

SPECIFICATION



159159

SURFACE TREATMENT COMPOSITION
AND
SURFACE TREATMENT METHOD
FOR METALLIC MATERIALS



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Technical Field

- 10 This invention relates to a surface treatment composition and a surface treatment method adapted to make the surface of a metallic material highly corrosion-resistant and paintable.

Background Art

- 15 Generally, metallic materials such as Zinc plated steel plates and aluminium plates find a wide variety of applications including automobiles, building materials and electric appliances for home use. However, both zinc and aluminium have a drawback that they can easily corrode in air to produce a corrosion
20 product (so-called white rust), which by turn degrades the appearance of the metallic material and adversely affects the adhesion of the paint applied thereto.

- In view of this problem, a chromate treatment process is generally used for treating the surface of the metallic material
25 with a treatment solution containing chromic acid, dichromic acid or a salt of either of them as principal ingredient in order to improve the corrosion-resistance and the paint adhesion of the surface of the metallic material.

However, in the trend of tighter environment protection in

recent years, the chromate treatment has become rapidly unpopular mainly because hexavalent chromium contained in the chromate treatment solution hurts the human body. Additionally, waste water containing hexavalent chromium is required to be subjected to a specific treatment process conforming to the provision of Water Pollution Control Law, which by turn raises the overall manufacturing cost. Furthermore, chromate-treated metallic materials are classified as chromium-contaminated industrial wastes after use and cannot be recycled. These problems and other problems of chromate treatment now make the use of such a treatment process a significant social issue.

Meanwhile, known surface treatment methods that does not involve the use of chromate include those using a surface treatment agent containing tannic acid and one or more than one polyphenol carboxylic acids. A metallic material treated with aqueous solution of tannic acid improves the corrosion-resistance of the metallic material because the reaction product of tannic acid and the metallic material operates as protective coat and prevents the invasion of corrosive substances.

As a result of the increasing demand for high quality metallic materials in recent years, the protective coat is currently required to be highly corrosion-resistant. However, protective coats of metallic materials formed by using tannic acid alone or in combination with one or more than one inorganic substances cannot meet the requirement of high corrosion-resistance. Therefore, currently, the use of tannic acid for the surface treatment of metallic materials is not industrially feasible.

JPA 53-121034 discloses a surface treatment method of applying an aqueous solution of water-dispersible silica, alkyd resin and a

trialkoxo silane compound to the surface of a metallic material in order to improve the corrosion-resistance.

A number of patent documents including JPA 57-44751 and JPA 1-177380 disclose surface treatment methods for providing a metallic material with corrosion-resistance by using water-soluble resin of a derivative of a hydroxy pyrone compound and methods for providing a metallic material with corrosion-resistance by using a water-soluble or water-dispersible polymer of a hydroxy styrene compound.

However, none of the above listed methods can satisfactorily form a coat on the surface of a metallic material to such a level of corrosion-resistance that it can replace a chromate coat. Thus, the above pointed out problems remain unsolved. In short, there has not been realized any non-chromium type surface treatment agent nor surface treatment method to date that provides metallic materials with a remarkable level of corrosion-resistance.

Disclosure Of The Invention

In view of the above identified circumstances, it is therefore the object of the present invention to provide a non-chromium type surface treatment agent that makes metallic materials highly corrosion-resistant and paintable.

