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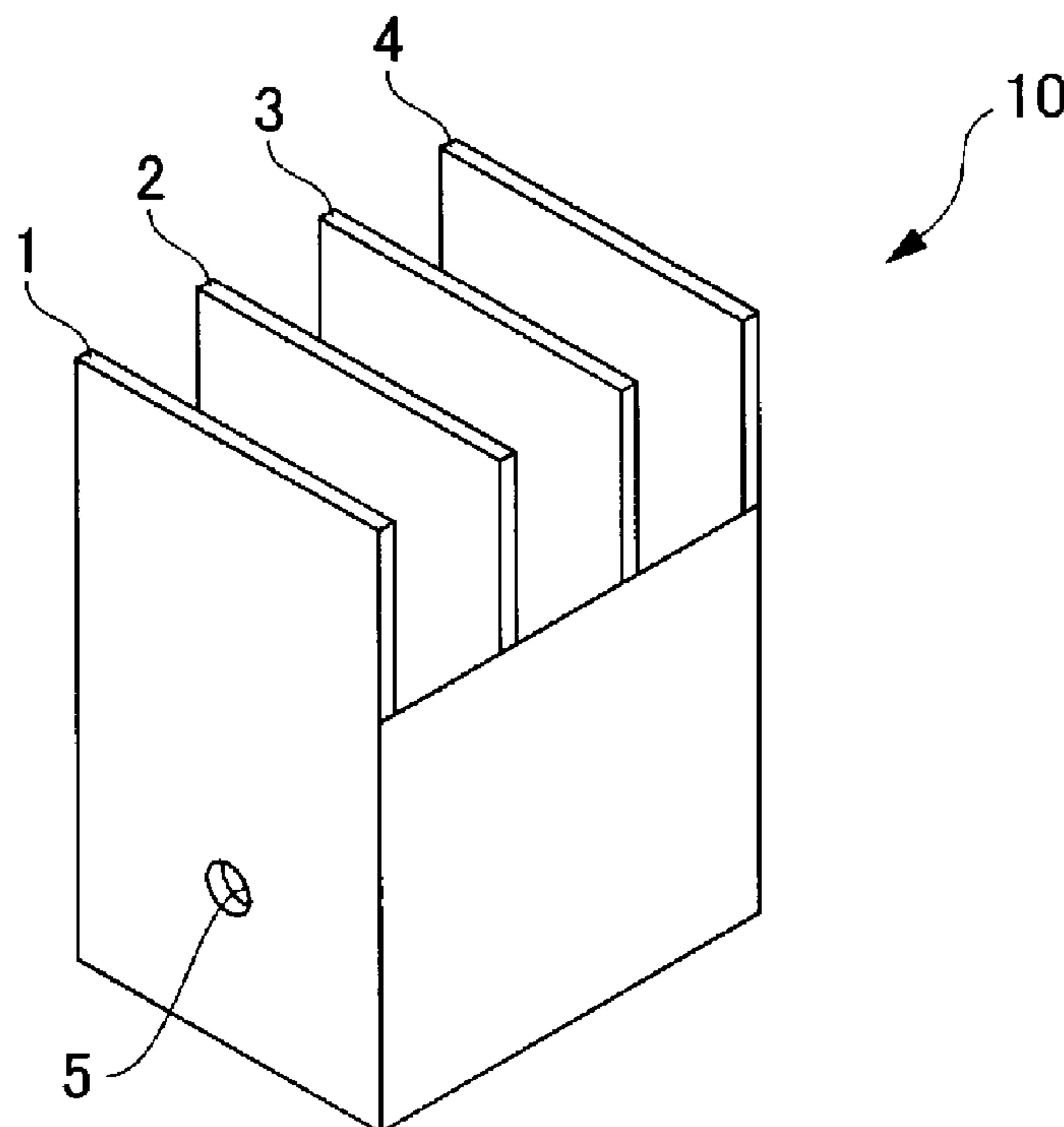
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(54) Titre : FLUIDE DE PRETRAITEMENT DE SURFACE POUR UN METAL DEVANT ETRE REVETU PAR
ELECTRODEPOSITION CATIONIQUE
(54) Title: SURFACE PRETREATMENT FLUID FOR THE METAL TO BE COATED BY CATIONIC
ELECTRODEPOSITION



(57) Abrégé/Abstract:

A surface treatment with a zirconium ion that enables sufficient throwing power, and superior anti-corrosion properties to be exhibited when thus surface treated metal base material is subjected to cation electrodeposition coating is provided. A metal surface treatment liquid for cation electrodeposition coating includes zirconium ions and tin ions, and has a pH of 1.5 to 6.5, in which: the concentration of zirconium ions is in the range of 10 to 10,000 ppm; and the content of the tin ions to the zirconium ions is 0.005 to 1 on a mass basis. Furthermore, a polyamine compound, copper ions, fluorine ions, and a chelate compound may also be included.

ABSTRACT

A surface treatment with a zirconium ion that enables sufficient throwing power, and superior anti-corrosion properties to be exhibited when thus surface treated metal base material is subjected to cation electrodeposition coating is provided. A metal surface treatment liquid for cation electrodeposition coating includes zirconium ions and tin ions, and has a pH of 1.5 to 6.5, in which: the concentration of zirconium ions is in the range of 10 to 10,000 ppm; and the content of the tin ions to the zirconium ions is 0.005 to 1 on a mass basis. Furthermore, a polyamine compound, copper ions, fluorine ions, and a chelate compound may also be included.

SURFACE PRETREATMENT FLUID FOR THE METAL TO BE COATED BY
CATIONIC ELECTRODEPOSITION

TECHNICAL FIELD

The present invention relates to a metal surface treatment liquid, particularly to a metal surface treatment liquid suited for cation electrodeposition coating, and a method of metal surface treatment.

BACKGROUND ART

In order to impart anti-corrosion properties to various metal base materials, surface treatments have thus far been performed. Particularly, a zinc phosphate treatment has been generally employed on metal base materials which constitute automobiles. However, this zinc phosphate treatment has a problem of sludge generation as a by-product. Accordingly, a surface treatment without use of zinc phosphate for a next generation has been demanded, and a surface treatment with zirconium ions is one of such treatments (see, for example, Patent Document 1).

Meanwhile, metal base materials which constitute automobiles and necessitate high anti-corrosion properties are subjected to cation electrodeposition coating following the surface treatment. The cation electrodeposition coating is carried out on the grounds that the coated film obtained by cation electrodeposition coating has superior anti-corrosion properties, and it has "throwing power", generally referred to,

that is a property of allowing automobile bodies having a complicated shape to be completely coated.

However, it has been recently proven that when a metal base material which had been surface treated with the zirconium ions is subjected to the cation electrodeposition coating, there may be a case in which no significant effect in terms of the throwing power is achieved, for example, the throwing power may not be sufficient for cold-rolled steel plates in some cases. Accordingly, when the cation electrodeposition coating is carried out, sufficient anticorrosion properties cannot be achieved if the throwing power is insufficient. See Japanese Patent Publication No. 2004-218070.

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

An object of the present invention is to provide a surface treatment with zirconium ions that enables sufficient throwing power and exhibit superior anti-corrosion properties to be exhibited, when thus surface treated metal base material is subjected to cation electrodeposition coating.

Means for Solving the Problems

Aspects of the present invention are as follows.

In a first aspect of the present invention, a metal surface treatment liquid for cation electrodeposition coating contains zirconium ions, and tin ions, and has a pH of in the range of 1.5 to 6.5, in which: the concentration of the zirconium ions

is in the range of 10 to 10,000 ppm; and the concentration ratio of the tin ions to the zirconium ions is 0.005 to 1 on a mass basis, and further comprises fluorine ions; and A) a chelate compound, wherein the chelate compound is selected from the group consisting of amino acid, aminocarboxylic acid, ascorbic acid and sulfonic acid, wherein the sulfonic acid is selected from the group consisting of methanesulfonic acid, isethionic acid, taurine, naphthalenedisulfonic acid, aminonaphthalenedisulfonic acid, sulfosalicylic acid, a naphthalenesulfonic acid-formaldehyde condensate, alkyl naphthalenesulfonic acid, a salt of any of these and sodium polystyrenesulfonate, or B) a nitrogenous, sulfur and/or phenolic rust-preventive agent selected from the group consisting of hydroquinone, ethyleneurea, quinolinol, thiourea, benzotriazole, a salt of any of these and mercaptobenzothiazole; or C) indium ions, wherein the amount of free fluorine ions at a pH of 3.0 is in the range of 0.1 to 50 ppm.

In a second aspect of the present invention, a metal surface treatment liquid for cation electrodeposition coating according to the first aspect further includes a polyamine compound.

In a third aspect of the present invention, a metal surface treatment liquid for cation electrodeposition coating according to the first or second aspect further includes copper ions.

In a fourth aspect of the present invention, a metal surface

treatment liquid for cation electrodeposition coating according to any one of the first to third aspects further includes an oxidizing agent.

In a fifth aspect of the present invention, a metal surface treatment liquid for cation electrodeposition coating according to any one of the first to fourth aspects further includes aluminum ions.

In a sixth aspect of the present invention, a method of metal surface treatment includes a step of subjecting a metal base material to a surface treatment with the metal surface treatment liquid for cation electrodeposition coating according to any one of the first to fifth aspects.

In a seventh aspect of the present invention, the method according to the sixth aspect further includes the step of subjecting the surface treated metal base material to cation electrodeposition coating.

In an eighth aspect of the present invention, a metal base material includes a coating film formed by a surface treatment obtained by the method according to the sixth or seventh aspects.

In a ninth aspect of the present invention, a metal base material according to the eighth aspect includes an element ratio of zirconium/tin on a mass basis in the coating film is in the range of 1/10 to 10/1.

Accordingly, the metal surface treatment liquid for cation electrodeposition coating of the present invention is a chemical conversion treatment liquid containing zirconium ions

and tin ions, and having a pH in the range of 1.5 to 6.5, in which the concentration of zirconium ions in the range of 10 to 10,000 ppm, and the content of the tin ions with respect to the zirconium ions is 0.005 to 1 on a mass basis. Moreover, the metal surface treatment liquid for cation electrodeposition coating may further contain a polyamine compound, copper ions, fluorine ions, a chelate compound, an oxidizing agent, and a rust-preventive agent. When the fluorine ions are included, the amount of free fluorine ions at a pH of 3.0 may be 0.1 to 50 ppm.

The method of metal surface treatment of the present invention includes the step of subjecting a metal base material to a surface treatment with the abovementioned metal surface treatment liquid.

A coating film obtained by the surface treatment is formed on the surface treated metal base material of the present invention. The element ratio of zirconium/tin on mass basis in the coating film may be 1/10 to 10/1.

The method of cation electrodeposition coating of the present invention includes a step of subjecting a metal base

material to a surface treatment with the abovementioned metal surface treatment liquid, and a step of subjecting the surface treated metal base material to cation electrodeposition coating.

The metal base material coated by the cation electrodeposition of the present invention is obtained by the abovementioned method of coating.

Effects of the Invention

It is believed that the throwing power attained by the metal surface treatment liquid for cation electrodeposition coating of the present invention can be improved by including tin ions in addition to zirconium ions when the cation electrodeposition coating is carried out after forming a conversion coating film with this treatment liquid. Although not clarified, the grounds are conceived as follows.

