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(54) Method of treating metal surfaces

Verfahren zur Oberflächenbehandlung von Metallen

Méthode de traitement de surfaces métalliques

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Description

[0001] The present invention relates to a method of metal surface treatment.

[0002] Generally, the surface of a metal is provided with surface treatment for the purpose of enhancing characteristics such as corrosion resistance and the like. As one species of such the surface treatment, there is known surface treatment with a chemical conversion treatment agent containing a zirconium compound. Such a method of surface treatment is performed by an electroless reaction, and an insoluble zirconium salt and a salt of the component metal of the article to be treated, consisting of hydroxides/fluorides of zirconium and fluorides of metal of an article to be treated, are deposited on the metal surface by means of a reaction inwhich the component metal of the article to be treated is eluted by the treatment solution, the production of fluorides based on a reaction of the eluted metal ions with fluorine ions, the formation of hydrogen through the reduction of hydrogen ions and the increase in a pH in the vicinity of the surface of an article to be treated resulting from the substitution of a fluorine ion for a hydroxide ion associated with the hydrolysis of zirconium complex ions.

[0003] In such an electroless reaction using a zirconium-based chemical conversion treatment agent, since it is extremely difficult to cause a homogeneous reaction to occur over the entire said surface, it is difficult to form an adequately dense and uniform coat and the resulting coat becomes one containing a high proportion of oxides and fluorides due to etching of substrates, and therefore the corrosion resistance is deteriorated. And, in the electroless reaction, since an anodic reaction and a cathodic reaction are simultaneously occurred on the same surface, reactivity is reduced when the chemical conversion coat is being formed. Therefore, only a rough and thin chemical conversion coat composed of a substrate metal or an alkali metal can be attained and it is difficult to attain a uniform and dense protection coat.

[0004] consequently, it was difficult that a chemical conversion coat obtained by using the electroless treatment with a zirconium-based chemical conversion treatment agent provide a sufficient rust prevention property particularly for an article to be treated such as an iron-based substrate and a zinc-based substrate, having low reactivity with the chemical conversion treatment agent. And, also in surface treatment of an aluminum-based substrate and a magnesium-based substrate, it is required to attain a higher level of corrosion resistance by forming a chemical conversion coat having better characteristics. Thus, a method of metal surface treatment, which can form a more uniform and denser chemical conversion coat, is desired.

[0005] Moreover, as a method of metal surface treatment, there is disclosed a method of surface treatment based on an electrolysis reaction (cf. for example, Japanese Kokai Publication 2000-234200 and Japanese Kokai Publication 2002-194589). However, these methods concern a treatment method of phosphate compounds and titanium-based compounds, but are not methods for forming a uniform and dense zirconium chemical conversion coat. Particularly, in a method of chemical conversion treatment in which phosphate compounds are used, there is a problem of placing a burden on the environment due to issues of the eutrophication. Additionally, in this method, sludge is formed through a reaction with metal ions in a phosphate treatment bath. Further, in chemical conversion treatment using a titanium-based compound, a high degree of corrosion resistance cannot be attained.

[0006] Further, in International Publication WO 02/103080, there is disclosed a composition for surface treatment, which contains a compound (A) including at least one species of Ti, Zr, Hf and Si, and a fluorine-containing compound (B) as a source of HF, and in which a ratio of the total molar weight A of metal elements of Ti, Zr, Hf and Si in the compound (A) to the molar weight B in converting the total fluorine atoms in the fluorine-containing compound (B) to HF, K=A/B, is within a range from 0.06 to 0.18, andamethodof metal surface treatment, in which a metal surface is contacted with the above-mentioned composition.

[0007] However, in this method, when the chemical conversion treatment is conducted by the electrolysis treatment using a composition for surface treatment, which is formed by dissolving compounds containing fluorine and zirconium, it is difficult to attain an effect of protecting a cathode in applying an electrolysis voltage to a substrate to be treated and a chemical conversion coat, containing a relatively large amount of fluorides and alkali metal compound, is formed since a large amount of and excessive fluorine and alkali metals are present in the solution. Therefore, the corrosion resistance becomes unsatisfactory. Further, a corrosion problem of facilities arises due to a large amount of fluorine.

[0008] In view of the above-mentioned state of the art, it is an obj ect of the present invention to provide a method of metal surface treatment and a surface treated metal thereby, which has excellent corrosion resistance and can form a coat having high corrosion resistance on metal substrates such as iron, zinc, aluminum and magnesium.

[0009] The present invention concerns a method of metal surface treatment comprising

the step of forming a chemical conversion coat on the surface of a metal article to be treated by a chemical conversion treatment reaction by a chemical conversion treatment agent containing a zirconium-containing compound and a fluorine-containing compound,

wherein said chemical conversion treatment reaction is conducted through cathodic electrolysis treatment under the condition that a ratio of weight as the total zirconium metal to weight of the total fluorine (amount of zirconium/amount of fluorine) is adjusted to within 0.2 to 1.0.

[0010] Preferably, the cathodic electrolysis treatment is conducted in conditions that the concentration of the zirconium-containing compound in the chemical conversion treatment agent is adjusted to 10 to 100000 ppm on the zirconium metal equivalent basis,

and a pH of the chemical conversion treatment agent is adjusted to within 1 to 6.

[0011] Preferably, the cathodic electrolysis treatment is conducted in conditions of voltage of 0.1 to 40 V and current density of 0.1 to 30 A/dm^2.

[0012] Preferably, the metal article to be treated is at least one species selected from the group consisting of an aluminum-based substrate, a zinc-based substrate, an iron-based substrate, and a magnesium-based substrate.

[0013] The present invention also concerns a surface treated metal having a chemical conversion coat attained by the method of the present invention.

Detailed description of the invention

[0014] Hereinafter, the present invention will be described in detail.

[0015] The method of metal surface treatment of the present invention is a method in which a chemical conversion coat is formed by treating the metal surface with a chemical conversion treatment agent containing a zirconium-containing compound and a fluorine-containing compound by a cathodic electrolysis technique. When the chemical conversion treatment reaction is conducted through cathodic electrolysis treatment, coats to be obtained will be dense and excellent in uniformity compared with a chemical conversion coat obtained by using electroless treatment. Therefore, there is formed the chemical conversion coat having high corrosion resistance even when an amount of a coat formed is identical to that of the chemical conversion coat obtained by using the electroless treatment.