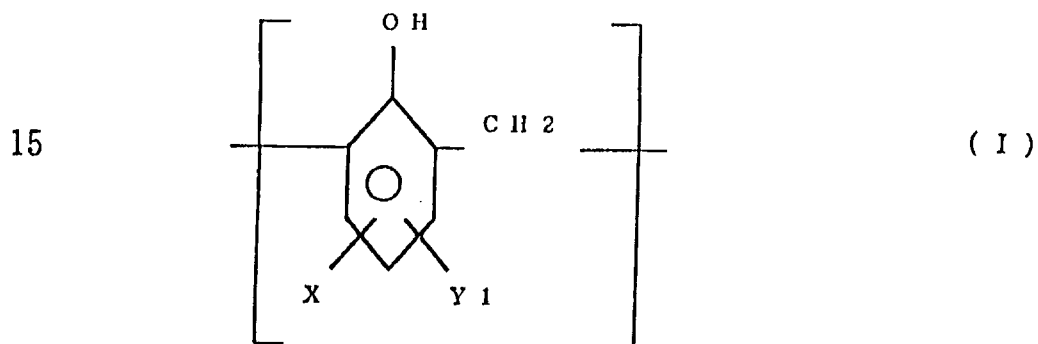
As a result of intensive efforts for solving the problems of the prior art, the inventors of the present invention came to find that a highly corrosion-resistant, paintable and coin-scratch-resistant coat can be formed on the surface of a metallic material by using a surface treatment agent containing as ingredients a silane coupling agent, a water-soluble polymer having a specific chemical structure and a colloidally dispersed inorganic compound.

The present invention is based on this finding.

Thus, according to the invention, there is provided a surface treatment composition to be used for a metallic material, said aqueous composition comprising:

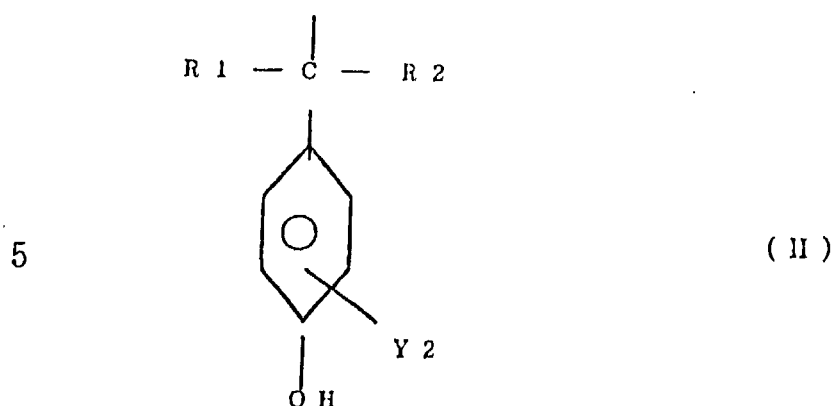
5 (A) a silane coupling agent containing one or more than one silane coupling compounds having at least a reactive functional group selected from an active-hydrogen-containing amino group, an epoxy group, a vinyl group, a mercapto group and a methacryloxy group:

10 (B) one or more than one water-soluble polymers, each being expressed by general formula (I) below and showing an average degree of polymerisation between 2 and 50:

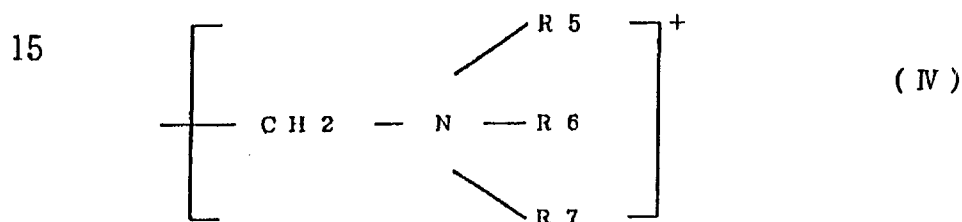
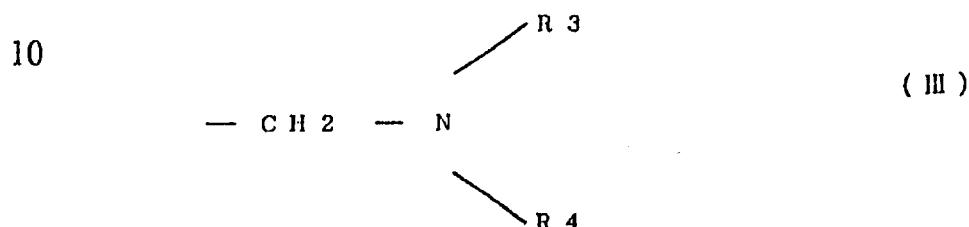


where X bonded to the benzene ring represents a hydrogen atom, a
 20 hydroxyl group, an alkyl group with any of C1 through C5, a hydroxyalkyl group with any of C1 through C5, an aryl group with any of C6 through C12, a benzyl group, a benzal group, an unsaturated hydrocarbon group adapted to be condensed with said benzene ring and form a naphthalene ring or a group expressed by
 25 formula (II) below:

where each of R1 and R2 represents a hydrogen atom, a hydroxyl group, an alkyl group with any of C1 through C5 or a hydroxyalkyl group with any of C1 through C10, each of Y1 and Y2 bonded to the respective benzene rings in formulas (I) and (II) representing a Z



group expressed independently by formula (III) or (IV) below:



where each of R₃, R₄, R₅, R₆ and R₇ represents a hydrogen atom, an
 20 alkyl group with any of C₁ through C₁₀ or a hydroxyalkyl group
 with any of C₁ through C₁₀ independently relative to each other
 and the average number of substitutions of Z group in each of the
 benzene rings of said polymer molecule is between 0.2 and 1.0; and

(C) one or more than one inorganic compound selected from a
 25 group of silica, silicates, compounds of metal salts and a mixture
 of any of them, each are being dispersed in said aqueous medium in
 a colloidal state.

In a surface treatment composition according to the invention,
 preferably, the ratio by weight of said component (A) that is

silane coupling agent to said component (B) that is water-soluble polymers, namely (A) : (B) is between 1:10 and 10:1, and the ratio by weight of said component (C) that is inorganic compound to [(A) + (B)], namely (C) : [(A) + (B)] is preferably between 1:5 and 5:5 1.

In a surface treatment composition according to the invention, preferably, said component (A) of said silane coupling agent contains (a) a silane coupling agent containing one or more than one silane coupling compounds having one or more than one active-10 hydrogen-containing amino groups and (b) a silane coupling agent containing one or more than one silane coupling compounds having one or more than one epoxysilane groups.

In a surface treatment composition according to the invention, preferably, the equivalent ratio of the active-hydrogen-containing15 amino groups contained in said silane coupling agent (a) to the epoxysilane groups contained in said silane coupling agent (b) is between 3:1 and 1:3.

In a surface treatment composition according to the invention, preferably, the ratio by weight of the sum of said silane coupling20 agent (a) and said silane coupling agent (b) to said water-soluble polymer component (B), namely [(a) + (b)] : (B) is between 1:5 and 5:1.

In another aspect of the invention, there is provided a surface treatment method to be used for a metallic material25 comprising:

using a surface treatment aqueous composition according to the invention with the pH value regulated to between 2.0 and 6.5 to put and adhere to the surface of the metallic

material and drying it to form a coat having a dried weight of between 0.01 and 2.0g/m².

With a surface treatment method according to the invention, preferably, the surface of the metallic material to be treated is
5 preliminarily treated by means of a phosphating or a plating process before adhering said aqueous surface treatment solution to the surface of the metallic material.

As described above, a surface treatment composition to be used for a metallic material according to the invention is an aqueous
10 solution containing component (A) which is a silane coupling agent containing one or more than one silane coupling compounds having a specific reactive functional group, component (B) which is one or more than one water-soluble phenol resin type polymers having a specific amino group and component (C) which is one or more than
15 one inorganic compound selected from a group of silica, silicates, compounds of metal salts and a mixture of any of them each are being dispersed in said aqueous medium in a colloidal state.

The silane coupling compounds contained in the component (A) are not subjected to any structural limitations so long as each of
20 them has at least a reactive functional group selected from an active-hydrogen-containing amino group, an epoxy group, a vinyl group, a mercapto group and a methacryloxy group. Specific examples of silane coupling compounds that can be used for the purpose of the invention include those listed in ① through ⑤
25 below:

① compounds having an amino group:

N-(2-aminoethyl)3-aminopropylmethyldimethoxysilane,
N-(aminoethyl)3-aminopropyltrimethoxysilane and
3-aminopropyltriethoxysilane.

② compounds having an epoxy group:

3-glycidioxypropyltrimethoxysilane,
3-glycidioxypropylmethyldimethoxysilane and
2-(3, 4epoxycyclohexyl)ethyltrimethoxysilane.

5 ③ compounds having a vinyl group:

vinyltriethoxysilane.

④ compounds having a mercapto group:

3-mercaptopropyltrimethoxysilane.

⑤ compounds having a methacryloxy group:

10 3-methacryloxypropyltrimethoxysilane and
3-methacryloxypropylmethyldimethoxysilane.

Preferably, the component (A) that is a silane coupling agent to be used for the purpose of the invention contains (a) a silane coupling agent containing one or more than one silane coupling
15 compounds having one or more than one active-hydrogen-containing amino groups and (b) a silane coupling agent containing one or more than one silane coupling compounds having one ore more than one epoxysilane groups.

When the component (A) in a surface treatment composition
20 according to the invention contains (a) a silane coupling agent containing active-hydrogen-containing amino groups and (b) a silane coupling agent containing epoxysilane groups, preferably, the equivalent ratio of the active-hydrogen-containing amino groups to the epoxysilane groups contained in said silane coupling
25 agent is between 3:1 and 1:3. The coat obtained from the surface treatment composition performs only poorly in terms of corrosion-resistance and paintability if the equivalent ratio of the active-hydrogen-containing amino groups to the epoxy groups exceeds 3:1, whereas the corrosion-resistance and the paintability of the

produced coat can be saturated if the equivalent ratio of the active-hydrogen-containing amino groups to the epoxy groups is lower than 1:3.

Secondly, each of the water-soluble polymers of the component 5 (B) to be used for the purpose of the invention is either an oligomer or a polymer and the average degree of polymerisation of the formula (I) is between 2 and 50.

In the formula (I), X bonded to the benzene ring represents a hydroxyl group, an alkyl group with any of C1 through C5 such as 10 methyl group, ethyl group or propyl group, a hydroxyalkyl group with any of C1 through C5 such as hydroxymethyl group, hydroxyethyl group or hydroxypropyl group, an aryl group with any of C6 through C12 such as phenyl group or naphthyl group, a benzyl group, a benzal group, an unsaturated hydrocarbon group adapted to 15 be condensed with said benzene ring and form a naphthalene ring such as $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$ group or $=\text{CH}-\text{CH}=\text{CH}-\text{CH}=-$ group or a group expressed by the above formula (II).

Each of R1 and R2 represents independently relative to each other a hydrogen atom, a hydroxyl group, an alkyl group with any 20 of C1 through C5 such as methyl group, ethyl group or propyl group or a hydroxyalkyl group with any of C1 through C10 such as hydroxymethyl group, hydroxyethyl group or hydroxypropyl group.

Each of Y1 and Y2 bonded to the respective benzene rings in the formulas (I) and (II) represents a Z group expressed 25 independently relative to each other by the above formula (III) or (IV). Each of R3, R4, R5, R6 and R7 in the above formulas (III) and (IV) represents an alkyl group with any of C1 through C10 such as methyl group, ethyl group or propyl group or a hydroxyalkyl group with any of C1 through C5 such as hydroxymethyl group,

hydroxyethyl group or hydroxypropyl group independently relative to each other.

Each of X and Y1 in the formula (I) and Y2 in the formula (II) bonded to a benzene ring in the polymer molecule may be the same
5 as or different from X, Y1 or Y2 bonded to some other benzene ring of the molecule.

The average number of substitutions of Z group in each of the benzene rings of said polymer molecule is between 0.2 and 1.0. The n represents the average degree of polymerisation
10 which is between 2 and 50. The molecular weight of the obtained polymer is too small to make the produced coat satisfactorily corrosion-resistant if the value of n is smaller than 2, whereas both the obtained surface treatment composition and the aqueous treatment solution containing such a composition
15 are unstable and disadvantageous in practical applications if the value of n exceeds 50.

The average number of substitutions of Z group as used herein refers to the average value of the numbers of the Z groups introduced into the entire benzene rings of the polymer molecule.
20 If, for example, $n = 10$ in the formula (I) and X represents a benzene-ring-containing group as expressed by the formula (II), the number of benzene rings per polymer molecule is twenty (20). If a Z group is introduced to each of ten (10) benzene rings out of the twenty benzene rings, the average number of substitutions
25 of Z group of the polymer molecule will be $[(1 \times 10) + (0 \times 10)] / 20 = 0.5$.

The obtained polymer does not show a sufficient degree of solubility to water and make the surface treatment composition unstable if the average number of substitutions of Z group is less

than 0.2, whereas the obtained polymer will be excessively water-soluble and the produced coat will not be satisfactorily corrosion-resistant nor paintable if the average number of substitutions of Z group exceeds 1.0.

- 5 Each of R3 through R7 in the Z group as expressed by the formula (III) or (IV) represents an alkyl group with any of C1 through C10 or a hydroxyalkyl group with any of C1 through C10. The produced coat performs only poorly in terms of corrosion-resistance and paintability if the number of carbon atoms is equal
10 to or greater than 11.

- Thirdly, C that is at least one inorganic compound selected from a group of silica, silicates, compounds of metal salts and a mixture of any of them for the purpose of the invention should be apt to be dispersed in said aqueous medium in a colloidal state.
- 15 Therefore, the compound is preferably supplied in the form of fine particles. Specific substances that can be used for the purpose of the invention include fumed silica or colloidal silica, precipitated silica, natural powdery quartz, diatomaceous earth, loess, silicates such as montmorillonite, synthetic magnesium
20 silicate such as Labonite (trademark), titaniasol, zirconiasol, aluminazol, barium sulfate, zinc phosphate and iron oxide red.

- In a surface treatment composition according to the invention, the ratio by weight of said component (A) that is silane coupling agent to said component (B) that is water-soluble polymers, namely
25 (A) : (B) is preferably between 1:10 and 10:1 and more preferably between 1:5 and 5:1. The adhesion of the composition to the underlying metallic material is reduced to make the coat perform unsatisfactorily in terms of corrosion-resistance and paintability when the ratio by weight is less than 1:10. The produced coat

performs only poorly in terms of corrosion-resistance and paintability when the ratio by weight exceeds 10:1 and the content ratio of the component (A) is very high.

In a surface treatment composition according to the invention,
5 the ratio by weight of said component (C) to the sum of said component (A) and (B) namely $C : [(A) + (B)]$, is preferably between 1:5 and 5:1. The obtained coat shows insufficient physical strength and is unsatisfactory in terms of paintability and coin-scratch-resistance when the ratio by weight is less than 1:5 and
10 the content of the inorganic compound (C) is very low, whereas the obtained coat of the surface treatment composition performs only poorly in terms of corrosion-resistance, paintability and adhesion when the ratio exceeds 5:1 and the content ratio of the inorganic compound (C) is very high.

15 Now, a surface treatment method according to the invention will be described in detail. A method according to the invention uses an aqueous surface treatment solution containing a surface treatment composition of above and with its pH value regulated to between 2.0 and 6.5 to put and adhere to the surface of the
20 metallic material and drying it to form a coat having a dried weight per unit area between 0.01 and 2.0g/m², preferably between 0.05 and 1.0g/m². Preferably, the aqueous surface treatment solution is made to contact the surface of the metallic material at temperature between 10 and 60°C for 0.1 to 30 seconds before it
25 is heated and dried.

With a surface treatment method according to the invention, the aqueous surface treatment solution is regulated by diluting the surface treatment composition with a water when necessary. At this time, the pH value is regulated to between 2.0 and 6.5 by

using phosphoric acid, sulphuric acid, hydrochloric acid, nitric acid, hydrofluoric acid, complex fluoride and/or an organic acid.

For the purpose of the invention, preferably, the pH value of the aqueous surface treatment solution is regulated by using
5 phosphoric acid, an acidic phosphate and/or a fluoride which may be a fluoride of a complex. More preferably, the pH value is regulated to between 3.0 and 5.0. The composition in the treatment solution and the surface of the metal material react each other excessively to produce a defective coat that is only
10 insufficiently corrosion-resistant and paintable when the pH value is less than 2.0, whereas the service life of the aqueous treatment solution is curtailed because the component (B) that is water-soluble polymers is apt to precipitate and deposit out of the aqueous surface treatment solution when the pH value exceeds
15 6.5.

Techniques that can be used for contacting the surface of a metallic material with a surface treatment composition according to the invention are not particularly limited. Techniques that can be used for the purpose of the invention include immersion,
20 spraying and roll-coating. While the treatment temperature and the treatment time are not subjected to particular limitations. However, the treatment temperature is preferably between 10 and 60 °C and the treatment time is preferably between 0.1 and 20 seconds.

The treated metallic material is preferably heated and dried.
25 The heating temperature is preferably between 50 and 280°C.

It should be noted that, when the surface treatment composition according to the invention is brought into contact with the metallic material, some of the metal ions arise from the metallic material mixed with the surface treatment composition and reacted

with component (B) to form a complex precipitates. If such is the case, a metal sealing agent may be added to the surface treatment composition. Effective metal sealing agents that can be used for the purpose of the invention include EDTA, Cy-DTA, 5 triethanolamine, gluconic acid, heptgluconic acid, oxalic acid, tartaric acid, malic acid and organic phosphonic acid.

A surface active agent may be added to the aqueous surface treatment solution according to the invention in order to improve the contact with the metallic material. Surface active agents 10 that can be used for the purpose of the invention include commercially available anionic surface active agents of the carbonic acidate type, the sulfate type, the sulfonate and the phosphate type, non-ionic surface active agents of the polyethyleneglycol type and the cationic surface active agents of 15 the polyalcohol type and amine type.

For the purpose of the invention, the metallic material may be selected from an iron sheet, a galvanized iron sheet, an aluminium sheet, an aluminium alloy sheet and a stainless steel sheet. Additionally, it may be selected from pre-treated steel sheet by 20 a phosphate film formation process or chemical plating process.

A pre-treated steel plate provides improvement in terms of corrosion-resistance and paintability. Chemical plating includes substitutional plating of cobalt, nickel, copper, iron, silver or gold.

25 While the reason why the corrosion-resistance and the paintability of a metallic material treated by means of a surface treatment composition according to the invention are improved is not clear yet. However, the following theory may be thought to be true. Firstly, the surface of the metallic material is etched by

the phosphoric acid, an acidic phosphate, fluoride and fluoride complex contained in the surface treatment composition. As a result, the pH of the interface rises and metal ions are appeared to react the component of the water-soluble polymers and form a
5 hardly soluble coat along the surface of the metallic material. Then, the hardly soluble coat operates as barrier to remarkably improve the corrosion-resistance of the metallic material. However, since the coat would not strongly adhere to the metallic material, the component of the silane coupling agent is used so that the
10 functional group (-OR group) in the hydrolysed silane coupling agent may form an oxane bond on the surface of the metallic material, and further the other functional group in the silane coupling agent may react with the component of the water-soluble polymers to improve the adhesion of the water-soluble polymers to
15 the surface of the metallic material.

Additionally, the component of the inorganic compound that is colloiddally dispersed in the solution produces fine undulations on the surface of the metallic material, which fine undulations effectively anchor the paint film formed on the surface to ensure
20 a satisfactory paintability and the strong coin-scratch resistance of the surface of the metallic material.

Examples And Comparative Examples

Now, the present invention will be described in greater detail
25 by way of examples, which by no means limit the scope of the present invention.

1. Metallic Materials Used in the Examples

- ① cold rolled steel sheet (SPC)

commercially available grade of JIS G3141, 0.6mm thickness.

② galvanized steel sheet,

commercially available hot dip galvanized steel sheet,
0.6mm thickness. (GI)

5 commercially available electric galvanized steel sheet,
0.6mm thickness (EG)

③ aluminium sheet (AL)

commercially available grade of JIS A 5052 0.6mm thickness.

10 2. Method of Pre-Cleaning of Metallic Materials.

The surface of all of the above listed metallic materials was treated by spraying a medium-alkaline degreasing agent (Fine Cleaner 4336: Product by Nihon Parcalizing Co., Ltd.) onto the surface of the metallic material at temperature of 60°C for 20
15 seconds to pre-clean the surface and remove the dirt and oil adhering to the surface. