared by joining three metal materials of SPC, GA and Al by a spot welding was used. For the evaluation of adhesion amount of surface treated film layer, each test plate of SPC, GA, Al and Mg, and the test plate prepared by joining three metal materials of SPC, GA and Al by a spot welding were used. For the evaluation of the coating property, the test plate prepared by joining three metal materials of SPC, GA and Al by a spot welding was used and the test from surface treatment, coating and evaluation of coating property were carried out in series. Fig.1 is the plane view of the test plate prepared by joining three metal materials of SPC, GA and Al by a spot welding, and Fig.2 is an elevation view of it. The numeral 1 indicates a spot welded portion.

- SPC: cold rolled steel plate (JIS-G-3141)
- GA: both-side alloyed hot-dip zinc-coated steel plate (45 g/m^2)
- Al: aluminum alloy plate (6000 series aluminum alloy)
- Mg: magnesium alloy plate (JIS-H-4201)

[Treating process]

[0046] Treating process of Examples and Comparative Examples are shown as follows.

Examples 1-4, Example 7 and Comparative Examples 1-4: alkali degreasing → rinsing by water → film forming treatment → rinsing by water → rinsing by pure water → drying
 Example 5: alkali degreasing → rinsing by water → electrolysis formation treatment → rinsing by water → rinsing by Pure water → drying
 Example 6: film formation treatment (used both as degreasing) → rinsing by water → rinsing by pure water → drying
 Example 8: alkali degreasing → rinsing by water → film formation treatment → rinsing by water → after treatment → rinsing by pure water → drying
 Example 9: film formation treatment (and degreasing) → rinsing by water → after treatment → rinsing by pure water → drying
 Comparative Example 5: alkali degreasing → rinsing by water → surface conditioning → zinc phosphate treatment → rinsing by water → rinsing by pure water → drying

[0047] In above mentioned processes for Examples and Comparative Examples, alkali degreasing was carried out as follows. That is, Fine Cleaner L4460 (Trade Mark: Product of Nihon Parkerizing) was diluted to 2% concentration by city water, and was sprayed to a plate to be treated at $40\text{ }^{\circ}\text{C}$ for 120 sec. Rinsing by water and rinsing by pure water after film formation treatment were performed by spraying water and pure water on the plate to be treated at a room temperature for 30 sec both in Examples and Comparative Examples.

Example 1

[0048] Aqueous solution of zirconium with concentration of 200 ppm was prepared using zirconium oxynitrate reagent and nitric acid. After heating the aqueous solution to $45\text{ }^{\circ}\text{C}$, the pH was adjusted to 3.0 using sodium hydroxide reagent and hydrofluoric acid, and the concentration of free fluorine ion measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd) was adjusted to 1 ppm, thus obtaining the treating solution for surface treatment of

metal. The total fluorine concentration in the treating solution for surface treatment of metal after adjusting free fluorine ion was 50 ppm.

[0049] The test plate rinsed by water after degreasing was immersed into the treating solution for surface treatment of metal for 120 seconds so as to carry out the surface treatment.

Example 2.

[0050] Aqueous solution of zirconium with concentration of 100 ppm, magnesium with concentration of 5000 ppm, strontium with concentration of 2000 ppm and nitric acid group with concentration of 28470 ppm was prepared using zirconium oxynitrate reagent, magnesium nitrate reagent and strontium nitrate reagent. After heating the aqueous solution to 50°C, the pH was adjusted to 4.0 using ammonium water reagent and hydrofluoric acid, and the concentration of free fluorine ion measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd) was adjusted to 80 ppm, thus obtaining the treating solution for surface treatment of metal. The total fluorine concentration in the treating solution for surface treatment of metal after adjusting free fluorine ion was 2000 ppm.

[0051] The test plate rinsed by water after degreasing was immersed into the treating solution for surface treatment of metal for 60 seconds so as to carry out the surface treatment.