[0016] When an electrolytic reaction is conducted using the chemical conversion treatment agent containing a zirconium-containing compound and a fluorine-containing compound, it is possible to attain a corrosion resistant chemical conversion coat having extremely excellent corrosion resistance and to attain better corrosion resistance than a chemical conversion coat obtained by the electrolytic reaction of a titanic chemical conversion treatment agent or a phosphate salt chemical conversion treatment agent. Accordingly, this method is expected to be applied to a wide range of uses and preferred.

[0017] When it is done to form a chemical conversion coat on an aluminum-based substrate by electroless treatment using the chemical conversion treatment agent containing a zirconium-containing compound and a fluorine-containing compound, etching of a substrate as expressed by the following reaction equations (1) and (2) occurs at first, and subsequently hydrolysis of fluorozirconium as mainly expressed by the following reaction equations (3) to (5) occurs. Thereby, a zirconium chemical conversion coat is formed.

$$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O \qquad (1)$$

$$2Al + 6H^+ \rightarrow 2Al^{3+} + 3H_2 \qquad (2)$$

$$2Al^{3+} + ZrF_6^{2-} + 3H_2O \rightarrow ZrO(OH)_2 \downarrow + 2AlF_3 + 4H^+ \qquad (3)$$

$$4/3Al^{3+} + ZrF_6^{2-} + H_2O \rightarrow ZrOF_2 \downarrow + 4/3AlF_3 + 2H^+ \qquad (4)$$

$$2Al(OH)_3 + ZrF_6^{2-} \rightarrow (AlO_2OH)_2ZrF_2 \downarrow + 2F^- + 2HF \qquad (5)$$

[0018] That is, when a coat is formed by the electroless treatment, since a chemical conversion coat is formed through the occurrence of reactions shown by the above-mentioned reaction equations (1) to (5), a zirconium chemical conversion coat, which contains relatively much fluorine and has the low corrosion resistance, is formed. On the other hand, when the cathodic electrolysis treatment is conducted using the chemical conversion treatment agent containing a zirconium-containing compound and a fluorine-containing compound, a reaction of generating hydrogen primarily occurs on the metal surface and a cathodic corrosion prevention is applied to a substrate metal. Therefore, the metal surface is not subjected to etching and fluoride of the component metal of the article to be treated is not generated. Accordingly, deposition of a coat containing relatively stable zirconium oxide occurs owing to the hydrolysis of the zirconium complex ion at the vicinity of metal surface, thus a dense and stable protection coat having a low fluorine content is formed. In addition, when the chemical conversion coat is formed on an iron-based substrate or a zinc-based substrate by the cathodic electrolysis treatment using the above-mentioned chemical conversion treatment agent, a coat, in which the amount of fluorine is reduced, can be formed and so it is assumed that the corrosion resistance can be enhanced.

[0019] In addition, when an aluminum-based substrate is surface treated, generally, aluminum ions are accumulated in an equilibrium bath composition. With respect to such a case, in the electroless treatment, a provision for supply water and waste water is required because the accumulation of aluminum of 500 ppm or more inhibits chemical conversion reactivity. On the other hand, in the cathodic electrolysis treatment, since a coat is formed in a state that an amount of etching of aluminum ions is relatively less (an efficiency of conversion to a coat is high) and there is less effect on accumulated aluminum ions, needless supply water and waste water become unnecessary.

[0020] The above-mentioned zirconium-containing compound is not particularly limited as long as it is a compound containing zirconium and for example, fluoro zirconic acid or lithium salt, sodium salt, potassium salt, or ammonium salt thereof, zirconium fluoride and zirconium oxide can be given. These compounds may be used alone or in combination of two or more species.

[0021] The above-mentioned fluorine-containing compound is not particularly limited as long as it is a compound containing fluorine and for example, the above-mentioned zirconium fluoride, hydrofluoric acid, ammonium fluoride, ammonium hydrogenfluoride, sodium fluoride and sodium hydrogenfluoride can be given. These compounds may be used alone or in combination of two or more species.

[0022] In method of metal surface treatment of the present invention, the above-mentioned cathodic electrolysis treatment is preferably conducted in conditions that the concentration of the zirconium-containing compound in the chemical conversion treatment agent is adjusted to 10 ppm as the lower limit and to 100000 ppm as the upper limit on the zirconium metal equivalent basis, : and a pH of the chemical conversion treatment agent is adjusted to 1 as the lower limit and to 6 as the upper limit. By conducting the cathodic electrolysis treatment in conditions adjusted like this, the corrosion resistance can be enhanced because a chemical conversion coat having relatively less fluorine content can be formed.

[0023] In the above-mentioned cathodic electrolysis treatment, as a method of adjusting the above-mentioned concentration of the zirconium-containing compound and the above-mentioned amount of zirconium/amount of fluorine within the above-mentioned specified ranges, there can be given, for example, a method of adjusting the concentration of total zirconium and the concentration of total fluorine in the chemical conversion treatment agent by replenishing the above-mentioned zirconium-containing compound and the fluorine-containing compound in the treatment bath while measuring the concentration of total zirconium and the concentration of total fluorine using an atomic absorption analyzer and using an ion chromatograph, respectively. As a method of adjusting the pH within the above-mentioned specified range, there can be given, for example, a method of adjusting the pH by replenishing nitric acid or ammonium hydroxide in the treatment bath while measuring the pH using a pH meter.

[0024] In the cathodic electrolysis treatment in the present invention, with respect to the chemical conversion treatment agent in the treatment bath, the above concentration of the zirconium-containing compound is preferably adjusted to within a range from 10 ppm as the lower limit to 100000 ppm as the upper limit on the zirconium metal equivalent basis. When the concentration is less than 10 ppm, the corrosion resistance may not be achieved since the zirconium compound is not adequately deposited on the metal surface. When it is more than 100000 ppm, it may be economically disadvantageous since further improvement is not recognized. More preferably, the above-mentioned lower limit is 30 ppm and the above-mentioned upper limit is 5000 ppm.