When zirconium ions are used alone, formation of their oxide coating film is believed to be executed simultaneously with etching of the metal base material in an acidic medium. However, since segregation materials and the like of compounds containing silicon or carbon in addition to silica may be present on cold-rolled steel plates, such parts are not susceptible to etching. Therefore, the coating film cannot be uniformly formed with zirconium oxide, whereby portions without coating film formation can be present. Since a difference in electric current flow is believed to be generated between the parts with and without formation of the coating film, the electrodeposition is not uniformly executed,

and consequently, the throwing power cannot be sufficiently attained.

When tin ions are additionally present, it is further considered as in the following. Since the tin ions are less likely to be affected on the steel plate as compared with the zirconium ions, their oxide coating film can be more easily formed on the base material. Although formation of the coating film of the tin ions is not specific to the parts where the zirconium ions are not significantly deposited, formation of the oxide coating film of the tin ions is not restricted to a specific part while having another part remain without formation of the film. As a result, the tin ions would form the coating film such that it covers the part where the zirconium ion could not form the coating film.

The metal surface treatment liquid for cation electrodeposition coating of the present invention can improve adhesiveness to the coated film by cation electrodeposition through including the polyamine compound, and consequently, it can pass SDT test under more stringent conditions. In addition, the metal surface treatment liquid for cation electrodeposition coating of the present invention can improve anti-corrosion properties by including the copper ion. Although the grounds are not clarified, it is believed that some interaction may be caused between copper and zirconium in forming the coating film. Furthermore, the metal surface treatment liquid for cation electrodeposition coating of the present invention can form a zirconium oxide coating film in a

stable manner by including a chelate compound when a metal other than zirconium is included in large quantity. This occurrence is believed to result from capture by the chelate compound of metal ions that are more likely to be deposited than zirconium.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a perspective view illustrating one example of the box for use in evaluating the throwing power; and

Fig. 2 shows a view schematically illustrating evaluation of the throwing power.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

The metal surface treatment liquid for cation electrodeposition coating of the present invention is a chemical conversion treatment liquid that contains zirconium ions and tin ions, and has a pH in the range of 1.5 to 6.5.

The zirconium ions are included at a concentration in a range of 10 to 10,000 ppm. When the concentration is less than 10 ppm, sufficient anti-corrosion properties cannot be achieved since deposition of the zirconium coating film is not enough. In addition, even though the concentration may exceed 10,000 ppm, an effect to justify the amount cannot be exhibited since the deposition amount of the zirconium coated film is not increased, and adhesiveness of the coated film may be deteriorated, thereby leading to inferior anticorrosion performance such as those in SDT. The lower limit and the

upper limit of the concentration are preferably 100 ppm and 500 ppm, respectively.

The concentration of the metal ions herein, when a complex or oxide thereof was formed, is represented by the concentration based on the metal element, taking into account only of the metal atom in the complex or oxide. For example, the concentration based on the metal element of zirconium of 100 ppm complex ions ZrF_6^{2-} (molecular weight: 205) is calculated to be 44 ppm by the formula of $100 \times (91/205)$. In the metal surface treatment liquid for cation electrodeposition coating of the present invention, the metal compound (zirconium compound, tin compound, copper compound and other metal compounds) is included at just a slight proportion, if present, in the state of a nonionic state such as an oxide portion, and is believed to be present almost in the form of the metal ion. Therefore, the metal ion concentration referred to herein is, irrespective of the presence in the form of the nonionic portion, the metal ion concentration when it is assumed to be present as the metal ion dissociated at a level of 100%.

The tin ion included in the metal surface treatment liquid for cation electrodeposition coating of the present invention is preferably a bivalent cation. When the tin ion has other valence, the intended effect may not be exhibited. However, the tin ion is not limited to the bivalent cation, but can be used in the present invention as long as it can be deposited on the metal base material. For example, when the

tin ions form a complex, it may be a quadrivalent cation, which can also be used in the present invention. The concentration of the tin ions is 0.005 to 1 on a mass basis with respect to the concentration of the zirconium ions. When the ratio is less than 0.005, the effect by addition is not exhibited, while zirconium may not be significantly deposited when the ratio exceeds 1. The lower limit and the upper limit of the concentration are preferably 0.02 and 0.2, respectively. However, when the total amount of the zirconium ion and tin ion is too small, the effect of the present invention may not be exhibited. Therefore, the total concentration of the zirconium ion and the tin ion in the metal surface treatment liquid of the present invention is preferably no less than 15 ppm.

The content of the tin ions in the metal surface treatment liquid of the present invention is preferably is preferably 1 to 100 ppm. When the content is less than 1 ppm, deposition of tin at the portion where zirconium could not form the coating film may be insufficient, and the anti-corrosion properties such as those in SDT are likely to be inferior. When the content exceeds 100 ppm, deposition of the zirconium coating film may be difficult, whereby the anti-corrosion properties and the coating appearance are likely to be inferior. The concentration is more preferably 5 to 100 ppm, and still more preferably 5 to 50 ppm.

The metal surface treatment liquid for cation electrodeposition coating of the present invention has a pH in

the range of 1.5 to 6.5. When the pH is less than 1.5, the metal base material cannot be sufficiently etched to decrease the coating film amount, and sufficient anti-corrosion properties cannot be achieved. In addition, the stability of the treatment liquid may not be sufficient. In contrast, when the pH is higher than 6.5, excessive etching may lead to failure in formation of sufficient coating film, or an un-uniform adhesion amount and film thickness of the coating film may adversely affect the coating appearance and the like. The lower limit and the upper limit of pH are preferably 2.0 and 5.5, and still more preferably 2.5 and 5.0, respectively.

The metal surface treatment liquid for cation electrodeposition coating of the present invention may further include a polyamine compound for improving adhesiveness to the coated film by cation electrodeposition which is formed after the surface treatment. The polyamine compound used in the present invention is believed to be fundamentally significant in being an organic molecule having an amino group. Although speculative, the amino group is believed to be incorporated in the coating film by a chemical action with zirconium oxide deposited as a coating film on the metal base plate, or with the metal base plate. In addition, the polyamine compound that is an organic molecule is believed to be responsible for adhesiveness with the coated film provided on the metal base plate having the coating film formed thereon. Therefore, when the polyamine compound that is an organic molecule having an amino group is used, adhesiveness between the metal base plate

and the coated film is significantly improved, and superior corrosion resistance can be attained. Examples of the polyamine compound include hydrolysis condensates of aminosilane, polyvinylamine, polyallylamine, water soluble phenolic resins having an amino group, and the like. Since the amount of amine can be freely adjusted, the hydrolysis condensate of aminosilane is preferred. Therefore, exemplary metal surface treatment liquids for cation electrodeposition coating of the present invention include, for example, the metal surface treatment liquids for cation electrodeposition coating which contain zirconium ions, tin ions, and a hydrolysis condensate of aminosilane; the metal surface treatment liquids for cation electrodeposition coating which contain zirconium ions, tin ions, and polyallylamine; and the metal surface treatment liquids for cation electrodeposition coating which contain zirconium ions, tin ions, and a water soluble phenolic resin having an amino group. In addition, these metal surface treatment liquids for cation electrodeposition coating may contain fluorine as described later.

The hydrolysis condensate of aminosilane is obtained by carrying out hydrolysis condensation of an aminosilane compound. Examples of the aminosilane compound include vinyltrichlorosilane, vinyltrimethoxysilane, vinyltriethoxysilane, 2-(3,4 epoxycyclohexyl)-ethyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldiethoxysilane, 3-

glycidoxypropyltriethoxysilane, p-styryltrimethoxysilane, 3-methacryloxypropylmethyldimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropylmethyldiethoxysilane, 3-methacryloxypropyltriethoxysilane, 3-acryloxypropyltrimethoxysilane, N-2-(aminoethyl)-3-aminopropylmethyldimethoxysilane, N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, N-2-(aminoethyl)-3-aminopropyltriethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-triethoxysilyl-N-(1,3-dimethylbutylidene)-propylamine, N-phenyl-3-aminopropyltrimethoxysilane, N-(vinylbenzyl)-2-aminoethyl-3-aminopropyltrimethoxysilane hydrochloride, 3-ureidepropyltriethoxysilane, 3-chloropropyltrimethoxysilane, 3-mercaptopropylmethyldimethoxysilane, 3-mercaptopropyltrimethoxysilane, bis(triethoxysilylpropyl)tetrasulfide, and 3-isocyanate propyltriethoxysilane, which are silane coupling agents having an amino group. In addition, examples of commercially available products which can be used include "KBM-403", "KBM-602", "KBM-603", "KBE-603", "KBM-903", "KBE-903", "KBE-9103", "KBM-573", "KBP-90" (all trade names, manufactured by Shin-Etsu Chemical Co.), "XS1003" (trade name, manufactured by Chisso Corporation), and the like.

The hydrolytic condensation of the aforementioned aminosilane can be carried out by a method well known to persons skilled in the art. Specifically, the hydrolytic

condensation can be carried out by adding water required for hydrolysis of the alkoxysilyl group to at least one kind of aminosilane compound, and stirring the mixture while heating as needed. The degree of condensation can be regulated with the amount of water used.

A higher degree of condensation of aminosilane hydrolysis condensate is preferred, since in this case where zirconium is deposited as an oxide, the above aminosilane hydrolysis condensate tends to be easily incorporated therein. For example, the portion on a mass basis of dimer or higher-order multimers of aminosilane in the total amount of the aminosilane is preferably no less than 40%, more preferably no less than 50%, still more preferably no less than 70%, and even more preferably no less than 80%. Therefore, when aminosilane is allowed to react in a hydrolytic condensation reaction, it is preferred to permit the reaction under conditions in which aminosilane is more likely to be hydrolysed and condensed such as those in which an aqueous solvent containing a catalyst such as acetic acid and alcohol is used as the solvent. In addition, by allowing for a reaction under conditions with a comparatively high aminosilane concentration, a hydrolysis condensate having a high degree of condensation is obtained. Specifically, it is preferred to allow for the hydrolytic condensation at an aminosilane concentration falling within the range of 5% by mass to 50% by mass. The degree of condensation can be determined by ^{29}Si -NMR measurement.

As the polyvinylamine and polyallylamine, commercially available products can be used. Examples of polyvinylamine include "PVAMTM-0595B" (manufactured by Mitsubishi Chemical Corporation) and the like, and examples of the polyallylamine include "PAATM-01", "PAATM-10C", "PAATM-H-10C", "PAATM-D-41HCl" (manufactured by Nitto Boseki Co., Ltd.) and the like.

The molecular weight of the polyamine compound is preferably in the range of 150 to 500,000. When the molecular weight is less than 150, a conversion coating film having sufficient adhesiveness may not be obtained. When the molecular weight exceeds 500,000, formation of the coating film may be inhibited. The lower limit and the upper limit are more preferably 5,000 and 70,000, respectively. When the polyamine compound has the amino group in too large an amount, it may adversely influence the coating film, while the effect to improve the adhesiveness with the coating film provided by the amino group is not significantly achieved when the amount is too small. Therefore, the polyamine compound preferably has a primary and/or secondary amino group of no less than 0.1 mmol and no more than 17 mmol per gram of the solid content, and more preferably a primary and/or secondary amino group of no less than 3 mmol and no more than 15 mmol per gram of the solid content.