Example 3

[0052] Aqueous solution of zirconium with concentration of 1000 ppm, titanium with concentration of 2000 ppm, calcium with concentration of 5 ppm and nitric acid group with concentration of 1000 ppm was prepared using aqueous solution of hexafluorozirconic acid (IV), aqueous solution of titanium sulfate (IV) and calcium sulfate reagent. After heating the aqueous solution to 40°C, the pH was adjusted to 5.0 using potassium hydroxide reagent and hydrofluoric acid, and the concentration of free fluorine ion measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd) was adjusted to 25 ppm, thus obtaining the treating solution for surface treatment of metal. The total fluorine concentration in the treating solution for surface treatment of metal after adjusting free fluorine ion was 2250 ppm.

[0053] The test plate rinsed by water after degreasing was immersed into the treating solution for surface treatment of metal for 90 seconds so as to carry out the surface treatment.

Example 4

[0054] Aqueous solution of titanium with concentration of 5000 ppm, strontium with concentration of 5000 ppm, nitric acid group with concentration of 7080 ppm and nitrous acid group with concentration of 40 ppm was prepared using aqueous solution of hexafluorotitanium acid (IV), strontium nitrate reagent, and sodium nitrite reagent. After heating the aqueous solution to 35°C, the pH was adjusted to 4.0 using triethanol amine reagent and hydrofluoric acid, and the concentration of free fluorine ion measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd) was adjusted to 10 ppm, thus obtaining the treating solution for surface treatment of metal. The total fluorine concentration in the treating solution for surface treatment of metal after adjusting free fluorine ion was 11900 ppm.

[0055] The test plate was rinsed by water after degreasing, then the obtained treating solution for surface treatment of metal was sprayed to the surface thereof for 120 sec., thus carrying out the surface treatment.

Example 5

[0056] Aqueous solution of zirconium with concentration of 5 ppm, titanium with concentration of 5 ppm, magnesium with concentration of 100 ppm, nitric acid group with concentration of 30520 ppm and chloric acid group with concentration of 100 ppm was prepared using zirconium oxynitrate reagent, aqueous solution of hexafluorotitanic acid (IV), magnesium nitrate reagent, nitric acid and sodium chloric acid reagent. After heating the aqueous solution to 30°C, the pH was adjusted to 6.0 using ammonia water reagent and hydrofluoric acid, and the concentration of free fluorine ion measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd) was adjusted to 0.5 ppm, thus obtaining the treating solution for surface treatment of metal. The total fluorine concentration in the treating solution for surface treatment of metal after adjusting free fluorine ion was 12 ppm.

[0057] Using the test plate rinsed by water after degreasing as a cathode and a carbon electrode as an anode, the test plate was electrolyzed in the treating solution for surface treatment of metal for 5 seconds under the condition of 5A/dm², thus carrying out the surface treatment.

Example 6

[0058] Aqueous solution of zirconium with concentration of 150 ppm, magnesium with concentration of 10 ppm, nitric acid group with concentration of 5200 ppm and hydrogen peroxide concentration of 10 ppm was prepared using zirconium oxynitrate reagent, magnesium oxide reagent, nitric acid, and hydrogen peroxide reagent. After heating the aqueous solution to 50°C, the pH was adjusted to 5.0 using ammonia water reagent and hydrofluoric acid, the concentration of free fluorine ion measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd) was adjusted to 50 ppm and 2 g/L of polyoxyethylenonylphenylether (ethylene oxide addition mole number: 12 mol), which is nonionic surface active agent, was added, thus obtaining the treating solution for surface treatment of metal. The total fluorine concentration in the treating solution for surface treatment of metal after adjusting free fluorine ion was 170 ppm.

[0059] Undegreased test plate on which oil is coated, above mentioned treating solution for surface treatment of metal was applied to the surface by spray for 90 sec., thus the degreasing and surface treatment were carried out at the same time.

Example 7

[0060] Aqueous solution of titanium with concentration of 100 ppm, calcium with concentration of 50 ppm, magnesium with concentration of 5000 ppm, nitric acid group with concentration of 25660 ppm and permanganate with concentration of 10 ppm was prepared using aqueous solution of titanium sulfate (IV), calcium nitrate reagent, magnesium nitrate reagent and potassium permanganate reagent. Water soluble acrylic polymer compound (Jurymer AC-10L: product of Nihon Junyaku Co., Ltd.) was added in the aqueous solution so as the concentration of solid to be 1%, then the aqueous solution was heated to 50°C.