[0025] In the cathodic electrolysis treatment in the present invention, with respect to the chemical conversion treatment agent in the treatment bath, a ratio of weight as the total zirconium metal (the weight of total zirconium as zirconium metal contained in the chemical conversion treatment agent) to weight of the total fluorine (the weight of total fluorine contained in the chemical conversion treatment agent) (amount of zirconium/amount of fluorine) is adjusted to fall within a range from 0.2 as the lower limit to 1.0 as the upper limit. When the ratio is less than 0.2, the formation of the chemical conversion coat by the cathodic electrolysis treatment may be counteracted since the amount of fluorine becomes excessive. Further the corrosion resistance may be deteriorated since a chemical conversion coat having relatively much fluorine content. When it is more than 1.0, precipitation of metal salt may be occurred since the amount of the total fluorine becomes insufficient. Preferably, the above-mentioned lower limit is 0.25 and the above-mentioned upper limit is 0.8.

[0026] In the cathodic electrolysis treatment in the present invention, with respect to the chemical conversion treatment agent in the treatment bath, the pH is preferably adjusted to within a range from 1 as the lower limit to 6 as the upper limit. When the pH is less than 1, the zirconium compound becomes difficult to deposit, and therefore a sufficient amount of the coat cannot be obtained and the corrosion resistance maybe deteriorated. When it ismore than 6, it is not preferred since a sufficient amount of the coat cannot be obtained. More preferably, the above-mentioned lower limit is 2 and the above-mentioned upper limit is 5.

[0027] In addition to the above-mentioned ingredients, the above-mentioned chemical conversion treatment agent may contain metal ions such as titanium, manganese, silicon, zinc, cerium, iron, molybdenum, vanadium, trivalent chromium, magnesium and the like; another rust prevention materials such as a tannic acid, imidazoles, triazines, triazoles, guanines, hydrazines, biguanide, a phenolic resin, a silane coupling agent, colloidal silica, amines and phosphoric acid; a surfactant; chelator; and the resins.

[0028] In the method of metal surface treatment of the present invention, the above-mentioned cathodic electrolysis treatment conducts electrolysis treatment by using an article to be treated as a cathode.

[0029] With respect to the above-mentioned cathodic electrolysis treatment, its voltage is preferably within a range from 0.1 V as the lower limit to 40 V as the upper limit. When the voltage is less than 0.1 V, the amount of the coat is insufficient; therefore the corrosion resistance may be deteriorated. When it is more than 40 V, effect from increase in the amount of the coat becomes saturated and energy disadvantage may occur. More preferably, the above-mentioned lower limit is 1 V and the above-mentioned upper limit is 30 V.

[0030] With respect to the above-mentioned cathodic electrolysis treatment, its current density is preferably within a range from 0.1 A/dm^2 as the lower limit to 30 A/dm^2 as the upper limit. When the current density is less than 0.1 A/dm^2, the amount of the coat is insufficient; therefore the corrosion resistance may be deteriorated. When it is more than 30 A/dm^2, effect from increase in the amount of the coat becomes saturated and energy disadvantage may occur. More preferably, the above-mentioned lower limit is 0.2 A/dm^2 and the above-mentioned upper limit is 10 A/dm^2.

[0031] A treatment time of the above cathodic electrolysis treatment is preferably 3 seconds as the lower limit and 180 seconds as the upper limit. When the treatment time is less than 3 seconds, the amount of the coat is insufficient; therefore the corrosion resistance may be deteriorated. When it is more than 180 seconds, effect from increase in the amount of the coat becomes saturated and energy disadvantage may occur.

[0032] A treatment temperature of the above cathodic electrolysis treatment is preferably 10°C as the lower limit and 70°C as the upper limit. When the treatment temperature is less than 10°C, the amount of the coat is insufficient; therefore the corrosion resistance may be deteriorated. When it is more than 70°C, effect from increase in the amount of the coat becomes saturated and energy disadvantage may occur. In addition, the lower limit of the treatment temperature is not particularly controlled and the cathodic electrolysis treatment can be conducted at room temperature.

[0033] Material of an electrode used as a counter electrode in the above cathodic electrolysis treatment is not particularly limited as long as the electrode does not dissolve in the above chemical conversion treatment agent and for example, stainless steel, titanium plated with platinum, titanium plated with niobium, carbon, iron, nickel, and zinc can be given.

[0034] As an article to be treated to which the method of metal surface treatment of the present invention can be applied, there can be given an iron-based substrate, an aluminum-based substrate, a zinc-based substrate and a magnesium-based substrate. Iron, aluminum, zinc and magnesium-based substrates refer to an iron-based substrate in which a substrate consists of iron and/or its alloy, an aluminum-based substrate in which a substrate consists of aluminum and/or its alloy, a zinc-based substrate in which a substrate consists of zinc and/or its alloy, and a magnesium-based substrate in which a substrate consists of magnesium and/or its alloy, respectively. Particularly, the method of metal surface treatment of the present invention can also form a chemical conversion coat having sufficient corrosion resistance on an iron-based substrate and a zinc-based substrate, for which conventionally, phosphate salt chemical conversion treatment agents have been usually used because sufficient corrosion resistance could not be attained through zirconium chemical conversion treatment agents. Therefore, it can also be applied to the purpose of dephosphorylation. By applying the method of metal surface treatment of the present invention to the chemical conversion treatment of an article to be treated, consisting of a plurality of substrates of an iron-based substrate, an aluminum-based substrate, a zinc-based substrate and a magnesium-based substrate, the excellent corrosion resistance can be provided for each article to be treated.

[0035] The above-mentioned iron-based substrate is not particularly limited and, for example, a cold-rolled steel sheet and a hot-rolled steel sheet can be given. The above-mentioned aluminum-based substrate is not particularly limited and, for example, 5000 series aluminum alloys and 6000 series aluminum alloys can be given.

[0036] The above-mentioned zinc-based substrate is not particularly limited and, for example, steel sheets, which are plated with zinc or a zinc-based alloy through electroplating, hot dipping and vacuum evaporation coating, such as a galvanized steel sheet, a steel sheet plated with a zinc-nickel alloy, a steel sheet plated with a zinc-iron alloy, a steel sheet plated with a zinc-chromium alloy, a steel sheet plated with a zinc-aluminum alloy, a steel sheet plated with a zinc-titanium alloy, a steel sheet plated with a zinc-magnesium alloy and a steel sheet plated with a zinc-manganese alloy can be given.