The number of moles of the primary and/or secondary amino group per gram of the solid content of the polyamine compound can be determined according to the following formula (1).

$$\text{Amount of Amino Group} = (mX - nY) / (m + n) \dots \text{Formula (1)}$$

in which the mass ratio of solid contents of the polyamine compound and the compound having a functional group A and/or a functional group B is defined as $m:n$; the number of mmoles of the functional group A and/or the functional group B per gram of the compound having the functional group A and/or the functional group B is defined as Y ; and the number of mmoles of the primary and/or secondary amino group included per gram of the polyamine compound when the compound having the functional group A and/or the functional group B is not included in the composition for the metal surface treatment is defined as X .

The content of the polyamine compound in the metal surface treatment liquid for cation electrodeposition coating of the present invention can be in the range of 1 to 200% based on mass of the zirconium metal included in the surface treatment liquid. When the content is less than 1%, the intended effect cannot be exhibited, while the content exceeding 200% may lead to failure in sufficient formation of the coating film. The upper limit of the content is more preferably 120%, more preferably 100%, still more preferably 80%, and even more preferably 60%.

The metal surface treatment liquid for cation electrodeposition coating of the present invention may further contain a copper ion for improving the anti-corrosion properties. With respect to the amount of the copper ions, the concentration preferably accounts for 10 to 100% with respect to the concentration of the tin ions. When the concentration

is less than 10%, the intended effect may not be exhibited, while deposition of zirconium may be difficult, similarly to the case of the tin ions when it exceeds the concentration of the tin ions. Exemplary metal surface treatment liquids for cation electrodeposition coating of the present invention include, for example, the metal surface treatment liquids for cation electrodeposition coating which contain zirconium ions, tin ions and copper ions. In this case, the fluorine ions described later can be further included and the aforementioned polyamine compound can be included.

It is preferred that the metal surface treatment liquid for cation electrodeposition coating of the present invention contains fluorine ions. Since the concentration of the fluorine ions varies depending on the pH, the amount of free fluorine ions is defined at a specified pH. In the present invention, the amount of the free fluorine ions at a pH of 3.0 is in the range of 0.1 to 50 ppm. When the amount is less than 0.1 ppm, the metal base material cannot be sufficiently etched so that the coating film amount is decreased, and sufficient anticorrosion properties cannot be achieved. In addition, the treatment liquid may not have enough stability. In contrast, when the amount is above 50 ppm, excessive etching may lead to failure in formation of sufficient coating film, or an un-uniform adhesion amount and film thickness of the coating film may adversely affect the coating appearance and the like. The lower limit and the upper limit are preferably 0.5 ppm and 10 ppm, respectively. Exemplary metal surface treatment liquids

for cation electrodeposition coating of the present invention include, for example, the metal surface treatment liquids for cation electrodeposition coating which contain zirconium ions, tin ions, and fluorine ions.

The metal surface treatment liquid for cation electrodeposition coating of the present invention may include a chelate compound. By including the chelate compound, deposition of metals other than zirconium can be suppressed in the treatment liquid, and the coating film of zirconium oxide can be stably formed. As the chelate compound, amino acid, aminocarboxylic acid, a phenolic compound, aromatic carboxylic acid, sulfonic acid, ascorbic acid and the like can be exemplified. Carboxylic acid having a hydroxyl group such as citric acid and gluconic acid, conventionally known as chelating agents, cannot exert their function enough in the present invention.

As the amino acid, a variety of naturally occurring amino acids and synthetic amino acids, as well as amino acids having at least one amino group and at least one acid group (carboxyl group, sulfonic acid group or the like) in one molecule, can be extensively utilized. Among these, at least one selected from the group consisting of alanine, glycine, glutamic acid, aspartic acid, histidine, phenylalanine, asparagine, arginine, glutamine, cysteine, leucine, lysine, proline, serine, tryptophan, valine and tyrosine, and a salt thereof can be preferably used. Furthermore, when there is an optical isomer of the amino acid, any one can be suitably used irrespective

of the forms, i.e., L-form, D-form, or racemic bodies.

In addition, as the aminocarboxylic acid, a compound having both functional groups, an amino group and a carboxyl group in one molecule other than the amino acid described above can be extensively used. Among these, at least one selected from the group consisting of diethylenetriamine pentaacetic acid (DTPA), hydroxyethylethylenediamine triacetic acid (HEDTA), triethylenetetraamine hexaacetic acid (TTHA), 1,3-propanediamine tetraacetic acid (PDTA), 1,3-diamino-6-hydroxypropane tetraacetic acid (DPTA-OH), hydroxyethylimino diacetic acid (HIDA), dihydroxyethylglycine (DHEG), glycolether diamine tetraacetic acid (GEDTA), dicarboxymethyl glutamic acid (CMGA), (S,S)-ethylenediamine disuccinic acid (EDDS), ethylenediamine tetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and a salt thereof can be preferably used.

Furthermore, examples of the phenolic compound include compounds having two or more phenolic hydroxyl groups, and phenolic compounds including the same as a basic skeleton. Examples of the former include catechol, gallic acid, pyrogallol, tannic acid, and the like. Meanwhile, examples of the latter include flavonoids such as flavone, isoflavone, flavonol, flavanone, flavanol, anthocyanidin, aurone, chalcone, epigallocatechin gallate, gallocatechin, theaflavin, daidzin, genistin, rutin, and myricitrin, polyphenolic compounds including tannin, catechin and the like, polyvinylphenol, water soluble resol, novolak resins, lignin, and the like.

Among them, tannin, gallic acid, catechin and pyrogallol are particularly preferred.

As the sulfonic acid, at least one selected from the group consisting of methanesulfonic acid, isethionic acid, taurine, naphthalenedisulfonic acid, aminonaphthalenedisulfonic acid, sulfosalicylic acid, a naphthalenesulfonic acid-formaldehyde condensate, alkyl naphthalenesulfonic acid and the like, and a salt thereof can be preferably used.

When sulfonic acid is used, coating performance and corrosion resistance of the object following the chemical conversion treatment can be improved. Although the mechanism is not clarified, the following grounds are conceived.

First, since there exist silica segregation products and the like on the surface of the object such as steel plates to yield an un-uniform surface composition, a portion not susceptible to etching in the chemical conversion treatment may be present. However, it is speculated that such a portion not susceptible to etching can be particularly etched by adding sulfonic acid, and consequently, a uniform metal oxide film is likely to be formed on the object surface. In other words, sulfonic acid is believed to act as an etching accelerator.

Second, it is possible that in chemical conversion treatment, hydrogen gas which can be generated by the chemical conversion reaction inhibits the reaction at the interface, and sulfonic acid is speculated to remove the hydrogen gas

through a depolarizing action thereby accelerating the reaction.

Of these, use of taurine is preferred since it has both an amino group and a sulfone group. The content of sulfonic acid is preferably in the range of 0.1 to 10,000 ppm, and more preferably in the range of 1 to 1,000 ppm. When the content is less than 0.1 ppm, the effect is not significantly exhibited, while deposition of zirconium can be inhibited when the content exceeds 10,000 ppm.

Use of ascorbic acid leads to uniform formation of the metal oxide film such as zirconium oxide, tin oxide and the like on the object surface by the chemical conversion treatment, and the coating performance and corrosion resistance can be improved. Although the mechanism is not clarified, the etching action in the chemical conversion treatment is uniformly executed on the object such as steel plates, and consequently, it is speculated that zirconium oxide and/or tin oxide is deposited on the etched part to form an entirely uniform metal oxide film. In addition, tin is speculated to become apt to be deposited in the form of the tin metal at the metal interface due to some influence, and as a consequence, zirconium oxide is deposited at the part where the tin metal deposited, whereby surface concealability on the object may be improved as a whole. The content of ascorbic acid is preferably in the range of 5 to 5,000 ppm, and more preferably in the range of 20 to 200 ppm. When the content is less than 5 ppm, the effect is not significantly exhibited,

while deposition of zirconium can be inhibited when the content exceeds 5,000 ppm.

When the chelating agent is included, its content is preferably 0.5 to 10 times the concentration of the total concentration of other metal ions except for zirconium such as tin ion and copper ion. When the concentration is less than 0.5 times, the intended effect cannot be exhibited, while a concentration exceeding 10 times may adversely influence on formation of the coating film.

The metal surface treatment liquid for cation electrodeposition coating of the present invention can further contain a nitrogenous, sulfur and/or a phenolic rust-preventive agent. The rust-preventive agent can inhibit corrosion through forming an anti-corrosion coating film on the metal surface. As the nitrogenous, sulfurous, phenolic rust-preventive agent, at least one selected from the group consisting of hydroquinone, ethyleneurea, quinolinol, thioures, benzotriazole and the like, and a salt thereof can be used. Use of the nitrogenous, sulfurous, phenolic rust-preventive agent in the metal surface treatment liquid for cation electrodeposition coating of the present invention leads to uniform formation of the metal oxide film such as zirconium oxide, tin oxide and the like on the object surface by the chemical conversion treatment, whereby the coating performance, corrosion resistance can be improved. Although the mechanism is not clarified, the followings are conceived.

That is, since there exist silica segregation products

and the like on the steel plate surface to yield an un-uniform surface composition, a portion having the conversion coating film formed by etching in the chemical conversion treatment, and a portion without formation of the conversion coating film due to different etching behavior thereby having iron oxide may be present. The nitrogenous, sulfurous, phenolic rust-preventive agent improves primary rust-preventive properties through adsorbing to the portion without formation of the conversion coating film in the chemical conversion treatment to cover the metal interface. It is speculated that the coating performance, corrosion resistance of the object following the chemical conversion treatment can be consequently improved.

In addition, when copper is excessively deposited on the conversion coating film, this copper may serve as a cathode base point to form an electrically un-uniform conversion coating film. However, by allowing the rust-preventive agent to be adsorbed to the portion where an excessive amount of copper deposited, improvement of the corrosion resistance is expected to be enabled by attaining a uniform electrodeposition coating property on the object following the chemical conversion treatment.

The content of the nitrogenous, sulfurous and/or phenolic rust-preventive agent is preferably in the range of 0.1 to 10,000 ppm, and more preferably in the range of 1 to 1,000 ppm. When the content is less than 0.1 ppm, the effect is not significantly exhibited, while deposition of zirconium can be

inhibited when the content exceeds 10,000 ppm.

The metal surface treatment liquid for cation electrodeposition coating of the present invention may further contain aluminum ions and/or indium ions. Since these cations have similar functions to the tin ions, they can be used in combination when the use of the tin ions alone cannot exhibit the effect. Of these, aluminum is more preferred. The content of the aluminum ions and/or the indium ions is preferably in the range of 10 to 1,000 ppm, more preferably in the range of 50 to 500 ppm, and still more preferably in the range of 100 to 300 ppm. The amount of the aluminum ions and indium ions can be a concentration accounting for, for example, 2 to 1,000% of the zirconium ion concentration. Exemplary metal surface treatment liquids for cation electrodeposition coating of the present invention include, for example, the metal surface treatment liquids for cation electrodeposition coating which contain zirconium ions, tin ions and aluminum ions. These can further contain fluorine as described later, and can also contain the polyamine compound described later.