Thereafter, the pH was adjusted to 3.0 using sodium hydroxide reagent and hydrofluoric acid, and the total free fluorine ion concentration in the aqueous solution to be measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd) was adjusted to 95 ppm, thus obtaining the treating solution for surface treatment of metal. After adjusting the free fluorine ion concentration, the total fluorine concentration in the treating solution for surface treatment of metal was 2000 ppm.

[0061] The test plate rinsed by water after degreasing was immersed into the treating solution for surface treatment of metal for 60 seconds so as to carry out the surface treatment.

Example 8

[0062] The aqueous solution with 1% of water soluble acrylic polymer compound (Jurymer AC-10L: product of Nihon Junyaku Co., Ltd.) in solid concentration and 2g/L of phosphoric acid reagent as phosphoric acid group was prepared. This aqueous solution was heated to 40°C, then the pH was adjusted to 4.5 using ammonia water reagent, thus obtaining the after treating solution. The test plate on which film formation was carried out by the surface treatment of Example 5 and rinsed by water was dipped into the above mentioned after treating solution for 30 seconds so as to carry out the after treatment.

Example 9

[0063] The aqueous solution of zirconium with concentration of 50 ppm and cobalt with concentration of 50 ppm was prepared using aqueous solution of hexafluorozirconic acid (IV) and cobalt nitrate reagent. After heating the aqueous solution to 40°C, the pH was adjusted to 5.0 with ammonia water reagent, thus obtaining the after treating solution. The test plate on which film formation was carried out by the surface treatment of Example 6 and rinsed by water was immersed into the above mentioned after treating solution for 30 seconds so as to carry out the after treatment.

Comparative Example 1

[0064] The aqueous solution of zirconium with concentration of 500 ppm, magnesium with concentration of 1000 ppm and nitric acid group with concentration of 6780 ppm was prepared using zirconium oxynitrate reagent, magnesium nitrate and nitric acid. After heating the aqueous solution to 45°C, the pH was adjusted to 4.0 with sodium hydroxide solution, thus obtaining the treating solution for surface treatment of metal. The free fluorine ion concentration of the treating solution for surface treatment of metal was measured by a fluorine ion meter on the market (IM-55G; product of Toa Denpa Industries Co., Ltd), and the result was 0 ppm.

[0065] The test plate which was rinsed by water after degreasing was immersed into the above mentioned treating solution for surface treatment of metal for 120 seconds so as to carry out the surface treatment.

Comparative Example 2

[0066] The aqueous solution of titanium with concentration of 2000 ppm was prepared by using aqueous solution of titanium sulfate (IV). After heating the aqueous solution to 50°C, the pH was adjusted to 3.5 using ammonia water reagent and hydrofluoric acid, and the concentration of free fluorine ion measured by a fluorine ion meter (IM-55G; product of Toa Denpa Industries Co., Ltd) was adjusted to 400 ppm, thus obtaining the treating solution for surface treatment of metal.

[0067] The test plate which was rinsed by water after degreasing was immersed into the above mentioned treating solution for surface treatment of metal for 90 seconds so as to carry out the surface treatment.

Comparative Example 3

[0068] Alchrom 713 (Trade Mark, product of Nihon Parkerizing Co., Ltd.), which is the chromic chromate treating agent on the market, was diluted by city water to the concentration of 3.6%, then total acidity and free acid acidity were adjusted to the center value described in the brochure.

[0069] The test plate was rinsed by water after degreasing, then immersed into the chromate treating solution heated to the temperature of 35°C and chromate treatment was carried out for 60 sec.

Comparative Example 4

[0070] Palcoat 3756 (Trade Mark, product of Nihon Parkerizing Co., Ltd.), which is the chrome free treating agent on the market, was diluted by city water to the concentration of 2%, then total acidity and free acid acidity were adjusted to the center value described in the brochure. The test plate was rinsed by water after degreasing, then immersed into the chrome free treating solution heated to the temperature of 40°C and chrome free treatment was carried out for 60 sec.