[0037] The above-mentioned magnesium-based substrate is not particularly limited and, for example, magnesium metal and magnesium alloys prepared by rolling, die casting or a thixomolding process can be given. The above-mentioned magnesium alloy is not particularly limited and, for example, AZ 31, AZ 91, AZ 91D, AM 60, AM 50 and AZ 31B can be given. By using the above-mentionedmethodof metal surface treatment, iron, aluminum, zinc and magnesium-based substrates can be simultaneously chemical conversion treated.

[0038] An amount of zirconium in the chemical conversion coat formed by the above-mentionedmethodofmetal surface treatment is preferably within a range from 10 mg/m^2 as the lower limit to 300 mg/m^2 as the upper limit. Thereby, the excellent corrosion resistance can be provided. When this amount is less than 10 mg/m^2, the corrosion resistance maybe insufficient. When it is more than 300 mg/m^2, it may be economically disadvantageous since further improvement in the corrosion resistance is not recognized. More preferably, the above-mentioned lower limit is 20 mg/m^2 and the above-mentioned upper limit is 150 mg/m^2.

[0039] The surface of the above-mentioned metal substrate is preferablydegreased, rinsed with water after being degreased, acid cleaned and rinsed with water after acid cleaning before the cathodic electrolysis treatment is conducted using the chemical conversion treatment agent.

[0040] The degreasing is performed to remove an oil matter or a stain adhering to the surface of the substrate and immersion treatment is conducted usually at 30 to 55°C for about several minutes using a degreasing agent such as phosphate-free and nitrogen-free cleaning liquid for degreasing. It is also possible to perform pre-degreasing before degreasing as desired.

[0041] The above-mentioned rinsing with water after degreasing is performed by spraying once or more with a large amount of water for rinsing in order to rinse a degreasing agent after degreasing.

[0042] As the above-mentioned acid cleaning, immersion treatment is conducted usually at 30 to 60°C for about several minutes using, for example, an acid cleaning agent such as sulfuric acid containing an oxidizer or an mixed acid cleaning solution of sulfuric acid and nitric acid. The above-mentioned rinsing after acid cleaning can be conducted using the conventional method publicly known. Rinsing with water may be performed after the cathodic electrolysis treatment.

[0043] The present invention also concerns a surface treated metal having the chemical conversion coat attained by the above-mentioned method of metal surface treatment. The surface treated metal of the present invention exhibits the high corrosion resistance when corrosion resistant primer coating composition such as cation electrocoating compostion, powder coating composition and thermosetting resin-containing coating composition is applied on the above-mentioned chemical conversion coat. Coating, which can be applied to the surface treatedmetal of the present invention, is not particularly limited and the cation electrodeposition coating, the powder coating and roller coating can be conducted. The above-mentioned cation electrodeposition coating is not particularly limited and the conventional cation electrocoating composition publicly known, consisting of aminated epoxy resin, aminated acrylic resin, sulfonated epoxy resin and the like, can be applied.

[0044] Since the method of metal surface treatment of the present invention is a method in which the chemical conversion coat is formed by treating the surface of metal with a chemical conversion treatment agent containing a zirconium-containing compound and a fluorine-containing compound by the cathodic electrolysis technique, treated material having the high corrosion resistance can be attained. And, since the method of metal surface treatment of the present invention can provide the excellent corrosion resistance for all substrates of iron, zinc, aluminum and magnesium-based substrates and does not contain hexavalent chromium, it is also preferred in terms of the environmental protection.

[0045] Particularly, when the cathodic electrolysis treatment is conducted in conditions that the concentration of the zirconium-containing compound in the chemical conversion treatment agent is adjusted to 10 to 100000 ppm on the zirconium metal equivalent basis, a ratio of weight as the total zirconium metal to weight of the total fluorine (amount of zirconium/amount of fluorine) is adjusted to within 0.2 to 1.0 and a pH of the chemical conversion treatment agent is adjusted to within 1 to 6, a chemical conversion coat having relatively less fluorine content is formed, and therefore the corrosion resistance can be more enhanced.

[0046] Since the chemical conversion treatment agent used in the present invention can provide the excellent corrosion resistance even when it does not contain phosphate ions, the method of metal surface treatment of the present invention will not cause environmental issues of the eutrophication or the like and can also suppress the amount of sludge.

[0047] Since the method of metal surface treatment of the present invention is constituted as described above, the corrosion resistance can be more enhanced than the case where the electroless treatment is conducted, or the electrolysis treatment is conducted using a titanic treatment agent or a phosphate treatment agent. Since this method can provide the excellent corrosion resistance for all material such as an iron-based substrate, an aluminum-based substrate, a zinc-based substrate and a magnesium-based substrate, it can also be suitably used to articles to be treated, which consists of a plurality of substrates of an iron-based substrate, an aluminum-based substrate, a zinc-based substrate and a magnesium-based substrate, such as bodies and parts of automobiles. And, the method of the present invention is also a method which places a less burden on the environment and suppresses the formation of sludge.

[0048] The method of metal surface treatment of the present invention can be favorably applied to an article to be treated such as an iron-based substrate, a zinc-based substrate, an aluminum-based substrate and a magnesium-based substrate.

EXAMPLES

[0049] Hereinafter, the present invention will be described in more detail by way of examples, but the present invention is not limited to these examples. In addition, "part(s)" refers to "weight part (s) " and " %" means "weight %" in Examples, unless otherwise specified.

Examples 1 to 13 and Comparative Examples 1 to 7

Preparation of chemical conversion treatment agent

[0050] Chemical conversion treatment agents shown in Tables 1 and 2 were prepared by mixing fluorozirconic acid, ammonium fluorozirconate, fluorotitanic acid and hydrofluoric acid as a zirconium-containing compound and a fluorine-containing compound, phytic acid, aluminum nitrate, phosphoric acid, water-soluble phenol and tannic acid, and adding ion-exchanged water to the mixture.

Preparation of test sheet

[0051] Test sheets having a size of 70 mm × 150 mm × 0.8 mm (A1100 manufactured by Nippon Testpanel Co., Ltd.) were degreased by immersing at 70°C for 30 seconds using a 3% aqueous solution of an alkaline degreasing agent (SURFCLEANER 322N8 manufactured by NIPPON PAINT Co., Ltd.). After rinsing by spraying with running water for 30 seconds, the test sheets were acid-cleaned by immersing at 70°C for 30 seconds using a 25% aqueous solution of an acid cleaning agent (NP Conditioner 2000 manufactured by NIPPON PAINT Co., Ltd.). The test sheets were rinsed by spraying with running water for 30 seconds, and then treated in the prepared chemical conversion treatment agent under conditions shown in Tables 1 and 2 with the counter electrode as the SUS 304 anode by a cathodic electrolysis technique. In addition, the amount of zirconium (mg/m^2) in the coat and the weight ratio of fluorine to zirconium (F/Zr) in the coat were analyzed by using "XRF-1700" (X-ray fluorescence spectrometer manufactured by Shimadzu Corp.).

[0052] In addition, in cathodic electrolysis treatment, treatments conditions were adjusted according to'the following manners in such a way that the concentration of zirconiummetal, a weight ratio of zirconium to fluorine and a pH, in the chemical conversion treatment agent in the treatment bath, became values as shown in Tables 1 and 2.

[0053] The concentration of total zirconium in the chemical conversion treatment agent in the treatment bath was adjusted while being measured using NOVA A330 (an atomic absorption analyzer manufactured by Rigaku Corporation) and the concentration of total fluorine in the chemical conversion treatment agent in a treatment bath was adjusted while being measured using DX-120 (an ion chromatograph manufactured by Nippon Dionex K. K.) , by replenishing ammonium fluorozirconate and hydrofluoric acid in a treatment bath respectively. The pH of the chemical conversion treatment agent in a treatment bath was adjusted by replenishing nitric acid or ammonium hydroxide in the treatment bath while being measured using D-24 (a pH meter manufactured by HORIBA, Ltd.).

Evaluation of physical properties of test sheet

[0054] With respect to the above-mentioned test sheets, corrosion resistance was evaluated by an evaluation method described below.

<Corrosion resistance>

[0055] According to JIS Z 2371, the salt spray tests using 5% salt water (2000 hours) were conducted and the rust-formation rates of the treated sheets were checked after that test. Rust area on the surfaces of the treated sheets was evaluated visually according to the following criteria.

10: no white color rust
9: area with white color rust formed is less than 10%
8: likewise, less than 20%
7: likewise, less than 30%
6: likewise, less than 40%
5: likewise, less than 50%
4: likewise, less than 60%
3: likewise, less than 70%
2: likewise, less than 80%
1: likewise, less than 90%

Table 1

Item		Examples												
		1	2	3	4	5	6	7	8	9	10	11	12	13
Test sheet		A1100												
Treatment agent	Fluorozirconic acid (weight % as zirconium)	0.01	-	-	-	0.01	-	-	-	-	-	-	-	0.01
	Ammonium fluorozirconate (weight % as zirconium)	-	0.1	0.1	0.1	-	0.2	0.01	1.00	0.01	0.01	0.01	0.01	-
	Fluorotitanic acid (weight % as titanium)	-	-	-	-	-	-	-	-	-	-	-	-	-
	Phytic acid (weight %)	-	-	-	-	-	-	-	-	-	-	-	-	-
	Aluminum nitrate (weight % as aluminum)	-	0.1	-	-	-	-	-	-	-	-	-	-	-
	Weight ratio of Zr to F in a treatment agent	0.71	0.78	0.75	0.77	0.81	0.65	0.73	0.71	0.79	0.71	0.69	0.78	0.66
	Phosphoric acid (weight %)	-	-	0.001	-	-	-	-	-	-	-	-	-	-
	Water-soluble phenol (weight %)	-	-	-	0.05	-	-	- -	-	-	-	-	-	-
	Tannic acid (weight %)	-	-	-	-	0.05	-	-	-	-	0.05	-	-	-
Treatment condition	pH	3.5	3.5	3.5	3.5	3.5	4.5	3.5	3.5	3.5	2.0	3.5	3.5	3.5
	Temperature (°C)	50	50	50	50	50	50	50	50	50	50	RT	50	50
	Time (sec)	30	30	30	30	30	30	30	30	30	5	30	15	30
	Electrolysis condition (voltage: V)*	-10	-10	-10	-10	-10	-10	-10	-10	-5	-20	-20	-20	-10
	Electrolysis condition (current density: A/dm^2)*	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5	-0.3	-1.0	-1.0	-1.0	-0.5
Characteristic of a coat	Amount of zirconium in a coat (mg/m^2)	60	72	57	49	55	62	62	73	41	35	36	51	70
	Weight ratio of F/Zr in a coat	0.62	0.65	0.66	0.60	0.64	0.70	0.63	0.60	0.56	0.58	0.63	0.63	0.61
	SST rating (SST for 2000 hours)	8	9	8	8	9	7	8	8	7	7.5	7	9	8.5
*- (minus) indicates cathodic electrolysis treatment. Weight ratio of F/Zr indicates measurements by X-ray fluorescence spectrometer.														

Table 2

Item		Comprative Example						
		1	2	3	4	5	6	7
Test sheet		A1100						
Treatment agent	Fluorozirconic acid (weight % as zirconium)	0.01	0.01	0.01	-	-	-	Phosphate ion 2.1
	Ammonium fluorozirconate (weight % as zirconium)	-	-	-	0.01	-	-	Nitrate ion 2
	Fluorotitanic acid (weight % as titanium)	-	-	-	-	-	0.3	Nickel ion 0.025
	Phytic acid (weight %)	-	-	-	-	-	0.2	Zinc ion 1.7
	Aluminum nitrate (weight % as aluminum)	-	-	-	-	-	-	-
	Weight ratio of Zr to F in a treatment agent	0.11	0.18	0.12	0.14	-	0.17 (Ti/F)	-
	Phosphoric acid (weight %)	-	-	-	-	-	-	-
	Water-soluble phenol (weight %)	-	-	-	-	-	-	-
	Tannic acid (weight %)	-	-	0.05	-	0.05	-	-
Treatment condition	pH	3.5	3.5	2	3	3.5	3.5	2.2
	Temperature (° C)	50	50	50	RT	50	50	40
	Time (sec)	180	30	20	180	30	30	120
	Electrolysis condition (voltage: V)*	-	-	-	-	-10	-10	-10
	Electrolysis condition (current density:A/dm^2)*	-	-	-	-	-0.5	-0.5	-0.5
Characteristic of a coat	Amount of zirconium in a coat (mg/m^2)	58	37	39	35	0	70(Ti)	-
	Weight ratio of F/Zr in a coat	0.87	0.91	0.86	0.82	-	-	-
	SST rating (SST for 2000 hours)	3	2	2	2	1	3	1

*- (minus) indicates cathodic electrolysis treatment. Weight ratio of F/Zr indicates measurements by X-ray fluorescence spectrometer.

[0056] Tables 1 and 2 show that the test sheets obtained by using the electroless treatment (Comparative Examples 1 to 5) were inferior to the test sheets obtained by using the cathodic electrolysis treatment (Examples) in the corrosion resistance. Thereby, it was apparent that the corrosion resistance can be improved by conducting the'cathodic electrolysis treatment to form a coat. And, the test sheet using fluorotitanic acid (Comparative Example 6) was inferior to the test sheet using a chemical conversion treatment agent containing zirconium in the corrosion resistance.

Examples 14 to 21 and Comparative Examples 8 to 11

Preparation of chemical conversion treatment agent

[0057] Chemical conversion treatment agents shown in Table 3 were prepared by mixing fluorozirconic acid as a zirconium-containing compound and a fluorine-containing compound, and nitrate salt as another metal-containing compound, and adding ion-exchanged water to the mixture.

Preparation of test sheet

[0058] SPCC-SD of 70 mm × 150 mm × 0.8mm (manufactured by Nippon Testpanel Co., Ltd.), galvanized steel sheet of 70 mm × 150 mm × 0.8 mm (GA steel sheet, manufactured by Nippon Testpanel Co., Ltd.) and 5182 series aluminum of 70 mm × 150 mm × 0.8 mm (manufactured by Nippon Testpanel Co., Ltd.) were degreased by spraying at 40°C for 2 minutes using a 2% aqueous solution of an alkaline degreasing agent (SURFCLEANER 53 manufactured by NIPPON PAINT Co., Ltd.). After rinsing by spraying with running water for 30 seconds, these metal sheets were treated in the prepared chemical conversion treatment agent under conditions shown in Table 3 with the counter electrode as the SUS 304 anode by a cathodic electrolysis technique. Next, the metal sheets were rinsed by spraying with running water for 30 seconds, and then rinsed by spraying with pure water for 30 seconds. Then, electrocoating was applied to the metal sheets in such a way that a dried film thickness was 20 μm using "POWERNICS 110" (a cation electrocoating paint manufactured by NIPPON PAINT Co., Ltd.) and after rinsing with water, the metal sheets were heated and baked at 170°C for 20 minutes to prepare test sheets.

[0059] The concentration of total zirconium in'the chemical conversion treatment agent in the treatment bath was adjusted while being measured using NOVA A330 (an atomic absorption analyzer manufactured by Rigaku Corporation) and the concentration of total fluorine in the chemical conversion treatment agent in the treatment bath was adjusted while being measured using DX-120 (an ion chromatograph manufactured by Nippon Dionex K.K.), by replenishing ammonium fluorozirconate and hydrofluoric acid in the treatment bath respectively so as to become values as shown in Table 3. The pH of the chemical conversion treatment agent in the treatment bath was adjusted by replenishing nitric acid or ammonium hydroxide in the treatment bath while being measured using D-24 (a pH meter manufactured by HORIBA, Ltd.) so as to become values as shown in Table 3.

Comparative Example 12

Preparation of test sheet

[0060] SPCC-SD of 70 mm × 150 mm × 0.8 mm was degreased by spraying at 40°C for 2 minutes using a 2% aqueous solution of an alkaline degreasing agent (SURFCLEANER 53 manufactured by NIPPON PAINT Co., Ltd.). After rinsing by spraying with running water for 30 seconds, the metal sheet was surface treated at room temperature for 30 seconds using "SURFFINE 5N-8M" (a surface conditioner manufactured by NIPPON PAINT Co., Ltd.) . Then, the metal sheet was treated in "SURFDINE SD-6350" (a chemical conversion treatment agent based on zinc phosphate manufactured by NIPPON PAINT Co., Ltd.) under conditions shown in Table 3 with the counter electrode as the SUS 304 anode by a cathodic electrolysis technique. Next, the metal sheet was rinsed by spraying with running water for 30 seconds, and then rinsed by spraying with pure water for 30 seconds. Then, electrocoating was applied to the metal sheet in such a way that a dried film thickness was 20 μm using "POWERNICS 110" (an electrocoating paint manufactured by NIPPON PAINT Co., Ltd.) and after rinsing with water, the metal sheet was heated and baked at 170°C for 20 minutes to prepare a test sheet.

Comparative Example 13

[0061] A test sheet was prepared by following the same procedure as in Comparative Example 12 except for using electroless treatment in place of cathodic electrolysis treatment.

Evaluation of physical properties of test sheet

<Secondary adhesion test (SDT)>

[0062] With respect to the above-mentioned test sheets, secondary adhesion was evaluated by an evaluation method described below.

[0063] Two parallel lines, which have depth reaching the base material, were cut in a longitudinal direction on the test sheets and then the test sheets were immersed at 50°C for 480 hours in a 5% aqueous solution of NaCl. After immersion, cut portions were peeled off with an adhesive tape and peeling of a coating was observed. Results of observations are shown in Table 3.
O: width of peeling is narrow than 3 mm
×: width of peeling is 3 mm or wider

<sludge>

[0064] After the cold-rolled steel sheet (SPCC-SD), the galvanized steel sheet and the 5182 series aluminum were treated in conditions of their areas of 1 m^2 per liter of the chemical conversion treatment agent, haze in the chemical conversion treatment agents was visually observed.
O: there is not haze
×: there is haze

Table 3

Item		Examples								Comparative Examples					
		14	15	16	17	18	19	20	21	8	9	10	11	12	13
Test sheet		SPC	SPC	SPC	SPC	SPC	SPC	GA	5182	SPC	SPC	GA	5182	SPC	SPC
Treatment agent	Fluorozirconic acid (weight % as zirconium)	0.010	0.010	0.010	0.050	0.100	0.200	0.010	0.010	0.010	0.010	0.010	0.010	SURFDINE SD-6350	SURFDINE SD-6350
	Weight ratio of Zr/F in a treatment agent	0.769	0.769	0.769	0.794	0.769	0.769	0.769	0.769	0.167	0.067	0.063	0.111		
	Magnesium nitrate (weight % as magnesium)	—	0.01	0.01	0.01	0.01	0.01	—	—	—	—	—	—		
	Zinc nitrate (weight % as zinc)	—	0.05	0.05	0.05	0.05	0.05	—	—	—	—	—	—		
	Resin:water-soluble epoxy NV (weight %)	—	—	0.01	—	0.01	—	—	—	—	—	—	—		
Treatment condition	pH	3.5	4.0	4.0	4.3	4.1	3.9	3.5	3.5	3.5	3.5	3.5	3.5	—	—
	Temperature (° C)	40	RT	30	30	30	30	40	40	40	60	60	60	—	—
	Time (sec)	30	60	60	60	60	60	60	60	300	60	60	60	—	—
	Electrolysis condition (voltage: V)*	-10	-20	-15	-25	-20	-10	-10	-10	—	—	—	—	-10	—
	Electrolysis condition (current density:A/dm^2)*	-0.5	-0.8	-0.5	-1.1	-1.0	-0.6	-0.5	-0.5	—	—	—	—	-0.5	—
Characteristic of a coat	Amount of zirconium in a coat (mg/m^2)	60	124	122	128	135	121	133	70	65	29	25	31	—	—
	Weight ratio of F/Zr in a coat	0.70	0.66	0.64	0.59	0.69	0.62	0.65	0.60	0.82	0.88	0.81	0.80	—	—
	SDT	○	○	○	○	○	○	○	○	×	×	×	×	○	○
	Sludge	○	○	○	○	○	○	○	○	○	○	○	○	×	×

* -(minus) indicates cathodic electrolysis treatment.
Weight ratio of F/Zr indicates measurements by X-ray fluorescence spectrometer.

[0065] Table 3 shows that the test sheets obtained by using the electroless treatment (Comparative Examples 8 to 13) had lower adhesion (wider peeling width) than the test sheets obtained by using the cathodic electrolysis treatment

(Examples 14 to 21). Thereby, it became apparent that the adhesion can be improved by conducting the cathodic electrolysis treatment to form a coat. And, in Examples 14 to 18, the formation of sludge was suppressed compared with the cases where the electrolysis treatment was conducted (Comparative Example 12) and the electroless treatment was conducted (Comparative Example 13) using a zinc phosphate treatment agent, respectively.

Examples 22 to 23

Preparation of chemical conversion treatment agent

[0066] Chemical conversion treatment agents shown in Table 4 were prepared by mixing fluorozirconic acid and ammonium fluorozirconate as a zirconium-containing compound and a fluorine-containing compound, and γ-aminopropyltriethoxysilane, and adding ion-exchanged water to the mixture.

Preparation of test-sheet

[0067] Magnesium alloy AZ91D of 70 mm × 150 mm × 2.0 mm obtained by a thixomolding process was degreased by spraying at 50°C for 2 minutes using a 1% aqueous solution of an alkaline degreasing agent (SURF MAGDINE SF120 CLEANER manufactured by NIPPON PAINT Co., Ltd.). After rinsing by spraying with running water for 30 seconds, the metal sheet was acid-cleaned by spraying at 50°C for 2 minutes using a 1% aqueous solution of an acid cleaning agent (SURF MAGDINE SF400 manufactured by NIPPON PAINT Co., Ltd.). After rinsing by spraying with running water for 30 seconds, the metal sheet was acid-cleaned by spraying at 60°C for 5 minutes using a 10% aqueous solution of a desmutting treatment agent (SURF MAGDINE SF300 manufactured by NIPPON PAINT Co., Ltd.). After rinsing by spraying with running water for 30 seconds, the metal sheet was treated in the prepared chemical conversion treatment agent under conditions shown in Table 4 with the counter electrode as the SUS 304 anode by a cathodic electrolysis technique. Next, the metal sheets were rinsed by spraying'with running water for 30 seconds, and then rinsed by spraying with pure water for 30 seconds.

[0068] The concentration of total zirconium in the chemical conversion treatment agent in the treatment bath was adjusted while being measured using NOVA A330 (an atomic absorption analyzer manufactured by Rigaku Corporation) and the concentration of total fluorine in the chemical conversion treatment agent in the treatment bath was adjusted while being measured using DX-120 (an ion chromatograph manufactured by Nippon Dionex K.K.), by replenishing ammonium fluorozirconate and hydrofluoric acid in the treatment bath respectively so as to become values as shown in Table 4. The pH of the chemical conversion treatment agent in the treatment bath was adjusted by replenishing nitric acid or ammonium hydroxide in the treatment bath while being measured using D-24 (a pH meter manufactured by HORIBA, Ltd.) so as to become values as shown in Table 4.

Comparative Example 14

[0069] A test sheet was prepared by following the same procedure as in Example 22 except that immersion treatment was conducted at 50°C for 2 minutes using a 5% aqueous solution of a commercially available manganese phosphate treatment agent (SF572 manufactured by NIPPON PAINT Co., Ltd.) in place of chemical conversion treatment based on cathodic electrolysis treatment.

Comparative Example 15

[0070] A test sheet was prepared by following the same procedure as in Example 22 except that immersion treatment was conducted at 50°C for 2 minutes using a 5% aqueous solution of a commercially available zirconium phosphate treatment agent (ALSURF 440 manufactured by NIPPON PAINT Co., Ltd.) in place of chemical conversion treatment based on cathodic electrolysis treatment.

[0071] With respect to the test sheets obtained in Examples 22 and 23 and Comparative Examples 14 and 15, corrosion resistance was evaluated in a manner as described below.