The metal surface treatment liquid for cation electrodeposition coating of the present invention may contain various cations in addition to the aforementioned components. Examples of the cation include magnesium, zinc, calcium, gallium, iron, manganese, nickel, cobalt, silver, and the like. In addition, there exist cations and anions that are derived from a base or an acid added for adjusting the pH, or are included as the counter ion of the aforementioned components.

The metal surface treatment liquid for cation electrodeposition coating of the present invention can be produced by placing each of the components thereof, and/or compound containing the same into water, followed by mixing.

Examples of the compound for supplying the zirconium ions include fluorozirconic acid, salts of fluorozirconic acid such as potassium fluorozirconate and ammonium fluorozirconate, zirconium fluoride, zirconium oxide, zirconium oxide colloid, zirconyl nitrate, zirconium carbonate, and the like.

Examples of the compound that supplies the tin ions include tin sulfate, tin acetate, tin fluoride, tin chloride, tin nitrate, and the like. On the other hand, as the compound that supplies the fluorine ions, for example, fluorides such as hydrofluoric acid, ammonium fluoride, fluoboric acid, ammonium hydrogen fluoride, sodium fluoride, sodium hydrogen fluoride, and the like can be exemplified. Additionally, a complex fluoride can also be used as the source, and examples thereof include hexafluorosilicic acid salts, specifically, hydrofluosilicic acid, zinc hydrofluosilicate, manganese hydrofluosilicate, magnesium hydrofluosilicate, nickel hydrofluosilicate, iron hydrofluosilicate, calcium hydrofluosilicate, and the like. Furthermore, a compound that supplies zirconium ions, and is a complex fluoride is also acceptable. Moreover, copper acetate, copper nitrate, copper sulfate, copper chloride and the like as the compound that supplies copper ions; aluminum nitrate, aluminum fluoride and the like as the compound that supplies aluminum ions; and

indium nitrate, indium chloride and the like as the compound that supplies indium ions can be exemplified, respectively.

After mixing these components, the metal surface treatment liquid for cation electrodeposition coating of the present invention can be regulated to have a predetermined value of pH using an acidic compound such as nitric acid or sulfuric acid, and a basic compound such as sodium hydroxide, potassium hydroxide or ammonia.

The metal surface treatment liquid for cation electrodeposition coating of the present invention may contain an oxidizing agent. The oxidizing agent is particularly preferably at least one selected from the group consisting of nitric acid, nitrous acid, hydrogen peroxide, bromic acid, and salts of the same. The oxidizing agent allows a metal oxide film to be uniformly formed on the surface of an object, whereby coatability and corrosion resistance of the object can be improved.

Although the mechanism is not clarified, it is speculated that use of the oxidizing agent in a specified amount allows the etching action in the chemical conversion treatment to be uniformly executed on an object such as a steel plate, whereby zirconium oxide and/or tin oxide is deposited at the etched part to form an entirely uniform metal oxide film. It is also speculated that the oxidizing agent in the specified amount renders tin readily deposited as a tin metal at the metal interface, and thus zirconium oxide is deposited at the portions of deposition of the tin metal, whereby the surface

concealability on the entire object is improved.

In order to affect such an action, the content of each oxidizing agent is as in the following. Accordingly, the content of nitric acid is preferably in the range of 100 to 100,000 ppm, more preferably in the range of 1,000 to 20,000 ppm, and still more preferably in the range of 2,000 to 10,000 ppm. The content of nitrous acid and bromic acid is preferably in the range of 5 to 5,000 ppm, and more preferably in the range of 20 to 200 ppm. The content of nitrous acid and bromic acid is preferably in the range of 5 to 5,000 ppm, and more preferably in the range of 20 to 200 ppm. The content of hydrogen peroxide is preferably in the range of 1 to 1,000 ppm, and more preferably in the range of 5 to 100 ppm. When content of each is less than the lower limit, the aforementioned effect is not significantly exhibited, while the deposition of zirconium can be inhibited when the content exceeds the upper limit.

The method of the metal surface treatment of the present invention includes a step of subjecting a metal base material to a surface treatment using the metal surface treatment liquid described above.

The metal base material is not particularly limited as long as it can be cation electrodeposited, and for example, an iron-based metal base material, aluminum-based metal base material, zinc-based metal base material and the like can be exemplified.

Examples of the iron-based metal base material include

cold-rolled steel plates, hot-rolled steel plates, soft steel plates, high-tensile steel plates, and the like. Moreover, examples of the aluminum-based metal base material include 5,000 series aluminum alloys, 6,000 series aluminum alloys, and aluminum-coated steel plates treated by aluminum-based electroplating, hot dipping, or vapor deposition plating. Furthermore, examples of the zinc-based metal base material include zinc or zinc-based alloy coated steel plates treated by zinc-based electroplating, hot dipping, or vapor deposition plating such as zinc coated steel plate, zinc-nickel coated steel plate, zinc-titanium coated steel plate, zinc-magnesium coated steel plate, zinc-manganese coated steel plate, and the like. There are a variety of grades of the high-tensile steel plate depending on the strength and manufacture method, and examples thereof include JSC400J, JSC440P, JSC440W, JSC590R, JSC590T, JSC590Y, JSC780T, JSC780Y, JSC980Y, JSC1180Y, and the like.

Metal base materials including a combination of multiple kinds of metals such as iron-based, aluminum-based, zinc-based metals and the like (including joint area and contact area of different kinds of metals) can be simultaneously applied as the metal base material.

The surface treatment step may be carried out by bringing the metal surface treatment liquid into contact with the metal base material. Specific examples of the method include a dipping method, a spraying method, a roll coating method, a pouring method, and the like.

The treatment temperature in the surface treatment step preferably falls within the range of 20 to 70°C. When the temperature is lower than 20°C, it is possible to cause failure in formation of a sufficient coating film, while a corresponding effect cannot be expected at a temperature above 70°C. The lower limit and the upper limit are more preferably 30°C and 50°C, respectively.

The treatment time period in the surface treatment step is preferably 2 to 1100 seconds. When the time period is less than 2 seconds, a sufficient coating film amount may not be attained, while a corresponding effect cannot be expected even though it is longer than 1100 seconds. The lower limit and the upper limit are still more preferably 30 seconds and 120 seconds, respectively. Accordingly, a coating film is formed on the metal base material.

The surface treated metal base material of the present invention is obtained by the surface treatment method described above. On the surface of the metal base material is formed a coating film that contains zirconium and tin. The element ratio of zirconium/tin in the coating film is preferably in the range of 1/10 to 10/1 on a mass basis. When the ratio is out of this range, the intended performance may not be attained.

The content of zirconium in the coating film is preferably no less than 10 mg/m² in the case of iron-based metal base materials. When the content is less than 10 mg/m², sufficient anti-corrosion properties may not be achieved. The

content is more preferably no less than 20 mg/m², and still more preferably no less than 30 mg/m². Although the upper limit is not specifically defined, too large an amount of the coating film may lead to an increased likelihood of crack generation of the rust-preventive coating film, and may make it difficult to obtain a uniform coating film. In this respect, the content of zirconium in the coating film is preferably no greater than 1 g/m², and more preferably no greater than 800 mg/m².

When the coating film is formed using the metal surface treatment liquid which contains copper ions, the content of copper in the coating film is preferably no less than 0.5 mg/m² in order to achieve the intended effect.

The method of cation electrodeposition coating of the present invention includes a step of subjecting a metal base material to a surface treatment using the metal surface treatment liquid described above, and a step of subjecting the surface treated metal base material to cation electrodeposition coating.

The surface treatment step in the aforementioned cation electrodeposition coating is same as the surface treatment step in the surface treatment method described above. The surface treated metal base material obtained in the surface treatment step may be subjected to the cation electrodeposition coating step directly or after washing.

In the cation electrodeposition coating step, the surface treated metal base material is subjected to the cation

electrodeposition coating. In the cation electrodeposition coating, the surface treated metal base material is dipped in cation electrodeposition coating solution, and a voltage of 50 to 450 V is applied thereto using the same as a cathode for a certain period of time. Although the application time period of voltage may vary depending on the conditions of the electrodeposition, it is generally 2 to 4 minutes.

As the cation electrodeposition coating solution, a generally well known one can be used. Specifically, such general coating solutions are prepared by blending: a binder cationized through adding amine or sulfide to an epoxy group carried by an epoxy resin or an acrylic resin, followed by adding thereto a neutralizing acid such as acetic acid; block isocyanate as a curing agent; and a pigment dispersing paste including a rust-preventive pigment dispersed in a resin.

After completing the cation electrodeposition coating step, a hardened coated film can be obtained by baking at a predetermined temperature directly, or after washing with water. Although the baking conditions may vary depending on the type of the cation electrodeposition coating solution used, usually the baking may be conducted in the range of 120 to 260°C, and preferably in the range of 140 to 220°C. The baking time period can be 10 to 30 minutes. The resulting metal base material coated by the cation electrodeposition is also involved as an aspect of the present invention.

EXAMPLES

Production Example 1: Production of Hydrolysis Condensate of Aminosilane, Part 1

As aminosilane, 5 parts by mass of KBE603 (3-aminopropyl-triethoxysilane, effective concentration: 100%, manufactured by Shin-Etsu Chemical Co., Ltd.) was added dropwise using a dropping funnel to a mixed solvent (solvent temperature: 25°C) containing 47.5 parts by mass of deionized water and 47.5 parts by mass of isopropyl alcohol over 60 minutes to a homogenous state, followed by allowing for reaction under a nitrogen atmosphere at 25°C for 24 hours. Then, the reaction solution was subjected to a reduced pressure to allow for evaporation of isopropyl alcohol, and deionized water was further added thereto, whereby a hydrolysis condensate of aminosilane including 5% of the active ingredient was obtained.

Production Example 2: Production of Hydrolysis Condensate of Aminosilane, Part 2

In a similar manner to Production Example 1, except that the amounts were changed to 20 parts by mass of KBE603, 40 parts by mass of deionized water, and 40 parts by mass of isopropyl alcohol, a hydrolysis condensate of aminosilane including 20% of the active ingredient was obtained.

Example 1

A metal surface treatment liquid for cation electrodeposition coating was obtained by: mixing a 40% aqueous zircon acid solution as a zirconium ion source, tin sulfate as a tin ion source, and hydrofluoric acid; diluting the mixture so as to give a zirconium ion concentration of 500

ppm, and a tin ion concentration of 30 ppm; and adjusting the pH to 3.5 using nitric acid and sodium hydroxide. Measurement of free fluorine ion concentration using a fluorine ion meter after adjusting the pH of this treatment liquid to 3.0 revealed a value of 5 ppm.

Example 2

A metal surface treatment liquid for cation electrodeposition coating was obtained in a similar manner to Example 1 except that: the hydrolysis condensate of aminosilane obtained in Production Example 1 was further added to be 200 ppm; tin sulfate was changed to tin acetate so as to give the tin ion concentration of 10 ppm; and the pH was adjusted to 2.75. Measurement of the free fluorine ion concentration using a fluorine ion meter after adjusting the pH of this treatment liquid to 3.0 revealed a value of 5 ppm.