Comparative Example 5

[0071] The test plate was rinsed by water after degreasing, then the solution prepared by diluting Prepalene ZN (Trade Mark, product of Nihon Parkerizing Co., Ltd.), which is a surface conditioning agent, with city water to the concentration of 0.1% was sprayed thereon at the room temperature for 30 sec. Palbond L3020 (Trade Mark, product of Nihon Parkerizing Co., Ltd.) was diluted to the concentration of 4.8% with city water. Further, sodium hydrogen fluoride reagent as fluorine was added into the solution to 200 ppm, and then, total acidity and free acid acidity thereof were adjusted to the center value described in the brochure. Thus the zinc phosphate treating solution was prepared. Above mentioned test plate was immersed into the zinc phosphate chemical treating solution heated to the temperature of 42°C, and zinc phosphate film was deposited.

[Evaluation of surface treated film]

[0072] The appearance of surface treated plates of the Examples and Comparative Examples were evaluated by visual inspection. Results are summarized in Table 1. Further, adhesion amounts of surface treated film layers were measured by a fluorescent X-ray analyzer (System 3270, product of Rigaku Denki Kogyo Co., Ltd.). Results are summarized in Table 2 and Table 3. The adhesion amount of surface treated film layer was measured in the case where metal materials were not joined together and treated respectively (in the case without joining) and in the case where materials were subjected to joining treatment by means of spot welding (in the case with joining).

Table 1

	appearance after surface treatment		
	on SPC	on GA	on Al
Example 1	uniform interference color	uniform dark black	uniform white
Example 2	uniform interference color	uniform dark black	uniform white
Example 3	uniform interference color	uniform dark black	uniform white
Example 4	uniform interference color	uniform dark black	uniform white
Example 5	uniform interference color	uniform dark black	uniform white

Table 1 (continued)

	appearance after surface treatment		
	on SPC	on GA	on Al
Example 6	uniform interference color	uniform dark black	uniform white
Example 7	uniform interference color	uniform dark black	uniform white
Comparative Example 1	film not deposited	film not deposited	uneven white
Comparative Example 2	pale yellow	uneven gray	uneven white
Comparative Example 3	film not deposited	slightly turned to yellow	gold
Comparative Example 4	film not deposited	film not deposited	uniform white
Comparative Example 5	material partially exposed	uniform gray	uneven white

[0073] In Table 1, the appearance evaluation results of surface treated films obtained by Examples and Comparative Examples are shown. In the Examples, it is clear that the uniform films, were obtained on all metal materials in all test plates. Further, on the spot welded portions of test plates used in Examples, the deposition of surface treated film was observed too. On the contrary, in Comparative Examples, a uniform film was not formed on all test plates. Especially, in Comparative Examples 3, 4 and 5, the deposition of film on spot welded portions was not at all observed. Further, the Comparative Example 5 used the zinc phosphate chemical treating solution to be used in the case where cold rolled steel plate, zinc plated steel plate and aluminum alloy are treated at the same time. When the test plates were joined by spot welding as illustrated in the present test, the portion where the metal material was exposed, which is called as "Lack of Hiding", was observed on the cold rolled steel plate.

Table 2

	adhesion amount of surface treated film layer (without joining) (total adhesion amount of Zr and Ti: mg/m ²)			
	on SPC	on GA	on Al	on Mg
Example 1	122	67	48	45
Example 2	108	66	49	41
Example 3	61	58	42	38
Example 4	73	59	14	12
Example 5	41	52	38	26
Example 6	35	38	25	19
Example 7	31	29	24	18
Comparative Example 1	trace	trace	trace	trace
Comparative Example 2	25	15	15	10
Comparative Example 3	trace	Cr 33	Cr 95	Cr 75
Comparative Example 4	trace	trace	25	15
Comparative Example 5	weight of film 2.5g/m ²	weight of film 4.5g/m ²	weight of film 1.2g/m ²	weight of film 0.5g/m ²

Table 3

	Adhesion amount of surface treated film layer (with joining) (total adhesion amount of Zr and Ti: mg/m ²)		
	on SPC	on GA	on Al
Example 1	125	67	48
Example 2	118	66	49
Example 3	65	58	42
Example 4	72	59	14
Example 5	45	52	38
Example 6	38	38	25
Example 7	32	29	24
Comparative Example 1	trace	trace	trace
Comparative Example 2	28	17	12
Comparative Example 3	trace	Cr 35	Cr 85
Comparative Example 4	trace	trace	21
Comparative Example 5	weight of film 2.8 g/m ²	weight of film 4.7 g/m ²	Weight of film 0.7 g/m ²

[0074] In Table 2 and Table 3, the results by the measurement of adhesion amount of surface treated film obtained in Examples and Comparative Examples. In the Examples, the aimed adhesion amounts were obtained on all metal materials in all test plates. Further, the adhesion amount of surface treated film layer in Examples was constant regardless of whether the test plates were joined or not. On the contrary, as clearly understood from the evaluation results for appearance of film in Comparative Example, the uniform film was not deposited on all test plates.

[Evaluation of coating performance]

(Preparation of evaluation plate)

[0075] For the purpose to evaluate the coating property of surface treated plates obtained in Examples and Comparative Examples, coating was carried out by the following process: cationic electrodeposition coating → rinsing with pure water → baking → surfacer → baking → top coating → baking.

[0076] Details of the cationic electrodeposition coating, surfacer, and top coating are as follows:

· Cationic electrodeposition coating: epoxy type cationic electrodeposition coating (Elecron 9400, product of Kansai Paint CO., LTD), electric voltage 200V, thickness of film 20μm, baked at 175°C for 20 minutes,

· surfacer: aminoalkyd coating (AmilacTP-37 gray: product of Kansai Paint CO., LTD.), spray coating, thickness of film 35μm, baked at 140°C for 20 minutes, and

· top coating: aminoalkyd coating (AmilacTM-13 white, product of Kansai Paint CO., LTD.), spray coating, thickness of film 35μm, baked at 140°C for 20 minutes.

[Evaluation of coating performance]

[0077] The coating property in the Examples and Comparative Examples was evaluated and the results thereof are shown in Table 4 and Table 5. Items evaluated and the abbreviations are described below. Hereinafter, the coated film after electrodeposition coating process is called as electrodeposition coated film and the coated film after top coating is called as 3-coats film.

- (1) SST: salt water spray test (electrodeposition coated film)
- (2) SDT: warm salt water dipping test (electrodeposition coated film)

(3) 1st ADH: primary adhesion (3-coats film)

(4) 2nd ADH: water resistant secondary adhesion (3-coats film)

SST: Cross cut line is notched using a sharp knife on the electrodeposition coated plate, and 5% brine is sprayed to the plate for 840 hours (according to JIS-Z-2371). After spraying, maximum blister widths at both sides from the cross cut line were measured.

SDT: The electrodeposition coated plate was soaked into aqueous solution of 5 wt% of NaCl at 50°C for 840 hours. After soaking, the test plate washed with city water and dried at the room temperature. The whole surface of the test plate was peeled off using an adhesive tape, and the removed area of coated film on each metal material was evaluated by inspector's eye.

1st ADH: Checker lines of 100 squares with 2 mm intervals were marked using a sharpened knife on a 3-coats film. The squares in the checker were peeled using a cellophane tape, and numbers of peeled squares were counted.

2nd ADH: A 3-coats film was soaked in pure water of 40 °C for 240 hours. Then, 100 checker squares with 2mm interval were marked using a sharpened knife on it. The checker squares were peeled using a cellophane tape, and numbers of peeled squares were counted.

Table 4

	coating property of electro deposition film					
	SST max blister widths at both sides (mm)			SDT removed area (%)		
	on SPC	on GA	on Al	on SPC	on GA	on Al
Example 1	2.0	0.5	0.5	5>	5>	5>
Example 2	2.0	0.5	0.5	5>	5>	5>
Example 3	3.0	0.5	0.5	5>	5>	5>
Example 4	3.0	0.5	0.5	5>	5>	5>
Example 5	3.0	0.5	0.5	5	5>	5>
Example 6	3.5	1.0	0.5	10	5>	5>
Example 7	3.5	1.0	0.5	10	5>	5>
Example 8	2.5	0.5	0.5	5>	5>	5>
Example 9	2.5	0.5	0.5	5>	5>	5>
Comparative Example 1	6.5	3.5	3.0	70	40	15
Comparative Example 2	4.5	2.0	0.5	30	10	5
Comparative Example 3	10.0	5.0	0.5	80	40	5>
Comparative Example. 4	10.0	5.0	1.0	90	50	10
Comparative Example 5	5.0	2.0	2.0	40	10	20

[0078] The results for evaluation of coating property of the electrodeposition coated film are summarized in Table 4. Examples showed good corrosive resistance on all test plates. On the contrary, in Comparative Example 1, since free fluorine ions were not contained in the treating solution for surface treatment of metal at all, the deposition of surface treated film was not sufficient and thus the corrosion resistance was not so good. Further, in Comparative Example 2, since the concentration of free fluorine ion in the treating solution for surface treatment of metal was high, especially, the adhesion amount of film on SPC was small and the corrosion resistance was not so good. The coating properties of Examples 5 and 6 were superior to those of Comparative Examples, but when compared with other Examples, corrosive resistances after electrodeposition coating was inferior to those of other Examples. However, as shown in Examples 8 and 9, the corrosive resistance was further improved by carrying out the after treatment.

[0079] Because in Comparative Example 3, a chromate treating agent for aluminum alloy was used and in Comparative Example 4, a chrome free treating agent for aluminum alloy was used, the corrosion resistance of Al was good, but the corrosion resistance of other test plates were obviously inferior to those of Examples. In Comparative Example 5, a zinc phosphate treating agent, which is now usually used as the base for coating was used. However, Comparative Example 5, in the condition where each of the test plates was joined by welding, showed the test results inferior to

those of Examples.

Table 5

	coating properties of 3-coats film					
	1st ADH			2nd ADH		
	on SPC	on GA	on Al	on SPC	on GA	on Al
Example 1	0	0	0	0	0	0
Example 2	0	0	0	0	0	0
Example 3	0	0	0	0	0	0
Example 4	0	0	0	0	0	0
Example 5	0	0	0	0	0	0
Example 6	0	0	0	0	0	0
Example 7	0	0	0	0	0	0
Example 8	0	0	0	0	0	0
Example 9	0	0	0	0	0	0
Comparative Example 1	0	0	0	5	8	0
Comparative Example 2	0	0	0	0	0	0
Comparative Example 3	6	0	0	17	3	0
Comparative Example 4	0	0	0	5	0	0
Comparative Example 5	5	0	0	8	0	6

[0080] Table 5 shows the evaluation results of adhesion of a 3-coats plate. Examples showed good adhesion to all test plates. Regarding to 1st ADH, good results were obtained in all Comparative Examples. However, regarding to 2nd ADH, Comparative Examples did not show the good level of adhesion to all test plates same as the corrosive resistance of the electrodeposition coating. Further, in Comparative Example 5, the generation of sludge, which is the by-product of zinc phosphate treatment, was observed in the treating bath after surface treatment. However, in Examples of the present invention, the generation of sludge was not observed.

[0081] From above mentioned results, it is obviously understood following facts. That is, simultaneous treatments of SPC, GA, and Al and the deposition of surface treated film having good adhesion and corrosion resistance on the surface thereof without changing treating bath and treating condition are possible only by using the treating solution for surface treatment of metal and the surface treating method of the present invention. According to the present invention, it is possible to deposit the surface treated film having good corrosion resistance even on a welded portion. Further, since the method for surface treatment of the present invention requires only to bring the metal material to be treated in contact with the treating solution for surface treatment of metal, it is possible to deposit surface treated film and to improve the corrosive resistance in the portion where the solution may not be stirred such as inside of bag shape structure. Industrial Applicability

[0082] According to the treating solution for metal surface treatment and the method for surface treatment of the present invention, it is possible to deposit a surface treated film having excellent corrosion resistance after coating on the surface of a metal made of two or more, or each of ferriferous material, zinciferous material, aluminiferous material and magnesiferous material in the treating bath containing no harmful component to the environment and without generating sludge, which have never been achieved in the prior art. Further, since the present invention does not need a process for surface conditioning on the metal material to be treated, it is possible to shorten the treatment time and to reduce space for the treatment.

Claims

1. Treating solution for surface treatment of metal, which is aqueous surface treating solution to treat independently each metal material or simultaneously two or more metal materials selected from the group consisting of ferriferous material, zinciferous material, aluminiferous material and magnesiferous material, the treating solution containing

5 to 5000 ppm of at least one compound selected from the group consisting of zirconium compound and titanium compound calculated as metal element, and 0.1 to 100 ppm of free fluorine ion, and having pH 2 to 6.

2. The treating solution for surface treatment of metal according to claim 1, further containing at least one compound selected from the group consisting of calcium compound, magnesium compound and strontium compound, wherein concentration of the compound calculated as metal element is 5 to 100 ppm in the case of the calcium compound, 10 to 5000 ppm in the case of the magnesium and 10 to 5000 ppm in the case of the strontium compound.
3. The treating solution for surface treatment of metal according to claim 1 or 2, further containing 1000 to 50000 ppm of nitrate group.
4. The treating solution for surface treatment of metal according to any one of claims 1 to 3, further containing at least one oxygen acid and/or salt of oxygen acid selected from the group consisting of HClO_3 , HBrO_3 , HNO_2 , HNO_3 , HMnO_4 , HVO_3 , H_2O_2 , H_2WO_4 , H_2MoO_4 and salts thereof.
5. The treating solution for surface treatment of metal according to any one of claims 1 to 4, further containing at least one polymer compound selected from the group consisting of water soluble polymer compounds and water dispersible polymer compounds.
6. The treating solution for surface treatment of metal according to any one of claims 1 to 5, further containing at least one surface active agent selected from the group consisting of nonionic surface active agents, anionic surface active agents and cationic surface active agents.
7. A method for surface treatment of metal comprising, contacting independently each metal material or simultaneously two or more metal materials selected from the group consisting of ferriferous material, zinciferous material, aluminiferous material and magnesiferous material with the treating solution for surface treatment according to any one of claims 1 to 6.
8. The method for surface treatment of metal according to claim 7, comprising, further contacting the metal material or the two or more metal materials with acidic aqueous solution of compound containing at least one element selected from the group consisting of cobalt, nickel, tin, copper, titanium and zirconium, after contacting with the treating solution for surface treatment, with or without washing by water.
9. The method for surface treatment of metal according to claim 7, comprising, further contacting the metal material or the two or more metal materials with treating solution containing at least one polymer compound selected from water soluble polymer compounds and water dispersible polymer compounds, after contacting with the treating solution for surface treatment, with or without washing by water.
10. A method for surface treatment of metal comprising, electrolytic treating in the treating solution for surface treatment according to any one of claims 1 to 6, wherein independently each metal material or simultaneously two or more metal materials selected from the group consisting of ferriferous material, zinciferous material, aluminiferous material and magnesiferous material are a cathode.
11. The method for surface treatment of metal according to claim 10, comprising, further contacting the metal material or the two or more metal materials with acidic aqueous solution of compound containing at least one element selected from the group consisting of cobalt, nickel, tin, copper, titanium and zirconium, after electrolytic treating in the treating solution for surface treatment, with or without washing by water.
12. The method for surface treatment of metal according to claim 10, comprising, further contacting the metal material or the two or more metal materials with treating solution containing at least one polymer compound selected from water soluble polymer compounds and water dispersible polymer compounds, after electrolytic treating in the treating solution for surface treatment, with or without washing by water.
13. A method for surface treatment of metal comprising, contacting independently each metal material or simultaneously two or more metal materials selected from the group consisting of ferriferous material, zinciferous material, aluminiferous material and magnesiferous material, whose surface is not degreased and cleaned with the treating solution for surface treatment according to claim 6.

14. A metal material having a surface treated film containing at least one metal element selected from the group consisting of titanium and zirconium formed on a surface of iron metal material by the method for surface treatment according to any one of claims 7 to 13, wherein an adhesion amount of the surface treated film calculated as the metal element is 30mg/m² or more.

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15. A metal material having a surface treated film containing at least one metal element selected from the group consisting of titanium and zirconium formed on a surface of zinc metal material by the method for surface treatment according to any one of claims 7 to 13, wherein an adhesion amount of the surface treated film calculated as the metal element is 20mg/m² or more.

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16. A metal material having a surface treated film containing at least one metal element selected from the group consisting of titanium and zirconium formed on a surface of aluminum metal material by the method for surface treatment according to any one of claims 7 to 13, wherein an adhesion amount of the surface treated film calculated as the metal element is 10mg/m² or more.

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17. A metal material having a surface treated film containing at least one metal element selected from the group consisting of titanium and zirconium formed on a surface of magnesium metal material by the method for surface treatment according to any one of claims 7 to 13, wherein an adhesion amount of the surface treated film calculated as the metal element is 10mg/m² or more.

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Fig.1

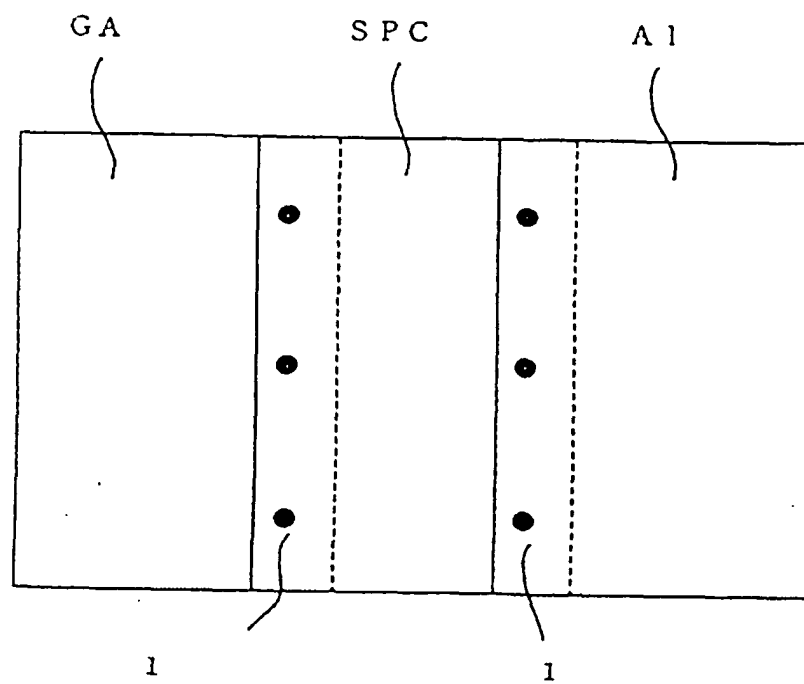
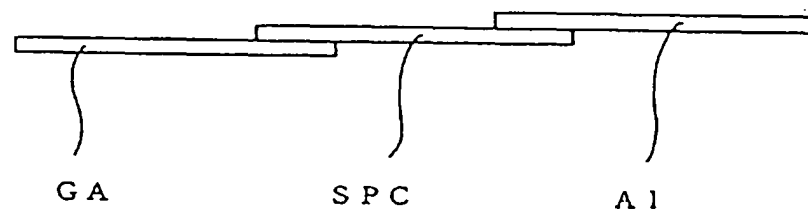


Fig.2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/15868

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl.⁷ C23C22/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl.⁷ C23C22/34Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2004
Kokai Jitsuyo Shinan Koho 1971-2004 Jitsuyo Shinan Toroku Koho 1996-2004

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	JP 2003-253461 A (NIPPON PAINT Co., Ltd.), 10 September, 2003 (10.09.03), (Family: none)	1, 3-5, 7, 14-16
A	US 2001/0050029 A1 (NIPPON PAINT Co., Ltd.), 13 December, 2001 (13.12.01), & JP 2001-303267 A	1-17

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
15 March, 2004 (15.03.04)Date of mailing of the international search report
30 March, 2004 (30.03.04)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

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Form PCT/ISA/210 (second sheet) (July 1998)