



(12) **EUROPEAN PATENT APPLICATION**

(21) Application number : **93302582.7**

(51) Int. Cl.⁵ : **C23C 22/36**

(22) Date of filing : **01.04.93**

(30) Priority : **03.04.92 JP 82509/92**

(43) Date of publication of application :
06.10.93 Bulletin 93/40

(84) Designated Contracting States :
DE FR GB

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(54) **Method for zinc-phosphating metal surface to be treated by the cationic electrodeposition coating.**

(57) By using a zinc-phosphating solution, which does not contain a nickel ion, but contains 0.1 to 4 g/l of a cobalt ion, 0.1 to 3 g/l of a manganese ion, a phosphating accelerator, 200 to 500 mg/l of a simple fluoride compound in terms of HF concentration and a complex fluoride compound in a mole ratio of 0.01 to 0.5 relative to the simple fluoride compound, a zinc phosphate coating film suitable for cationic electrodeposition coating and superior in coating film adhesiveness and corrosion resistance, especially in warm brine resistance and scab resistance, is formed on the metal surface simultaneously having an iron-based, a zinc-based and an aluminum-based surface by using an identical solution.

BACKGROUND OF THE INVENTION

The present invention relates to a conversion treating method for forming a zinc phosphate coating film on a metal surface. In detail, the invention relates to a treating method for forming a zinc phosphate coating film which does not contain any nickel ions, because of its recent trend in use to be limited according to environmental regulation, and which is suitable for cationic electrodeposition coating and superior in coating film adhesion and corrosion resistance, especially warm brine resistance and a property to prevent rust of a scab type (scab corrosion) (hereinafter, this property is referred to as "scab resistance") on a metal surface simultaneously having an iron-based, a zinc-based and an aluminum-based surface.

Metal materials have been used in various fields such as automobile bodies and other attachments, building materials, furniture, and the like. Metal is treated with zinc phosphate as coating pretreatment in order to prevent the metal from corrosion caused by oxygen or sulfur oxides in the air, rainwater, seawater, and so forth. A zinc phosphate coating film formed by this treatment is required to be superior in adhesion to a metal surface substrate, and also, to be superior in adhesion to a coating film further formed on the zinc phosphate coating film (secondary adhesion) and also, the zinc phosphate coating film is required to have sufficient rust preventability even if it is under corrosive environment. In particular, for an automobile body, the scab resistance, a high order of warm brine resistance and so on are desired since the body is repeatedly subjected to permeation of salt water or variation of dry and wet atmospheric conditions from a scar of the external plate part.

Recently, there has been increased a case of zinc phosphating a metallic material having two or more kinds of metal surfaces. For example, to elevate further the corrosion resistance of after-coating for the automobile body, a material plated by zinc or a zinc alloy is used on a surface of a steel material. If conventional zinc-phosphating is carried out on such a metal surface simultaneously having both of an iron-based and a zinc-based surfaces, the zinc-based surface is inferior in corrosion resistance and secondary adhesion (adhesion after aging test) compared with the iron-based surface.

A zinc phosphate coating film formed on a metal surface does not consist of only zinc phosphate, but contains various kinds of metal components besides zinc to elevate corrosion resistance. Especially, to obtain a zinc phosphate coating film superior in scab resistance and warm brine resistance, the zinc phosphate coating film has contained nickel as an essential component.

On the other hand, a method for forming a zinc phosphate coating film suitable for cationic electrodeposition coating on a surface of a metal material having two or more kinds of metal surfaces (for example, a metal surface simultaneously having both of an iron-based surface such as a steel sheet as well as a zinc-based surface such as a material made by plating a surface of a steel sheet with zinc or a zinc alloy) by zinc phosphating the metal surfaces using an acidic zinc phosphating solution which does not contain nickel as an essential component. In the zinc-phosphating method described in Japanese Official Patent Provisional Publication No. showa 57-152472, an acidic zinc-phosphating solution containing 0.5 to 1.5 g/l of a zinc ion, 1 to 30 g/l of a phosphate ion, 0.6 to 3 g/l of a manganese ion, and a coating film-converting accelerator as main components is used. In the zinc-phosphating method described in Japanese Official Patent Gazette No. showa 61-36588, an acidic zinc-phosphating solution containing 0.5 to 1.5 g/l of a zinc ion, 5 to 30 g/l of a phosphate ion, 0.6 to 3 g/l of a manganese ion, 0.05 g/l or more of a fluorine ion, and a coating film-converting accelerator as main components is used in order to form a further superior coating film on a metal surface simultaneously having both of an iron-based and a zinc-based surface and to lower a treating temperature. If necessary, the two kinds of phosphating solutions cited here contains 0.1 to 4 g/l of a nickel ion to elevate further the secondary adhesion and corrosion resistance compared with the case of using a manganese ion alone.