[0072] The corrosion resistance was evaluated by following the same procedure as in the evaluation in Example 1 except that 48 hours was used as an evaluation time of the corrosion resistance in place of 2000 hours.

Table 4

Mg chemical conversion treatment		Examples		Compar. Ex.	
		22	23	14	15
Test sheet		AZ91D			
Treatment agent	Fluorozirconic acid (weight % as zirconium)	1		SF572	ALSURF440
	Ammonium fluorozirconate (weight % as zirconium)		0.5		
	Weight ratio of Zr/F in a treatment agent	0.77	0.83		
	γ-aminopropyltriethoxysilane (ppm)	100	100		
Treatment condition	pH	3.5	3.5	-	-
	Temperature (° C)	30	30	50°C	50°C
	Time (sec)	30	30	120	120
	Electrolysis condition (voltage: V)*	-10	-10	-	-
	Electrolysis condition (current density:A/dm2) *	1.2	1.0	-	-
Characteristic of a coat	Coat resistance (Ω)	0.1	0.1	0.1	0.1
	SST評点 (SST48h)	10	9	2	2
*- (minus) indicates cathodic electrolysis treatment.					

[0073] Table 4 shows that the test sheets obtained in Examples 22 and 23 were superior to those obtained in Comparative Examples 14 and 15 in corrosion resistance.

Claims

1. A method of metal surface treatment comprising
   the step of forming a chemical conversion coat.on the surface of a metal article to be treated by a chemical conversion treatment reaction by a chemical conversion treatment agent containing a zirconium-containing compound and a fluorine-containing compound,
   wherein said chemical conversion treatment reaction is conducted through cathodic electrolysis treatment under the condition that a ratio of weight as the total zirconium metal to weight of the total fluorine (amount of zirconium/amount of fluorine) is adjusted to within 0.2 to 1.0.

2. The method of metal surface treatment according to Claim 1,
   wherein the cathodic electrolysis treatment is conducted in conditions that the concentration of the zirconium-containing compound in the chemical conversion treatment agent is adjusted to 10 to 100000 ppm on the zirconium metal equivalent basis,
   and a pH of the chemical conversion treatment agent is adjusted to within 1 to 6.

3. The method of metal surface treatment according to Claim 1 or 2,
   wherein the cathodic electrolysis treatment is conducted in conditions of voltage of 0.1 to 40 V and current density of 0.1 to 30 A/dm^2.

4. The method of metal surface treatment according to any of Claims 1 to 3,
   wherein the metal article to be treated is at least one species selected from the group consisting of an aluminum-based substrate, a zinc-based substrate, an iron-based substrate, and a magnesium-based substrate.

Patentansprüche

1. Verfahren zur Behandlung einer Metalloberfläche, umfassend den Schritt der Bildung einer chemischen Umwandlungsbeschichtung auf der Oberfläche eines zu behandelnden Metallgegenstands durch eine chemische Umwandlungsbehandlungsreaktion durch ein chemisches Umwandlungsmittel, umfassend eine zirkoniumhaltige Verbindung und eine fluorhaltige Verbindung, worin die chemische Umwandlungsbehandlungsreaktion durch kathodische Elektrolysebehandlung unter der Bedingung durchgeführt wird, daß das Verhältnis des Gewichts als gesamtes Zirkoniummetall zum Gewicht des gesamten Fluors (Menge an Zirkonium/Menge an Fluor) auf den Bereich von 0,2 bis 1,0 eingestellt wird.

2. Verfahren zur Behandlung einer Metalloberfläche gemäß Anspruch 1, worin die kathodische Elektrolysebehandlung unter Bedingungen durchgeführt wird, daß die Konzentration der zirkoniumhaltigen Verbindung in dem chemischen Umwandlungsbehandlungsmittel auf 10 bis 100.000 ppm auf der Basis von Zirkoniummetalläquivalenten eingestellt wird und der pH des chemischen Umwandlungsmittels auf 1 bis 6 eingestellt wird.

3. Verfahren zur Behandlung einer Metalloberfläche gemäß Anspruch 1 oder 2, worin die kathodische Elektrolysebehandlung bei einer Spannung von 0,1 bis 40 V und einer Stromdichte von 0,1 bis 30 A/dm^2 durchgeführt wird.

4. Verfahren zur Behandlung einer Metalloberfläche gemäß einem der Ansprüche 1 bis 3, worin der zu behandelnde Metallgegenstand zumindest eine Spezies ist, ausgewählt aus der Gruppe bestehend aus einem Substrat auf Aluminiumbasis, einem Substrat auf Zinkbasis, einem Substrat auf Eisenbasis und einem Substrat auf Magnesiumbasis.

Revendications

1. Procédé de traitement d'une surface métallique comprenant
l'étape de formation d'un enduit de conversion chimique sur la surface d'un article métallique à traiter par une réaction de traitement de conversion chimique par un agent de traitement de conversion chimique contenant un composé contenant du zirconium et un composé contenant du fluor,
dans lequel ladite réaction de traitement de conversion chimique est réalisée par l'intermédiaire d'un traitement d'électrolyse cathodique dans des conditions dans lesquelles un rapport du poids, en zirconium métallique total, au poids du fluor total (quantité de zirconium/quantité de fluor) est ajusté dans la gamme de 0,2 à 1,0.

2. Procédé de traitement d'une surface métallique selon la revendication 1,
dans lequel le traitement d'électrolyse cathodique est réalisé dans des conditions dans lesquelles la concentration du composé contenant du zirconium dans l'agent de traitement de conversion chimique est ajustée dans la gamme de 10 à 100 000 ppm, sur une base d'équivalent de zirconium métallique,
et le pH de l'agent de traitement de conversion chimique est ajusté dans la gamme de 1 à 6.

3. Procédé de traitement d'une surface métallique selon la revendication 1 ou 2,
dans lequel le traitement d'électrolyse cathodique est réalisé dans des conditions de tension de 0,1 à 40 V et de densité de courant de 0,1 à 30 A/dm^2.

4. Procédé de traitement d'une surface métallique selon l'une quelconque des revendications 1 à 3,
dans lequel l'article à traiter est au moins un élément choisi dans le groupe constitué par un substrat à base d'aluminium, un substrat à base de zinc, un substrat à base de fer et un substrat à base de magnésium.