Example 3

A metal surface treatment liquid for cation electrodeposition coating was obtained in a similar manner to Example 1 except that: polyallylamine "PAATM-H-10C" (manufactured by Nitto Boseki Co., Ltd.) was further added to be 25 ppm; zirconium ion concentration was changed to 250 ppm; and the pH was adjusted to 3.0. Measurement of the free fluorine ion concentration using a fluorine ion meter on this treatment liquid revealed a value of 5 ppm.

Example 4

A metal surface treatment liquid for cation electrodeposition coating was obtained in a similar manner to

Example 1, except that: copper nitrate was further added so as to give a copper ion concentration of 10 ppm; the tin ion concentration was changed to 10 ppm; and the pH was adjusted to 3.0. Measurement of the free fluorine ion concentration using a fluorine ion meter on this treatment liquid revealed a value of 5 ppm.

Example 5

A metal surface treatment liquid for cation electrodeposition coating was obtained in a similar manner to Example 4, except that: the hydrolysis condensate of aminosilane obtained in Production Example 2 was further added to be 200 ppm; and the tin ion concentration was changed to 30 ppm. Measurement of the free fluorine ion concentration using a fluorine ion meter on this treatment liquid revealed a value of 5 ppm.

Example 6

A metal surface treatment liquid for cation electrodeposition coating was obtained in a similar manner to Example 2, except that: aluminum nitrate was further added so as to give an aluminum ion concentration of 200 ppm; and tin sulfate was changed to tin acetate so as to give the tin ion concentration of 30 ppm. Measurement of the free fluorine ion concentration using a fluorine ion meter after adjusting the pH of this treatment liquid to 3.0 revealed a value of 5 ppm.

Examples 7 and 8

Metal surface treatment liquids for cation electrodeposition coating were obtained in a similar manner to

Example 6, except that the pH was adjusted to 3.5 and 4.0. The free fluorine ion concentration measured using a fluorine ion meter after adjusting the pH of this treatment liquid to 3.0 is shown in Table 1.

Examples 9 to 16

Metal surface treatment liquids for cation electrodeposition coating were obtained in a similar manner to Example 7, except that the amount of added 40% aqueous zirconic acid solution, tin sulfate, and aluminum nitrate was changed so as to give a zirconium ion concentration, a tin ion concentration, and an aluminum ion concentration as shown in Table 1. The free fluorine ion concentration measured using a fluorine ion meter after adjusting the pH of this treatment liquid to 3.0 is shown in Table 1.

Example 17

A metal surface treatment liquid for cation electrodeposition coating was obtained in a similar manner to Example 2, except that: indium nitrate was further added so as to give an indium ion concentration of 200 ppm; tin sulfate was changed to tin fluoride so as to give a tin ion concentration of 30 ppm; and the pH was adjusted to 3.5. Measurement of the free fluorine ion concentration using a fluorine ion meter after adjusting the pH of this treatment liquid to 3.0 revealed a value of 5 ppm.

Example 18

A metal surface treatment liquid for cation electrodeposition coating was obtained in a similar manner to

Example 2, except that: diethylenetriamine pentaacetic acid (DTPA) was further added as a chelating agent to give a concentration of 100 ppm; tin acetate was changed to tin sulfate, thereby changing the tin ion concentration to 30 ppm; and further, the zirconium ion concentration was changed to 1,000 ppm. Measurement of the free fluorine ion concentration using a fluorine ion meter after adjusting the pH of this treatment liquid to 3.0 revealed a value of 10 ppm.

Example 19

A metal surface treatment liquid for cation electrodeposition coating was obtained in a similar manner to Example 2, except that: sodium nitrate was further added so as to give a sodium ion concentration of 5,000 ppm; and the tin ion concentration was changed to 30 ppm. Measurement of the free fluorine ion concentration using a fluorine ion meter after adjusting the pH of this treatment liquid to 3.0 revealed a value of 5 ppm.

Example 20

A metal surface treatment liquid for cation electrodeposition coating was obtained in a similar manner to Example 5, except that: glycine as chelating agents and copper nitrate further added so as to give a concentration of 50 ppm and copper ion concentration of 10 ppm, respectively; and the concentration of polyamine was changed to 100 ppm. Measurement of the free fluorine ion concentration using a fluorine ion meter on this treatment liquid revealed a value of 5 ppm.

Examples 21 to 31

Metal surface treatment liquids for cation electrodeposition coating were respectively obtained in a similar manner to Example 1, except that: polyamine as described in Table 1 was added in a specified amount; and the concentration of the other component was changed as shown in Table 1. The free fluorine ion concentrations measured using a fluorine ion meter on these treatment liquids under a condition of pH 3.0 are shown together in Table 1.

Examples 32 to 50

Metal surface treatment liquids for cation electrodeposition coating were respectively obtained in a similar manner to Example 1, except that: sulfonic acid described in Table 2 was added in a specified amount; and polyamine and the other component were changed as shown in Table 2. The free fluorine ion concentrations measured using a fluorine ion meter on these treatment liquids under a condition of pH 3.0 are shown together in Table 2. In Table 2, the used naphthalenesulfonic acid-formaldehyde condensate was DEMOLTM NL manufactured by Kao Corporation; sodium alkylnaphthalenesulfonate was PELEXTM NBL manufactured by Kao Corporation; and sodium polystyrenesulfonate was P-NASS-1 manufactured by Tosoh Corporation.

Examples 51

Metal surface treatment liquids for cation electrodeposition coating were respectively obtained in a similar manner to Example 1, except that: ascorbic acid as described in Table 3 was added in a specified amount; and

polyamine and the other component were changed as shown in Table 3. The free fluorine ion concentrations measured using a fluorine ion meter on these treatment liquids under a condition of pH 3.0 are shown together in Table 3.

Examples 52 to 59

Metal surface treatment liquids for cation electrodeposition coating were respectively obtained in a similar manner to Example 1, except that: the oxidizing agent described in Table 3 was added in a specified amount; and polyamine and the other component were changed as shown in Table 3. The free fluorine ion concentrations measured using a fluorine ion meter on these treatment liquids under a condition of pH 3.0 are shown together in Table 3.

Examples 60 to 74

Metal surface treatment liquids for cation electrodeposition coating were respectively obtained in a similar manner to Example 1, except that: the nitrogen-based rust-preventive agent, the sulfur-based rust-preventive agent, or the phenol-based rust-preventive agent described in Table 3 was added in a specified amount; and polyamine and the other component were changed as shown in Table 3. The free fluorine ion concentrations measured using a fluorine ion meter on these treatment liquids under a condition of pH 3.0 are shown together in Table 3.

Examples 75 to 77

Metal surface treatment liquids for cation electrodeposition coating were respectively obtained in a

similar manner to Example 1, except that: instead of a cold-rolled steel plate (SPC) a high-tensile steel plate was used as the base plate that is the object; and polyamine and the other component described in Table 3 were changed as shown in Table 3. The free fluorine ion concentrations measured using a fluorine ion meter on these treatment liquids under a condition of pH 3.0 are shown together in Table 3.

Examples 78 to 106

With respect to Examples 2, 3, and 5 to 31, metal surface treatment liquids for cation electrodeposition coating were obtained in a similar manner to each Example, except that polyamine was not added. The free fluorine ion concentrations measured using a fluorine ion meter after adjusting the pH of the treatment liquids to 3.0 are shown in Table 4.

Comparative Examples 1 to 6: Preparation of Comparative Metal Surface Treatment Liquid

According to the description in Table 1 and Table 3, comparative metal surface treatment liquids were obtained, respectively, based on the aforementioned Examples. Thus resulting metal surface treatment liquids are summarized in Table 1 and Table 3.

Table 1

	Zr Concentration (ppm)	Tin ion supplying compound	Sn Concentration (ppm)	Sn/Zr ratio	pH	Added Component (Concentration in Parenthesis (ppm))		Free Fluorineion Concentration
						Polyamine Compound	Others	
Example 1	500	tin sulfate	30	0.06	3.5	absent		5
Example 2	500	tin sulfate	10	0.02	2.75	Production Exapmle 1(200)		5
Example 3	250	tin sulfate	30	0.12	3	poly allylamine(25)		5
Example 4	500	tin sulfate	10	0.02	3	absent	copper nitrate(10)	5
Example 5	500	tin sulfate	30	0.06	3	Production Exapmle 2(200)	copper nitrate(10)	5
Example 6	500	tin acetate	30	0.06	2.75	Production Exapmle 1(200)	aluminum nitrate(200)	5
Example 7	500	tin acetate	30	0.06	3.5	Production Exapmle 1(200)	aluminum nitrate(200)	5
Example 8	500	tin acetate	30	0.06	4	Production Exapmle 1(200)	aluminum nitrate(200)	5
Example 9	1000	tin acetate	30	0.03	3.5	Production Exapmle 1(200)	aluminum nitrate(200)	7
Example 10	500	tin acetate	30	0.06	3.5	Production Exapmle 1(200)	aluminum nitrate(500)	5
Example 11	500	tin acetate	30	0.06	3.5	Production Exapmle 1(200)	aluminum nitrate(1000)	5
Example 12	500	tin acetate	10	0.02	3.5	Production Exapmle 1(200)	aluminum nitrate(500)	5
Example 13	500	tin acetate	200	0.4	3.5	Production Exapmle 1(200)	aluminum nitrate(500)	5
Example 14	200	tin acetate	10	0.05	3.5	Production Exapmle 1(200)	aluminum nitrate(200)	7
Example 15	200	tin acetate	30	0.15	3.5	Production Exapmle 1(200)	aluminum nitrate(200)	5
Example 16	200	tin acetate	70	0.35	3.5	Production Exapmle 1(200)	aluminum nitrate(200)	5
Example 17	500	tin fluoride	30	0.06	3.5	Production Exapmle 1(200)	indium nitrate(50)	5
Example 18	1000	tin sulfate	30	0.03	2.75	Production Exapmle 1(200)	DTPA(100)	10
Example 19	500	tin sulfate	30	0.06	2.75	Production Exapmle 1(200)	sodium nitrate(5000)	5
Example 20	500	tin sulfate	30	0.06	3	Production Exapmle 2(100)	coppoer sulfate(10), glycine(50)	5

	Zr Concentration (ppm)	Tin ion supplying compound	Sn Concentration (ppm)	Sn/Zr ratio	pH	Added Component (Concentration in Parenthesis (ppm))		Free Fluorine ion Concentration
						Polyamine Compound	Others	
Example 21	20	tin sulfate	5	0.25	3	Production Exapmle 1(10)		2
Example 22	500	tin sulfate	20	0.04	2	Production Exapmle 1(200)		1
Example 23	500	tin sulfate	30	0.06	5.5	Production Exapmle 1(200)		20
Example 24	5000	tin sulfate	25	0.005	3	Production Exapmle 1(2000)		10
Example 25	50	tin sulfate	10	0.2	3	Production Exapmle 2(50)		3
Example 26	50	tin sulfate	50	1	3	Production Exapmle 2(25)		1
Example 27	500	tin sulfate	30	0.06	3	Production Exapmle 1(50)		0
Example 28	500	tin sulfate	30	0.06	2.75	Production Exapmle 2(50)		0.1
Example 29	500	tin sulfate	30	0.06	2.75	Production Exapmle 2(50)		0.6
Example 30	500	tin sulfate	30	0.06	4	Production Exapmle 1(200)		20
Example 31	500	tin sulfate	30	0.06	4.5	Production Exapmle 1(200)		50
Comparative Example 1	500	absent	0	0	3.5	Production Exapmle 1(200)		7
Comparative Example 2	500	absent	0	0	3	Production Exapmle 1(200)	aluminum nitrate(500)	5
Comparative Example 3	50	absent	0	0	3.5	Production Exapmle 1(200)		5
Comparative Example 4	500	tin sulfate	250	0.5	1	Production Exapmle 1(200)		5
Comparative Example 5	500	tin sulfate	250	0.5	8	Production Exapmle 1(200)		5

Table 2

	Zr Concentration (ppm)	Tin ion supplying compound	Sn Concentration (ppm)	Sn/Zr ratio	pH	Added Component (Concentration in Parenthesis (ppm))			Free Fluorine ion Concentration
						Polyamine Compounds	Other Metal	Others	
Example 32	500	tin sulfate	30	0.06	3.5	Production Exapmple 1(200)		taurine(100)	5
Example 33	500	tin sulfate	30	0.06	3.5	Production Exapmple 1(200)		methan sulfonic acid(100)	5
Example 34	500	tin sulfate	30	0.06	3.5	Production Exapmple 1(200)		isethionic acid(100)	5
Example 35	500	tin sulfate	30	0.06	3.5	Production Exapmple 1(200)		sodium naphthalenedisulfonate (100)	5
Example 36	500	tin sulfate	30	0.06	3.5	Production Exapmple 1(200)		sodium amino naphthalenedisulfonate (100)	5
Example 37	500	tin sulfate	30	0.06	3.5	Production Exapmple 1(200)		sulfosalicylic acid(100)	5
Example 38	500	tin sulfate	30	0.06	3.5	Production Exapmple 1(200)		naphthalene sulfonic acid - formaldehyde condensate (100)	5
Example 39	500	tin sulfate	30	0.06	3.5	Production Exapmple 1(200)		sodium alkyl naphthalene sulfonate(100)	5
Example 40	500	tin sulfate	30	0.06	3.5	Production Exapmple 1(200)	copper nitrate(10)	taurine(100)	5

	Zr Concentration (ppm)	Tin ion supplying compound	Sn Concentration (ppm)	Sn/Zr ratio	pH	Added Component (Concentration in Parenthesis(ppm))			Free Fluorineion Concentration
						Polyamine Compounds	Other Metal	Others	
Example 41	500	tin sulfate	30	0.06	3.5	-	copper nitrate (10)	taurine (100)	5
Example 42	500	tin sulfate	30	0.06	3.5	-	aluminum nitrate (200)	methan sulfonic acid(100)	5
Example 43	500	tin sulfate	30	0.06	3.5	-	copper nitrate(10)	isethionic acid(100)	5
Example 44	500	tin sulfate	30	0.06	3.5	-	aluminum nitrate (200)	sodium naphthalenedisulfonate (100)	5
Example 45	500	tin sulfate	30	0.06	3.5	-	copper nitrate(10)	sodium aminonaphthalenedisulfo nate(100)	5
Example 46	500	tin sulfate	30	0.06	3.5	-	aluminum nitrate (200)	sulfosalicylic acid(100)	5
Example 47	500	tin sulfate	30	0.06	3.5	-	copper nitrate(10)	naphthalene sulfonic acid - formaldehyde condensate(100)	5
Example 48	500	tin sulfate	30	0.06	3.5	-	aluminum nitrate (200)	sodium alkyl naphthalene sulfonate(100)	5
Example 49	500	tin sulfate	30	0.06	3.5	-	copper nitrate(10)	sodium styrenesulfonate (100)	5
Example 50	500	tin sulfate	30	0.06	3.5	-	aluminum nitrate (200)	sodium polystyrene sulfonate(100)	5

Table 3

	Zr Concentration (ppm)	Tin ion supplying compound	Sn Concentration (ppm)	Sn/Zr ratio	pH	Added Component (Concentration in Parenthesis(ppm))			Free Fluorineion Concentration
						Polyamine Compounds	Other Metal	Others	
Example 51	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	-	sodium ascorbate (50)	5
Example 52	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	-	as sodium nitrate (10000)	5
Example 53	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	-	hydrogen peroxide(10)	5
Example 54	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	-	sodium nitrite(50)	5
Example 55	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	-	sodium bromate(100)	5
Example 56	500	tin sulfate	30	0.06	3.5	-	copper nitrate(10)	as sodium nitrate (10000)	5
Example 57	500	tin sulfate	30	0.06	3.5	-	aluminum nitrate (200)	hydrogen peroxide(10)	5
Example 58	500	tin sulfate	30	0.06	3.5	-	copper nitrate(10)	sodium nitrite(50)	5
Example 59	500	tin sulfate	30	0.06	3.5	-	aluminum nitrate (200)	sodium bromate(100)	5

	Zr Concentration (ppm)	Tin ion supplying compound	Sn Concentration (ppm)	Sn/Zr ratio	pH	Added Component (Concentration in Parenthesis (ppm))			Free Fluorine ion Concentration
						Polyamine Compounds	Other Metal	Others	
Example 60	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	-	hydroquinone(100)	5
Example 61	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	-	ethylene urea(100)	5
Example 62	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	-	quinolinol(100)	5
Example 63	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	-	thiourea(100)	5
Example 64	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	-	benzotriazole(100)	5
Example 65	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	-	mercaptobenzothiazole (100)	5
Example 66	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	-	KBM803(100)	5
Example 67	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	copper nitrate(10)	benzotriazole(100)	5
Example 68	500	tin sulfate	30	0.06	3.5	-	copper nitrate(10)	hydroquinone(100)	5

	Zr Concentration (ppm)	Tin ion supplying compound	Sn Concentration (ppm)	Sn/Zr ratio	pH	Added Component (Concentration in Parenthesis (ppm))			Free Fluorine Ion Concentration
						Polyamine Compounds	Other Metal	Others	
Example 69	500	tin sulfate	30	0.06	3.5	-	copper nitrate(10)	ethylene urea(100)	5
Example 70	500	tin sulfate	30	0.06	3.5	-	copper nitrate(10)	quinolinol(100)	5
Example 71	500	tin sulfate	30	0.06	3.5	-	copper nitrate(10)	thiourea(100)	5
Example 72	500	tin sulfate	30	0.06	3.5	-	copper nitrate(10)	benzotriazole(100)	5
Example 73	500	tin sulfate	30	0.06	3.5	-	copper nitrate(10)	mercaptobenzothiazole (100)	5
Example 74	500	tin sulfate	30	0.06	3.5	-	copper nitrate(10)	KEM803(100)	5
Example 75	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	copper nitrate(10)	as sodium nitrate (10000)	5
Example 76	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	copper nitrate(10)	taurine(100)	5
Example 77	500	tin sulfate	30	0.06	3.5	Production Example 1(200)	copper nitrate(10)	benzotriazole(100)	5
Comparative Example 6	500	-	-	-	3.5	Production Example 1(200)	-		5

Table 4

	Zr Concentration (ppm)	Tin ion supplying compound	Sn Concentration (ppm)	Sn/Zr ratio	pH	Added Component (Concentration in Parenthesis (ppm))		Free Fluorine ion Concentration
						Polyamine Compound	Others	
Example 78	500	tin sulfate	10	0.02	2.75	-		5
Example 79	250	tin sulfate	30	0.12	3	-		5
Example 80	500	tin sulfate	30	0.06	3	-	copper nitrate(10)	5
Example 81	500	tin sulfate	30	0.06	2.75	-	aluminum nitrate(200)	5
Example 82	500	tin acetate	30	0.06	3.5	-	aluminum nitrate(200)	5
Example 83	500	tin acetate	30	0.06	4	-	aluminum nitrate(200)	5
Example 84	1000	tin acetate	30	0.03	3.5	-	aluminum nitrate(200)	7
Example 85	500	tin acetate	30	0.06	3.5	-	aluminum nitrate(500)	5
Example 86	500	tin acetate	30	0.06	3.5	-	aluminum nitrate(1000)	5
Example 87	500	tin acetate	10	0.02	3.5	-	aluminum nitrate(500)	5
Example 88	500	tin acetate	200	0.4	3.5	-	aluminum nitrate(500)	5
Example 89	200	tin acetate	10	0.05	3.5	-	aluminum nitrate(200)	7
Example 90	200	tin acetate	30	0.15	3.5	-	aluminum nitrate(200)	5
Example 91	200	tin acetate	70	0.35	3.5	-	aluminum nitrate(200)	5
Example 92	500	tin fluoride	30	0.06	3.5	-	indium nitrate(50)	5
Example 93	1000	tin sulfate	30	0.03	2.75	-	DTPA(100)	10
Example 94	500	tin sulfate	30	0.06	2.75	-	sodium nitrate(5000)	5

	Zr Concentration (ppm)	Tin ion supplying compound	Sn Concentration (ppm)	Sn/Zr ratio	pH	Added Component (Concentration in Parenthesis(ppm))		Free Fluorineion Concentration
						Polyamine Compound	Others	
Example 95	500	tin sulfate	30	0.06	3	-	copper nitrate(10), glycine(50)	5
Example 96	20	tin sulfate	5	0.25	3	-		2
Example 97	500	tin sulfate	20	0.04	2	-		1
Example 98	500	tin sulfate	30	0.06	5.5	-		20
Example 99	5000	tin sulfate	25	0.005	3	-		10
Example 100	50	tin sulfate	10	0.2	3	-		3
Example 101	50	tin sulfate	50	1	3	-		1
Example 102	500	tin sulfate	30	0.06	3	-		0
Example 103	500	tin sulfate	30	0.06	2.75	-		0.1
Example 104	500	tin sulfate	30	0.06	2.75	-		0.6
Example 105	500	tin sulfate	30	0.06	4	-		20
Example 106	500	tin sulfate	30	0.06	4.5	-		50

Surface Treatment

As metal base materials, a commercially available cold-rolled steel plate (SPC, manufactured by Nippon Testpanel Co., Ltd., 70 mm x 150 mm x 0.8 mm) was provided for Examples 1 to 74, Examples 78 to 106, and Comparative Examples 1 to 5, and a high-tensile steel plate (70 mm x 150 mm x 1.0 mm) was provided for Examples 75 to 77, and Comparative Example 6. These plates were subjected to a degreasing treatment using "SURFCLEANERTM EC92" (manufactured by Nippon Paint Co., Ltd.) as an alkali degreasing treatment agent at 40°C for 2 minutes. This plate was dipped and washed in a water washing bath, and then washed by spraying tap water thereon for approximately 30 seconds.

The metal base material following the degreasing treatment was subjected to a surface treatment by dipping thereof in the metal surface treatment liquid prepared in Examples and Comparative Examples at 40°C for 90 seconds. However, the treatment time period was 240 seconds and 15 seconds, respectively, in Examples 21 and 22. After completing the surface treatment, the plate was dried at 40°C for 5 minutes, and the thus surface treated metal base material was obtained. Unless specifically stated, this surface treated metal base material was used as a test plate in the following evaluation.

Measurement of Element Content in Coating Film

The content of each element included in the coating film was measured using an X-ray fluorescence spectrometer

"XRF1700" manufactured by Shimadzu Corporation.

Primary Rust Prevention

After immersing the test plate in pure water at 25°C for 5 hours, the generation state of rust was visually observed.

A: no rust generation observed

B: slightly generated rust observed

C: rust generation clearly identified

Observation of Sludge

With 10 L of the surface treatment liquids of the Examples and Comparative Examples, 200 test panels were subjected to the surface treatment and evaluation was made according to the following standards through visual observation as to whether the surface treatment liquid became turbid due to generation of sludge following the lapse of 30 days at room temperature.

A: transparent liquid

B: slightly turbid

C: turbid

D: precipitate (sludge) generated

Evaluation of Throwing Power

The throwing power was evaluated according to a "four-plate box method" described in Japanese Patent Publication No. 2000-038525. More specifically, as shown in Fig. 1, test plates 1 to 4 were arranged to stand up in parallel with intervals of 20 mm to produce a box 10 sealed with an insulator such as cloth adhesive tape at the underneath of both side faces and the bottom face. Through-holes 5 having a

diameter of 8 mm were provided underneath the metal materials 1, 2 and 3, except for metal material 4.

This box 10 was dipped into an electrodeposition coating vessel 20 filled with a cation electrodeposition coating solution "POWERNICS™ 110" (manufactured by Nippon Paint Co., Ltd.). In this case, the cation electrodeposition coating solution entered inside the box 10 only from each through-hole 5.

Each of the test plates 1 to 4 was electrically connected while stirring the cation electrodeposition coating solution with a magnetic stirrer, and a counter electrode 21 was arranged such that the distance from the test plate 1 became 150 mm. Voltage was applied with each of the test plates 1 to 4 as cathodes, and the counter electrode 21 as an anode to execute cation electrodeposition coating. The coating was carried out by elevating to the intended voltage (210 V and 160 V) over 30 seconds from initiation of the application, and thereafter maintaining the voltage for 150 seconds. The bath temperature in this process was regulated to 30°C.

After washing each of the test plates 1 to 4 with water after coating, they were baked at 170°C for 25 minutes, followed by air cooling. The throwing power was then evaluated by measuring the film thickness of the coated film formed on side A of the test plate 1 that is the closest to the counter electrode 21, and the film thickness of the coated film formed on side G of the test plate 4 that is the farthest from the counter electrode 21 to determine a ratio of the film

thickness (side G)/film thickness (side A). As this value becomes greater, better evaluation of the throwing power can be decided. The acceptable level was no less than 40%.

Coating Voltage

Using the surface treatment liquids of Examples and Comparative Examples, cold-rolled steel plates and zinc coated steel plates were subjected to a surface treatment, whereby test plates were obtained. Using the cation electrodeposition coating solution "POWERNICS™ 110" described above on these test plates, the voltage required for obtaining a 20 μm electrodeposition coated film was determined. The difference in coating voltage required for obtaining the 20 μm electrodeposition coated film was then determined between the case in which the metal base material was a zinc coated steel plate, and the case of the cold-rolled steel plate. As the difference becomes smaller, superiority as a surface treated coating film is suggested. A difference of no greater than 40 V is acceptable.

The voltage required for obtaining a 20 μm electrodeposition coated film was determined as in the following manner. Under the electrodeposition condition, the voltage was elevated to a specified voltage over 30 seconds, and thereafter maintaining for 150 seconds. The resulting film thickness was measured. Such a procedure was conducted for 150 V, 200 V, and 250 V. Thus, a voltage to give a 20 μm film thickness was derived from the formula of relationship between the determined voltage and the film thickness.

Appearance of Coating

The test plate was subjected to cation electrodeposition coating, and the appearance of the resulting electrodeposition coated film was evaluated according to the following standards. The results are shown in Tables 5 to 8.

- A: uniform coated film obtained
- B: nearly uniform coated film obtained
- C: some non-uniformity of the coated film found
- D: non-uniformity of the coated film found

Secondary Adhesion Test (SDT)

After forming a 20 μm electrodeposition coated film, the test plates were incised to provide two parallel cut lines that ran longitudinally, with the depth to reach to the metal basis material, and then immersed in a 5% aqueous sodium chloride solution at 55°C for 240 hours. After water washing and air drying, an adhesive tape "L-PACK™ LP-24" (manufactured by Nichiban Co., Ltd.) was adhered to the portion including the cuts. Then, the adhesive tape was peeled off abruptly. The maximum width (one side) of the coating adhered to the stripped adhesive tape was measured.

- A: 0 mm
- B: less than 2 mm
- C: at least 2 mm to less than 5 mm
- D: no less than 5 mm

Cycle Corrosion Test (CCT)

After forming the 20 μm electrodeposition coated film on the test plate, the edge and back face was sealed with a tape,

thereby providing cross cuttings that reached to the metal basis material. A 5% aqueous sodium chloride solution incubated at 35°C was continuously sprayed for 2 hours onto this sample in a salt spray tester kept at 35°C, and with a humidity of 95%. Subsequently, it was dried under conditions of 60°C and with a humidity of 20 to 30% for 4 hours. Such a sequence of procedures repeated three times in 24 hours was defined as one cycle, and 200 cycles were carried out. Thereafter, the width of the swelling portion of the coated film (both sides) was measured.

A: less than 6 mm

B: at least 6 mm to less than 8 mm

C: at least 8 mm to less than 10 mm

D: no less than 10 mm

Salt Spray Test (SST)

After forming the 20 μ m electrodeposition coated film on the test plate, the edge and the back face were sealed with a tape, thereby providing cross cuttings that reached to the metal basis material. A 5% aqueous sodium chloride solution incubated at 35°C was continuously sprayed for 840 hours to this sample in a salt spray tester kept at 35°C, and with a humidity of 95%. After washing with water and air drying, an adhesive tape "L-PACKTM LP-24" (manufactured by Nichiban Co., Ltd.) was adhered on the portion including the cuts. Then, the adhesive tape was peeled off quickly. The maximum width (one side) of the coating adhered to the stripped adhesive tape was measured.

A: less than 2 mm

B: at least 2 mm to less than 5 mm

C: no less than 5 mm

The evaluation results are summarized in Tables 5 to 8.

Table 5

	Content of Element				Primary Rust Prevention	Observation of sludge	Throwing Power(%)		Difference in Coating Voltage (V)	Appearance of Coating	SDT	CCT	SST
	Zr	Si	Sn	Cu			210V	160V					
Example 1	45		22		A	B	60%	52%	30	A	-	B	A
Example 2	51	3.3	13		A	B	57%	25%	40	B	A	B	A
Example 3	44		24		A	B	57%	44%	40	A	B	B	A
Example 4	55		16	8	A	B	58%	51%	40	A	A	A	A
Example 5	46	6.2	27	11	A	B	61%	55%	20	A	A	A	A
Example 6	42	3.5	19		A	B	57%	47%	40	A	A	B	A
Example 7	56	3.7	15	-	A	B	53%	42%	30	B	A	B	A
Example 8	62	4.1	12	-	A	C	51%	39%	30	B	A	B	A
Example 9	41	2.3	16	-	A	B	53%	41%	30	B	B	B	A
Example 10	72	2.4	15	-	A	C	54%	43%	30	B	A	B	A
Example 11	62	2.4	15	-	A	C	53%	43%	30	B	B	B	A
Example 12	75	3.2	10	-	A	C	49%	40%	30	B	A	A	A
Example 13	32	2.1	31	-	A	B	59%	51%	20	B	B	B	A
Example 14	52	2.5	12	-	A	B	58%	30%	40	B	A	B	A
Example 15	38	2.3	18		A	B	59%	48%	20	B	B	B	A
Example 16	31	2.1	23		A	B	62%	50%	20	B	B	B	A
Example 17	55	3	22		A	B	59%	50%	20	A	A	B	A
Example 18	51	3.3	19		A	A	56%	51%	30	A	B	B	A
Example 19	44	2.5	23		A	B	56%	49%	30	A	A	B	A
Example 20	48	4.8	22	6	A	A	58%	52%	20	A	B	A	A
Example 21	28	1.8	21		A	B	52%	44%	30	B	B	B	A
Example 22	63	4.2	28		A	B	55%	49%	30	B	B	B	A
Example 23	44	2.9	26		A	B	60%	43%	30	B	B	B	A
Example 24	77	5.1	31		A	B	52%	52%	20	B	A	A	A
Example 25	34	2.6	26		A	B	51%	41%	30	B	B	B	A

	Content of Element				Primary Rust Prevention	Observation of sludge	Throwing Power(%)		Difference in Coating Voltage (V)	Appearance of Coating	SDT	CCT	SST
	Zr	Si	Sn	Cu			210V	160V					
Example 26	42	2.6	27		A	B	62%	48%	20	B	B	B	A
Example 27	38	2.7	18		A	B	52%	29%	40	B	B	B	A
Example 28	38	3.5	21		A	B	53%	36%	30	B	B	B	A
Example 29	41	3	26		A	B	55%	42%	30	B	B	B	A
Example 30	44	3	22		A	B	58%	41%	30	B	A	A	A
Example 31	47	3.5	25		A	B	57%	48%	20	B	A	A	A
Comparative Example 1	52	3.5			B	B	21%	12%	80	C	B	C	A
Comparative Example 2	55	3.3			B	B	36%	15%	50	B	D	C	B
Comparative Example 3	5.2	0.1	38		A	B	60%	55%	30	B	D	D	C
Comparative Example 4	1.2	0.1	0.2		C	D	57%	45%	30	B	D	D	C
Comparative Example 5	0	0	0		C	-	38%	-	-	B	D	D	C

Table 6

	Content of Element				Primary Rust Prevention	Observation of sludge	Throwing Power(%)		Difference in Coating Voltage (V)	Appearance of Coating	SDT	CCT	SST
	Zr	Si	Sn	Cu			210V	160V					
Example 32	42	3.2	18		A	B	69%	61%	10	A	A	A	A
Example 33	45	3.3	16		A	B	62%	57%	20	A	A	A	A
Example 34	41	3	15		A	B	62%	55%	20	A	A	A	A
Example 35	38	2.9	16		A	B	64%	51%	30	A	A	A	A
Example 36	44	3.1	19		A	B	61%	53%	30	A	A	A	A
Example 37	51	3.6	21		A	B	59%	52%	30	A	A	A	A
Example 38	48	3.5	16		A	B	60%	47%	30	A	A	A	A
Example 39	42	32	22		A	B	60%	46%	20	A	A	A	A
Example 40	55	3.8	18	8	A	B	69%	62%	10	A	A	A	A
Example 41	48		18	8	A	B	68%	65%	10	A	A	A	A
Example 42	41		16		A	B	65%	60%	20	A	B	B	A
Example 43	52		17	7	A	B	65%	60%	20	A	B	A	A
Example 44	43		18		A	B	62%	55%	30	A	B	B	A
Example 45	55		18	9	A	B	60%	56%	30	A	B	A	A
Example 46	43		16		A	B	59%	53%	30	A	B	B	A
Example 47	58		20	6	A	B	61%	49%	30	A	B	A	A
Example 48	45		19		A	B	62%	47%	30	A	B	B	A
Example 49	56		17	7	A	B	58%	44%	40	A	B	A	A
Example 50	41		16		A	B	58%	45%	40	A	B	B	A

Table 7

	Content of Element				Primary Rust Prevention	Observation of sludge	Throwing Power (%)		Difference in Coating Voltage (V)	Appearance of Coating	SDT	CCT	SST
	Zr	Si	Sn	Cu			210V	160V					
Example 51	91	5.7	19		A	B	62%	55%	30	A	A	A	A
Example 52	75	5.1	21		A	B	57%	50%	30	A	A	A	A
Example 53	81	5.3	18		A	B	56%	51%	30	A	A	A	A
Example 54	88	5.7	14		A	B	59%	47%	30	A	A	A	A
Example 55	72	4.8	17		A	B	60%	50%	30	A	A	A	A
Example 56	72		18	6	A	B	59%	51%	20	A	B	B	A
Example 57	85		21		A	B	57%	48%	30	A	B	B	A
Example 58	91		20	7	A	B	59%	51%	20	A	B	B	A
Example 59	94		18		A	B	60%	52%	30	A	B	B	A
Example 60	44	3.2	15		A	B	62%	55%	30	A	A	A	A
Example 61	46	3.1	19		A	B	61%	51%	30	A	A	A	A
Example 62	49	3.6	18		A	B	60%	53%	30	A	A	A	A
Example 63	38	3	20		A	B	65%	57%	20	A	A	A	A
Example 64	44	3.2	16		A	B	66%	55%	20	A	A	A	A
Example 65	41	3.5	17		A	B	61%	58%	20	A	A	A	A
Example 66	49	3.2	16		A	B	62%	55%	30	A	A	A	A
Example 67	41	3.2	15	7	A	B	68%	59%	20	A	A	A	A
Example 68	51		18	7	A	B	59%	53%	30	A	B	A	A
Example 69	52		18	5	A	B	63%	51%	30	A	B	A	A
Example 70	48		19	9	A	B	61%	53%	30	A	B	A	A
Example 71	55		17	6	A	B	65%	55%	30	A	B	A	A
Example 72	43		16	10	A	B	62%	58%	20	A	B	A	A
Example 73	49		20	7	A	B	66%	54%	20	A	B	A	A
Example 74	52		17	5	A	B	62%	52%	30	A	B	A	A
Example 75	67	4.7	18		A	B	59%	52%	30	A	A	A	A
Example 76	54	3.2	16		A	B	62%	58%	20	A	A	A	A
Example 77	48	2.8	17		A	B	59%	50%	30	A	A	A	A
Comparative Example 6	58	4.2			B	B	22%	10%	80	C	B	D	B

Table 8

	Content of Element				Primary Rust Prevention	Observation of sludge	Throwing Power (%)		Difference in Coating Voltage (V)	Appearance of Coating	SDT	CCT	SST
	Zr	Si	Sn	Cu			210V	160V					
Example 78	55		13		A	B	58%	50%	40	B	C	B	B
Example 79	44		24		A	B	58%	25%	40	B	C	B	B
Example 80	49		21		A	B	69%	55%	30	A	C	A	B
Example 81	45		18		A	B	59%	50%	20	A	C	A	B
Example 82	38		26		A	B	60%	50%	20	A	C	A	B
Example 83	45		9		A	B	59%	51%	20	A	C	A	B
Example 84	51		18		A	B	58%	52%	20	A	C	A	B
Example 85	43		21		A	B	60%	54%	20	A	C	A	B
Example 86	36		18		A	B	61%	53%	10	A	C	A	B
Example 87	47		23		A	B	59%	51%	10	A	C	A	B
Example 88	32		33		A	B	60%	53%	20	A	C	A	B
Example 89	52		12		A	B	61%	53%	20	A	C	A	B
Example 90	42		21		A	B	60%	51%	20	A	C	A	B
Example 91	36		28		A	B	59%	53%	20	A	C	A	B
Example 92	50		22		A	B	60%	51%	30	A	C	B	B
Example 93	50		24		A	A	55%	48%	30	B	C	B	B
Example 94	46		26		A	B	58%	49%	30	B	C	B	B
Example 95	46		15		A	A	60%	51%	20	A	C	A	B
Example 96	30		21		A	B	56%	48%	40	B	C	B	B
Example 97	65		26		A	B	57%	47%	30	A	C	B	B
Example 98	42		19		A	B	53%	50%	30	A	C	B	B
Example 99	72		21		A	B	52%	49%	30	A	C	B	B
Example 100	33		10		A	B	56%	32%	40	B	C	B	B
Example 101	43		22		A	B	52%	52%	20	A	C	B	B
Example 102	40		24		A	B	58%	42%	20	A	C	B	B
Example 103	43		16		A	B	57%	48%	30	B	C	B	B
Example 104	41		17		A	B	54%	34%	30	A	C	B	B
Example 105	40		21		A	B	57%	33%	30	A	C	B	B
Example 106	40		11		A	B	55%	45%	30	A	C	B	B

INDUSTRIAL APPLICABILITY

The metal surface treatment liquid for cation electrodeposition coating of the present invention is applicable to metal base materials, such as automobile bodies and parts to be subjected to cation electrodeposition.

CLAIMS

1. A metal surface treatment liquid for treating a metal base material prior to cation electrodeposition coating of the metal base material, the liquid having a pH of 1.5 to 6.5 and comprising:

(i) fluorine ions, wherein the amount of free fluorine ions at a pH of 3.0 is 1 to 50 ppm;

(ii) 10 to 10,000 ppm zirconium ions;

(iii) tin ions, wherein a concentration ratio of the tin ions to the zirconium ions is in the range of 0.005 to 1 on a mass basis;

(iii) a polyamine compound selected from the group consisting of hydrolysis condensates of aminosilane, polyvinylamine, and polyallylamine; and

A) a chelate compound, wherein the chelate compound is selected from the group consisting of amino acid, aminocarboxylic acid, and a sulfonic acid selected from the group consisting of methanesulfonic acid, isethionic acid, taurine, naphthalenedisulfonic acid, aminonaphthalenedisulfonic acid, sulfosalicylic acid, a naphthalenesulfonic acid-formaldehyde condensate, alkyl naphthalenesulfonic acid, salts thereof, and sodium polystyrenesulfonate, or

B) a nitrogenous, sulfur and/or phenolic rust-preventive agent selected from the group consisting of hydroquinone, ethyleneurea, quinolinol, thiourea, benzotriazole, salts

thereof, and mercaptobenzothiazole; or

C) indium ions.

2. The metal surface treatment liquid of claim 1, further comprising copper ions.

3. The metal surface treatment liquid of claim 1 or 2, further comprising an oxidizing agent.

4. The metal surface treatment liquid of any one of claims 1 to 3, further comprising aluminum ions.

5. A method of metal surface treatment comprising a step of subjecting a metal base material to a surface treatment with the metal surface treatment liquid according to any one of claims 1 to 4.

6. The method of claim 5, further comprising the step of subjecting the surface treated metal base material to cation electrodeposition coating.

7. A metal base material comprising a coating film formed by the method of metal surface treatment according to claim 5 or 6.

8. The metal base material according to claim 7, wherein an element ratio of zirconium/tin on a mass basis in the coating

film is in the range of 1/10 to 10/1.

FIG. 1

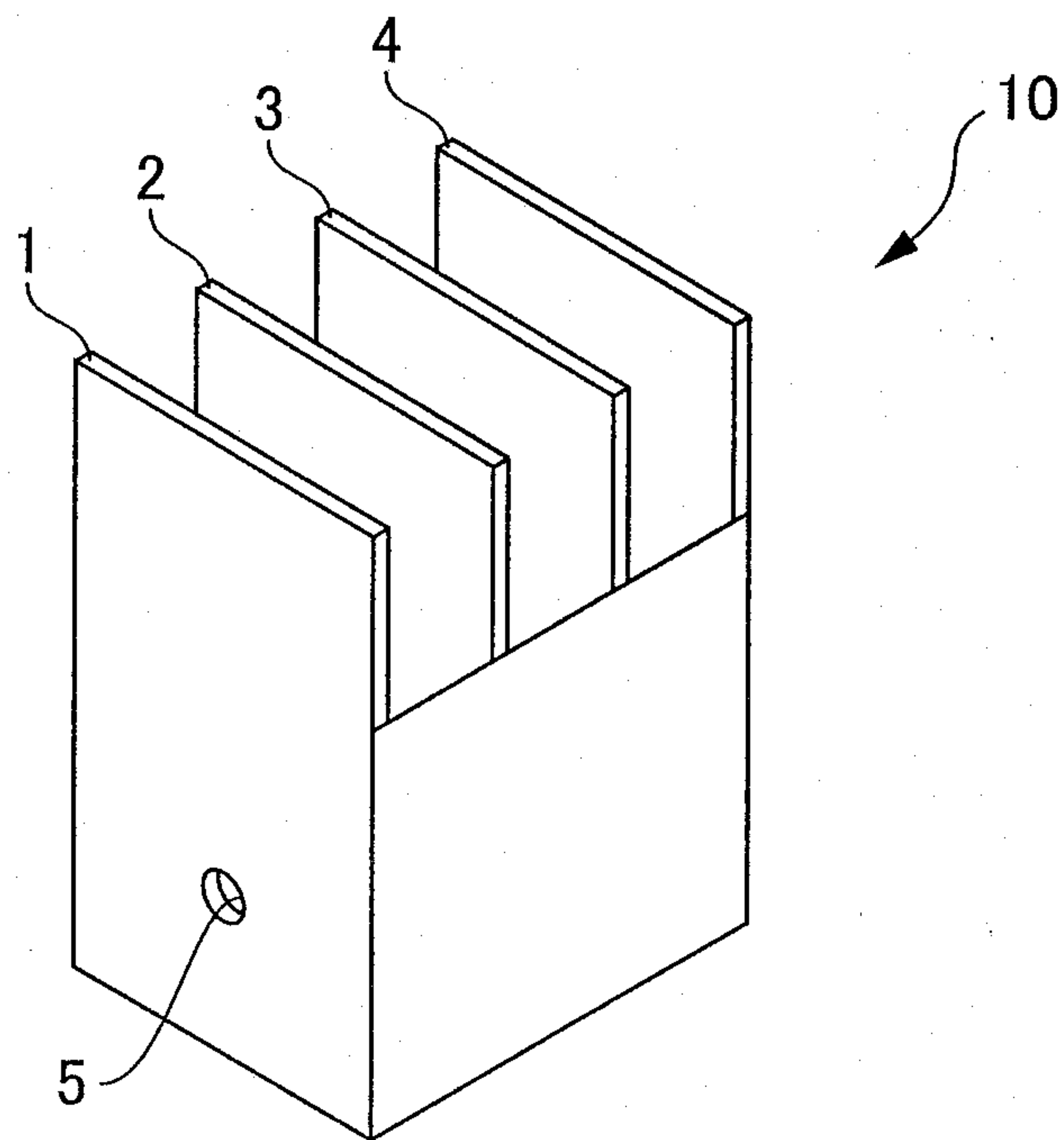


FIG. 2