A material made by combining an aluminum material with at least one of an iron material and a zinc material also has been practically used in various fields such as automobiles, building materials and so forth. It is desired to form a coating film having superior adhesion and high corrosion resistance on these metal surfaces by conversion treatment of the surfaces with the same zinc phosphating solution.

There has been increased a case of forming a zinc phosphate coating film on a metal surface simultaneously having an iron-based, a zinc-based and an aluminum-based surfaces.

In recent years, environmental regulation has tended to become strict and, because of this, use of nickel necessary for forming a zinc phosphate coating film superior in scab resistance and warm brine resistance has tended to be limited. However, the zinc phosphating treatments described in the above two publications, if they do not comprise use of a nickel ion, forms zinc phosphate coating films of low performance as mentioned above and, therefore, the treatments require to use a nickel ion in order to elevate the performance and, although applicable to the iron-based and zinc-based surfaces, so, they have no effect on the aluminum-based surface,

At present, there is no method for forming, on a metal surface comprising all of the iron-based, zinc-based and aluminum-based surface, a zinc phosphate coating film which is suitable for cationic electrodeposition

coating and superior in film adhesion and corrosion resistance, by using a zinc-phosphating solution not containing a nickel ion.

Accordingly, it is an object to provide a treating method for forming a zinc phosphate coating film which is suitable for cationic electrodeposition coating and superior in coating film adhesion and corrosion resistance, especially warm brine resistance, scab resistance, by using a zinc-phosphating solution which does not contain nickel because of its limitation in use according to environmental regulation, and which is capable of treating a metal surface simultaneously having an iron-based, a zinc based and an aluminum-based surface with an identical solution.

To solve the object, the present invention provides a method for zinc-phosphating a metal surface to be treated by the cationic electrodeposition coating, which comprises bringing a metal surface having all of an iron-based, a zinc-based and an aluminum-based surface in contact with an acidic zinc-phosphating solution to make a zinc phosphate coating film; said method is characterized in that the acidic zinc phosphate solution does not contain a nickel ion, but 0.1 to 4 g/liter of a cobalt ion, 0.1 to 3 g/liter of a manganese ion, a coating film-converting accelerator (a), 200 to 500 mg/liter of a simple fluoride compound in terms of HF concentration, and a complex fluoride in a mole ratio of 0.01 to 0.5 relative to the simple fluoride compound.

A metal material to be treated with the zinc-phosphating method of this invention is a metal surface simultaneously having an iron-based, a zinc based and an aluminum-based surfaces.

The cobalt ion concentration of the acidic zinc phosphating solution is in a range of from 0.1 to 4 g/l and preferably in a range of from 0.3 to 3 g/l. If the cobalt ion concentration is less than 0.1 g/l, an elevating effect on the corrosion resistance becomes insufficient. If it exceeds 4 g/l, an elevating effect on the corrosion resistance decreases. The manganese ion concentration is in a range of from 0.1 to 3 g/l and preferably in a range of from 0.3 to 3 g/l. If it is less than 0.1 g/l, the adhesion a zinc-based surface and an elevating effect on the warm brine resistance become insufficient. If it exceeds 3 g/l, further increased effect than that in this invention be expected and it is economically disadvantageous.

The concentration of a simple fluoride compound in the acidic zinc-phosphating solution in this invention should be adjusted in a range of 200 to 500 mg/l in terms of HF and preferably in a range of from 250 to 500 mg/l. If it is less than 200 mg/l, the aluminum ion concentration in the treating solution increases due to formation of a water-soluble complex fluoride compound, and deterioration of the conversion treating occurs. If it exceeds 500 mg/l, zinc phosphate coating film formed on an aluminum-based surface is contaminated with Na_3AlF_6 and warm brine resistance of the cationic electrodeposition coating film deteriorates.

A complex fluoride compound contained in the acidic zinc-phosphating solution must be adjusted so that the mole ratio relative to simple fluoride concentration in terms of HF is satisfactory for the following equation (1).

$$0.01 \leq (\text{complex compound})/(\text{simple compound}) \leq 0.5 \quad (1)$$

The amount of the complex fluoride compound in the equation 1 does not comprise the complex fluoride containing aluminum. If the mole ratio of complex fluoride to simple fluoride exceeds 0.5, eluted aluminum ions form a water-soluble complex and the aluminum ion concentration in the treating solution increases and, accompanying with these, deterioration of conversion occurs. Also, even if a water-insoluble complex is formed, because of its having floating and suspending characters, the removal by filtration of precipitate becomes difficult, and it makes a reason of inferior electrodeposition coating (for example, uniformity lack in the coating film and deterioration in the corrosion resistance of a coating film) by its attaching with a matter to be treated. If the above molar ratio is less than 0.01, Na_3AlF_6 is mingled in a zinc phosphate coating film formed on an aluminum-based surface and the warm brine resistance of the coating film formed by the cationic electrodeposition coating decreases.

Though the concentration of a simple fluoride compound in terms of HF in an acidic zinc-phosphating solution can be measured by a commercially available silicon electrode meter or fluorine ion meter, it is preferable to control the concentration by measuring the active fluorine concentration using a silicon electrode meter. The concentration is preferably controlled so as to be in a range of from 15 to 130 μA in a value indicated by the silicon electrode meter, more preferably in a range of 40 to 140 μA . The silicon electrode meter shows high sensitivity in the pH region of an acidic zinc-phosphating solution used in this invention (an acidic region, preferably $\text{pH} \leq 4$) and has such advantage as the indicated value becomes large in proportion to the active fluorine concentration. If the indicated value is less than 15 μA , an uniform zinc phosphate coating film is not formed on an aluminum-based surface and also, because aluminum ions dissolved into a treating solution form a water-soluble fluoride complex, the aluminum ion concentration in the treating solution increased and, accompanying with this, the conversion deterioration occurs. If the indicated value exceeds 130 μA , the zinc phosphate coating film formed on an aluminum-based surface is contaminated with Na_3AlF_6 component and the warm brine resistance of the electrocoating film decreases. A silicon electrode meter described above is, for example, the one disclosed in Japanese Official Patent Gazette, showa 42-17632, but not limited to this

type. The silicon electrode meter is commercially available with the trade name of product of Surfproguard 101N made by Nippon Paint Co., Ltd. and easily obtainable. A silicon electrode meter is generally arranged so as to read an electric current value by bringing a p-type silicon electrode and an inactive electrode made of platinum in contact with a solution to be measured under a condition where the solution is not in light and by connecting a direct current source between both of these electrodes. The solution to be measured is arranged so as to be at a stationary state or to be in a constant current. Then, under these conditions a direct current is impressed between both the electrodes, so that the active fluorine concentration is known by reading an electric current when it becomes a steady state.

As a simple fluoride, for example, HF, NaF, KF, NH_4F , NaHF_2 , KHF_2 and NH_4HF_2 and so on are used. As a fluoride complex, for example, H_2SiF_6 , HBF_4 , and these metal salts such as a nickel salt and a zinc salt and so on are used.

In the main components in the acidic zinc-phosphating solution used in this invention, components other than a cobalt ion, a manganese ion, a simple fluoride compound and a complex fluoride compound are, for example, a zinc ion, a phosphate ion and the accelerator for converting a coating film.

As the accelerator for converting a coating film (a) is used at least one kind selected from a nitrite ion, a meta-nitrobenzenesulfonate ion, and hydrogen peroxide. Their preferable concentrations are as follows: 0.1 to 2.0 (0.3 to 1.5) g/l for a zinc ion, 5 to 40 (10 to 30) g/l for a phosphate ion, 0.01 to 0.5 (0.01 to 0.4) g/l for a nitrite ion, 0.05 to 5 (0.1 to 4) g/l for a m-nitrobenzenesulfonate ion, and 0.5 to 10 g/l for hydrogen peroxide on a basis converted into 100 % H_2O_2 . Values in parentheses are more preferable concentrations.

If the zinc ion concentration is less than 0.1 g/l, a uniform zinc phosphate coating film does not form on a metal surface. Lack of hiding is much and, a coating film of a blue color type in part sometimes forms. Also, if the zinc ion concentration exceeds 2.0 g/l, a uniform zinc phosphate coating film is formed, but the coating film is apt to dissolve easily in an alkali and, especially under an alkali atmosphere where the film is exposed during a cationic electrodeposition process, the coating film sometimes easily dissolves. As a result, the warm brine resistance generally lowers and, especially in a case of treating an iron-based surface, the scab resistance deteriorates, and thus, desired properties are not obtained.

Therefore, it is not suitable as a substrate for electrodeposition coating, especially for cationic electrodeposition coating.

If the phosphate ion concentration is less than 5 g/l, a non-uniform coating film is apt to be formed. If it exceeds 40 g/l, elevation of effects can not be expected and the amount of using drugs becomes large leading to an economical disadvantage.

When the concentration of an accelerator for converting a coating film (a) is lower than the forementioned range, sufficient coating film-conversion is not possible on an iron-based surface and yellow rust is easily formed. If the concentration exceeds the range, a non-uniform coating film of a blue color type is easily formed on an iron-based surface.

Also, the zinc-phosphating solution used in this invention is desired to contain one or more kinds selected from magnesium ion, calcium ion and copper ion in a specially defined concentration range besides the main components described above.

A preferable range of the magnesium ion is from 0.01 to 3 g/l and a more preferable one is from 0.1 to 2.5 g/l. If the ion is less than 0.01 g/l, an effect upon elevating the corrosion resistance becomes insufficient and if it exceeds 3 g/l, there is a trend that the effect upon elevating the corrosion-resistance decreases. The calcium ion prefers to be in a range of from 0.01 to 3 g/l and more prefers to be in a range from 0.1 to 2.5 g/l. If it is less than 0.01 g/l, the effect on elevating the corrosion resistance becomes insufficient and if it exceeds 3 g/l, there is a trend that the effect upon elevating the corrosion-resistance decreases. The copper ion prefers to be in a range from 0.005 to 0.2 g/l and more prefers to be in a range from 0.01 to 0.1 g/l. If it is less than 0.005 g/l, the effect upon elevating the corrosion-resistance becomes insufficient and if it exceeds 0.2 g/l, there is a trend that the scab resistance elevates, but the effect upon elevating the warm brine resistance decreases.

The zinc-phosphate treating solution used in this invention prefers to contain a sulfuric acid ion. It is desirable to contain a sulfuric acid ion so that the mole ratio of a sulfuric acid ion to a cobalt ion is in the range from 0.1 to 2. If this ratio is less than 0.1, the effect on the improvement of scab resistance is insufficient and if exceeds 2, there is a trend that the effect on the improvement of scab resistance decreases.

Furthermore, if necessary, the zinc phosphating solution used in this invention may contain an accelerator for converting a coating film (b). As the accelerator for converting a coating film (b) is cited, for example, a nitrate ion and a chlorate ion and so forth. The nitrate ion prefers to be in a range from 0.1 to 15 g/l and more prefers to be in a range from 2.0 to 10 g/l. The chlorate ion prefers to be in a range from 0.05 to 2.0 g/l and more prefers to be in a range from 0.2 to 1.5 g/l. These components may be contained alone or in combination of two or more kinds. The accelerator for converting a coating film (b) may be used in combination with the accelerator for converting a coating film (a) or without combination with this (a).

As a supplying source of the aforementioned components are used the following compounds.

Zinc ion

5 Zinc oxide, zinc carbonate and zinc nitrate, etc.

Phosphate ion

10 Phosphoric acid, zinc phosphate, manganese phosphate and cobalt phosphate, etc.

Cobalt ion

Cobalt nitrate, cobalt sulfate, cobalt phosphate, cobalt hydroxide, cobalt chloride and cobalt fluoride, etc.

15 Manganese ion

Manganese carbonate, manganese nitrate, manganese chloride, manganese phosphate, and manganese sulfate, etc.

20 Accelerator for converting coating film (a)

Nitrous acid, sodium nitrite, ammonium nitrite, sodium meta-nitrobenzenesulfonate, and hydrogen peroxide, etc.

25 Magnesium ion

Magnesium nitrate, magnesium sulfonate, magnesium phosphate, magnesium fluoride, magnesium hydroxide and magnesium carbonate, etc.

30 Calcium ion

Calcium nitrate, calcium sulfate, calcium phosphate, calcium fluoride, calcium carbonate, calcium hydroxide and calcium chloride, etc.

35 Copper ion

Copper nitrate, copper chloride and copper sulfate, etc.

Accelerator for converting coating film (b)

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Sodium chlorate, ammonium chlorate, nitric acid, sodium nitrate, ammonium nitrate, zinc nitrate, manganese nitrate, cobalt nitrate, calcium nitrate, magnesium nitrate, and copper nitrate, etc.

Sulfate ion

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Sulfuric acid and the aforementioned metal salts of sulfuric acid.

In performing the zinc-phosphating process of this invention is performed, temperature of the phosphating solution prefers to be in a range of from 20 to 70 °C and more prefers a range of from 35 to 60°C. If it is lower than 20 °C, the coating film-converting is insufficient and it consumes a long time to complete the processing. Also, if it is higher than 70°C, balance of the phosphating solution is easily broken due to the decomposition of an accelerator for converting a coating film and a precipitate formation in the phosphating solution, so that it is difficult to obtain a good coating film.

50 A preferable time for treating with zinc phosphating solution is 15 seconds or more and a more preferable one is in a range of from 30 to 120 seconds. If it is less than 15 seconds, there is a case where a coating film having desired crystals is not sufficiently formed. Furthermore, in a case where an article having a complicate structure such as an automobile body is treated, it is practically preferred to combine the immersing treatment with the spraying treatment, and in this case, an article is at first subjected to the immersing treatment for 15 seconds or more, preferably, for a period of from 30 to 120 seconds and then to the spraying treatment for 2

seconds or more, preferably, for a period of from 5 to 45 seconds. Besides, to wash off sludge attached in the course of immersing treatment, it is preferable to carry out the spraying treatment as long as possible. Accordingly, a method for treating with zinc phosphate of this invention includes the immersing treatment and spraying treatment as well as treating embodiment made by combining those treatments.

A zinc phosphate coating film is formed on a metal surface simultaneously having an iron-based, a zinc-based and an aluminum-based surface by bringing it in contact with an acidic zinc-phosphating solution containing 0.1 to 4 g/l of a cobalt ion, 0.1 to 3 g/l of a manganese ion, the phosphating accelerator (a), 200 to 500 mg/l of a simple fluoride compound in terms of HF concentration, and a fluoride complex compound in 0.01 to 0.5 mole ratio relative to the simple fluoride. Thus, the coating film with conversion superior in adhesiveness and corrosion resistance after the cationic electrodeposition coating is obtained even using the zinc-phosphating solution not containing a nickel ion.

According to the present invention, an identical zinc-phosphating solution not containing nickel, use of which suffers limitation according to environmental regulation, can be applied to a metal surface simultaneously having an iron-based, a zinc-based and an aluminum-based surface, and a zinc phosphate coating film suitable for cationic electrodeposition coating and superior in film adhesiveness and corrosion resistance, especially in warm brine resistance and scab resistance can be formed.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, practical examples and comparative examples in the present invention are shown, but the present invention is not limited to the undermentioned examples.

Practical Examples 1 to 9 and Comparative Examples 1 to 7

(1) Metal to be treated and treating area ratio

(A)Cold rolled steel sheet (iron-based surface)	20%
(B)Alloyed melt zinc-plated steel sheet (zinc-based surface)	50%
(C)Aluminum-magnesium alloy sheet (aluminum-based surface)	30%
total area 0.07 m ² per treatment	

(2)Treating solution

An aqueous acidic zinc phosphating solution having compositions shown in Table 1 and 2 was used. The volume 5 l of the solution was used for the treatments.

Table 1

	Example								
	1	2	3	4	5	6	7	8	9
Zn ion (g/l)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
PO ₄ ion (g/l)	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Co ion (g/l)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.5	2.0
Mn ion (g/l)	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Ni ion (g/l)	—	—	—	—	—	—	—	—	—
Mg ion (g/l)	—	—	0.6	—	—	—	—	—	—
Ca ion (g/l)	—	—	—	0.5	—	—	—	—	—
Cu ion (g/l)	—	—	—	—	0.01	—	—	—	—
SO ₄ ion (g/l)	—	—	—	—	—	2.0	—	—	—
HF (mg/l)	* 300	250	* 500	300	300	300	300	300	300
H ₂ SiF ₆ (mg/l)	500	800	200	500	500	500	500	500	500
NO ₂ ion (g/l)	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
NO ₃ ion (g/l)	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Total acidity (point)	19.8	20.6	19.5	21.5	20.7	19.9	23.8	19.4	21.0
Acidity of free acid (point)	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Complex fluoride									
Simple fluoride (mole ratio)	0.23	0.44	0.06	0.23	0.23	0.23	0.23	0.23	0.23

Footnote 1;

*: The concentration of NH_4HF_2 is shown in terms of HF concentration. The concentration of NH_4HF_2 in example 1 was 430 mg/l and that in example 3 was 710 mg/l.

Footnote 2;

In example 7, (Sulfate ion):(cobalt ion)=1.23 : 1

Table 2

	Comparative example						
	1	2	3	4	5	6	7
Zn ion (g/l)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
PO ₄ ion (g/l)	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Co ion (g/l)	1.0	1.0	1.0	1.0	—	0.6	—
Mn ion (g/l)	0.6	0.6	0.6	—	0.6	0.6	0.6
Ni ion (g/l)	—	—	—	—	—	—	1.0
Mg ion (g/l)	—	—	—	—	—	0.2	—
Ca ion (g/l)	—	—	—	—	—	0.3	—
Cu ion (g/l)	—	—	—	—	—	—	—
SO ₄ ion (g/l)	—	—	—	—	—	—	—
HF (mg/l)	—	300	600	300	300	—	300
H ₂ SiF ₆ (mg/l)	500	1500	500	500	500	—	500
NO ₂ ion (g/l)	0.09	0.09	0.09	0.09	0.09	0.09	0.09
NO ₃ ion (g/l)	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Total acidity (point)	19.8	21.3	19.9	19.2	18.8	19.9	20.0
Acidity of free acid (point)	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Complex fluoride Simple fluoride (mole ratio)	—	0.69	0.11	0.23	0.23	—	0.23

(3) Treating process

Coated metal sheets were obtained by treating three kinds of the above-described metal with the following processes, (a)degreasing, (b)rinsing, (c)surface-conditioning, (d)phosphating (dipping process) (e)rinsing, (f)rinsing with pure water, (g)drying and (h)coating in this sequence.

Furthermore, in the conversion process (d) there were investigated the coating film conversion at an initial stage (when the first zinc-phosphating was carried out) and at a time passage (when the 150th zinc-phosphating was carried out), the aluminum ion concentration at an equilibrium, and properties of the sludge containing aluminum ions. Results obtained are shown in Tables 3 and 4.

Table 3

	Example								
	1	2	3	4	5	6	7	8	9
Simple fluoride (mg/l)	300	250	500	300	300	300	300	300	300
Complex fluoride (mg/l)	500	800	200	500	500	500	500	500	500
Complex fluoride / Simple fluoride (mole ratio)	0.23	0.44	0.06	0.23	0.23	0.23	0.23	0.23	0.23
Current (silicon electrode meter) (μA)	35	20	130	35	35	35	35	35	35
Film appearance (at an initial stage)	Aluminum	Aluminum	Aluminum	Aluminum	Aluminum	Aluminum	Aluminum	Aluminum	Aluminum
	iron zinc	iron zinc	iron zinc	iron zinc	iron zinc	iron zinc	iron zinc	iron zinc	iron zinc
Film appearance (at the 150th treatment)	Aluminum	Aluminum	Aluminum	Aluminum	Aluminum	Aluminum	Aluminum	Aluminum	Aluminum
	iron zinc	iron zinc	iron zinc	iron zinc	iron zinc	iron zinc	iron zinc	iron zinc	iron zinc
Aluminum ion concentration at equilibrium (mg/l)	25	35	15	25	25	30	30	25	25
Properties of sludge containing Aluminum ion	Aluminum ion	Aluminum ion	Aluminum ion	Aluminum ion	Aluminum ion	Aluminum ion	Aluminum ion	Aluminum ion	Aluminum ion

Table 4

		Comparative example						
		1	2	3	4	5	6	7
Control of fluoride concentration	Simple fluoride (mg/l)	—	300	600	300	300	—	300
	Complex fluoride (mg/l)	500	1500	500	500	500	—	500
	Complex fluoride							
	Simple fluoride (mole ratio)		0.69	0.11	0.23	0.23	—	0.23
	Current (silicon electrode meter) (μA)	—	35	180	35	35	—	35
Film Appearance (at an initial stage)	Aluminum	⊙	⊙	×	⊙	⊙	×	⊙
	iron zinc	⊙	⊙	○	⊙	⊙	○	⊙
Film appearance (at the 150th treatment)	Aluminum	×	×	×	⊙	⊙	×	⊙
	iron zinc	×	○	○	⊙	⊙	×	⊙
Aluminum ion concentration at equilibrium (mg/l)		300<	150<	10	30	30	10	25
Properties of sludge containing aluminum ion		×	×	⊙	⊙	⊙	×	⊙

(Evaluation of the coating film conversion)

5 ⊙:An uniform zinc phosphate coating film with fine crystals
was formed.

○:An uniform zinc phosphate coating film was formed.

10 ×:A coating film without uniformity was formed including
a case where the Na_3AlF_6 contaminant was mixed or the
coating film was not formed at all.

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(Evaluation of properties of the sludge containing an
aluminum ion)

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⊙:highly precipitating

○:precipitating

25 ×:floating and suspending

(4)Treating condition

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(a)Degreasing

Using a 2 % by weight aqueous solution of an alkaline degreasing agent (Surf Cleaner SD 250, made by Nippon Paint Co., Ltd.), a metal to be treated was immersed at 40 °C for 2 minutes. Then the reaction in the bath was controlled by maintaining alkalinity at an initial value, which was shown a milliliter amount of a 0.1 N NaOH solution required for neutralizing a 10 ml of the bath using bromophenolblue as an indicator. Surf Cleaner SD 250 was used as a supplementary reagent.

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(b)Rinsing

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Tap water was used with spraying by water pressure.

(c)Surface-conditioning

Using a 0.1 % by weight aqueous solution of a surface conditioner (Surf Fine 5N-5, made by Nippon Paint Co., Ltd.), a metal to be treated was immersed at room temperature for 15 seconds in the solution. The bath control was performed by adding Surf Fine 5N-5 to maintain the alkalinity.

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(d)Conversion (dipping treatment)

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Using a zinc phosphating solution described above, all metals to be treated were immersed at 40°C for 2 minutes. The bath control was performed by maintaining the concentration of each ion composition and the free acidity (which is shown by a milliliter number of a 0.1N-NaOH solution required for neutralizing a 10 ml of the bath using bromophenolblue as an indicator) at an initial value.

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To maintain each concentration of the Zn, PO_4 , Co, Mn and NO_3 ions and the complex fluoride, a concentrated solution for supplement A, which contains zinc oxide, phosphoric acid, cobalt nitrate, manganese carbonate, hydrosilicofluoric acid and nitric acid corresponding to each of the above ions was used. To maintain the concentration of a NO_2 ion, a concentrated solution for supplement B was used. Supplement C which con-

tains sodium hydrogen fluoride (NaHF_2) was used to control the simple fluoride concentration in terms of HF by an active fluorine concentration using a silicon electrode meter.

(e)Rinsing

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Using tap water, this was carried out at a room temperature for 15 minutes.

(f)Rinsing with pure water

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Using ion-exchanged water, this was carried out at room temperature for 15 seconds.

(g)Drying

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This was carried out at 100°C for 10 minutes.

(h)Coating

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A cationic electrodeposition coating reagent, Power Top U-1000 made by Nippon Paint Co., Ltd. was coated in film thickness of 30 μm by a cationic electrodeposition coating in the usual way. On this coated film, an intermediate coated film having 30 μm in film thickness was formed by coating an melamine alkyd intermediate coat made by Nippon Paint Co., Ltd. in the usual way. By coating a melamine alkyd-based top coating reagent made by Nippon Paint Co., Ltd in an usual way, a top coat film was formed in film thickness of 40 μm on the intermediate coated film.

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For a metal sheet treated with a 150th zinc-phosphating, the coated film was examined in quality after the above-described coatings. Results evaluated by the undermentioned are shown in Table 5 and Table 6. The procedure for testing is shown below.

(A)Warm brine resistance

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After making cuts reached to a metal surface, that is a substrate, an electrodeposition coated sheet was immersed in a 5 % sodium chloride solution for 480 hours at 55°C. Then an adhesive tape was pasted on the cut part and peeled off. A maximum peeled width (both sides of the cut part in mm) was measured.

(B)Water-resistant secondary adhesion

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Three coated sheets formed by cationic electrodeposition coating, intermediate coating and top coating were immersed in ion-exchanged water at 50°C for 20 days. Then cuts of checkerboard squares at an 1 mm interval (100 pieces) were made so as to reach the metal surface by a keen cutter. An adhesive tape was pasted up on these sheets and then peeled off. It was counted how many cut square pieces remained on the sheets.

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(C) Scab corrosion resistance

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Cuts reached to a metal surface, that is a substrate, were made on the three-coated sheets formed by cationic deposition coating, intermediate coating and top coating by using a keen cutter. Corrosion tests, one cycle of which consists of a 5 % brine spraying test (based on JIS-Z-2371 and for 2 minutes), drying at 60°C for 58 minutes and a wetting test at 50°C for 3 hours under an atmosphere of 95 % relative humidity, were repeated 200 cycles. After completing the cycle tests, a maximum width (one side width from the cut part in mm) of coating abnormality on the coated surface (filament type rust and blister, etc.) was examined.

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Table 5

Material	Test item	Example								
		1	2	3	4	5	6	7	8	9
Cold rolled steel sheet	Warm brine resistance (mm)	0.5	1.0	0.5	0.5	1.0	0.5	0.3	0.5	0.5
	Water-resistant secondary adhesion	100	100	100	100	100	100	100	100	100
	scab resistance (mm)	7.0	7.0	7.5	6.5	7.0	5.0	5.0	7.0	6.0
Alloyed melt zinc coated steel sheet	Warm brine resistance (mm)	2.5	2.0	2.0	2.0	2.5	2.5	2.0	3.0	2.5
	Water-resistant secondary adhesion	100	100	100	100	100	100	100	100	100
	scab resistance (mm)	1.0	1.5	1.0	1.5	1.0	1.0	1.0	1.0	1.0
Aluminum alloy sheet	Warm brine resistance (mm)	2.5	2.5	2.0	1.5	1.5	2.5	0.5	2.5	2.5
	Water-resistant secondary adhesion	100	100	100	100	100	100	100	100	100
	scab resistance (mm)	1.5	2.0	1.5	1.5	1.5	2.5	1.0	2.0	1.0

Table 6

Material	Test item	Comparative example						
		1	2	3	4	5	6	7
Cold rolled steel sheet	Warm brine resistance (mm)	15.0	3.0	1.0	2.0	2.0	1.0	1.0
	Water-resistant secondary adhesion	30	100	100	100	100	100	100
	scab resistance (mm)	20.0	9.0	8.0	11.0	16.0	8.0	8.0
Alloyed melt zinc coated steel sheet	Warm brine resistance (mm)	5.0	3.5	2.5	4.0	3.5	2.5	2.5
	Water-resistant secondary adhesion	60	100	100	40	100	100	100
	scab resistance (mm)	3.0	2.5	1.5	5.0	4.0	1.5	1.5
Aluminum alloy sheet	Warm brine resistance (mm)	4.0	3.5	8.0	5.5	7.0	7.0	3.0
	Water-resistant secondary adhesion	80	90	60	40	100	65	100
	scab resistance (mm)	9.0	9.5	6.0	5.5	8.0	6.0	3.0

As shown in Tables 1 to 6, the conversion treatment in which the used zinc-phosphating solution does not contain a nickel ion, resulted in an excellent adhesion and corrosion resistance for all the iron-based, zinc-based and aluminum-based surfaces, and the conversion was kept in excellent conditions. The results of comparative example 1 show that, because the solution did not contain a simple fluoride compound was used, aluminum ions accumulated in the phosphating solution and inferior phosphating occurs and that the phosphating can not be carried out continuously for a metal surface having all the iron-based, zinc-based and aluminum-based surfaces.

The results of comparative example 2 were similar to those of the example 1, because a solution in which the mole ratio of a complex fluoride compound to a simple fluoride compound is over the above-described range was used.

In the comparative example 3, because the simple fluoride concentration was too high, the phosphating for the aluminum-based surface was especially bad and also, the adhesion and corrosion resistance on the surface were bad.

In the comparative example 4, because a manganese ion was not used, the scab resistance on the iron-based surface was bad and both the adhesion and corrosion resistance on the zinc-based and aluminum-based surfaces were bad.

Although the comparative example 5 corresponds to a case where the nickel ion was eliminated from a

conventional zinc-phosphating solution, because the cobalt ion was not used, the corrosion resistance on the iron-based, zinc-based and aluminum-based surfaces was inferior.

In the comparative example 6, because a simple fluoride and complex fluoride compounds were not used, the conversion on the aluminum-based surface was especially bad and the adhesion and corrosion resistance on the surface were bad.

Claims

1. A process for zinc-phosphating metal surface to be treated by cationic electrodeposition coating, comprising forming a zinc phosphate coating film on a metal surface by bringing the metal surface into contact with an acidic zinc-phosphating solution, said metal surface simultaneously having an iron-based surface, a zinc-based surface and an aluminum-based surface;
being characterized in that said zinc-phosphating solution is free from a nickel ion and is composed of 0.1 to 2 g/l a zinc ion, 5 to 40 g/l of a phosphate ion, 0.1 to 4 g/l of a cobalt ion, 0.1 to 3 g/l of a manganese ion, a phosphating accelerator (a), a simple fluoride compound from 200 to 500 mg/l in terms of HF concentration and a complex fluoride compound of in a mole ratio of 0.01 to 0.5 relative to the simple fluoride compound.
2. A process according to Claim 1, wherein said solution contains the cobalt ion in a weight ratio of 0.5 to 2 relative to the zinc ion.
3. A process according to Claim 1 or 2, wherein said solution further contains one kind or more selected from 0.01 to 3 g/l of a magnesium ion, 0.01 to 3 g/l of a calcium ion and 0.005 to 0.2 g/l of a copper ion.
4. A process according to Claim 1 or 2, wherein said solution further contains a sulfate ion in a mole ratio of 0.1 to 2 relative to the cobalt ion.
5. A process according to Claim 3, wherein said solution further contains a sulfate ion in a mole ratio of 0.1 to 2 relative to the cobalt ion.
6. A process according to Claim 1 or 2, wherein said solution contains the simple fluoride compound so that the concentration of an active fluorine ion measured by a silicon electrode meter is in a range of from 15 to 130 μA .
7. A process according to Claim 3, wherein said solution contains the simple fluoride compound so that the concentration of an active fluorine ion measured by a silicon electrode meter is in a range of from 15 to 130 μA .
8. A process according to Claim 4, wherein said solution contains the simple fluoride compound so that the concentration of an active fluorine ion measured by a silicon electrode meter is in a range of from 15 to 130 μA .
9. A process according to Claim 5, wherein said solution contains the simple fluoride compound so that the concentration of an active fluorine ion measured by a silicon electrode meter is in a range of from 15 to 130 μA .
10. A process according to Claim 1, wherein said phosphating accelerator (a) is at least one kind selected from 0.01 to 0.5 g/l of a nitrite ion, 0.05 to 5 g/l of a m-nitrobenzenesulfonate ion and 0.5 to 10 g/l of hydrogen peroxide.
11. A process according to Claim 10, wherein said solution further contains at least one kind of phosphating accelerator (b) selected from 0.05 to 2 g/l of a chlorate ion and 0.1 to 15 g/l of a nitrate ion.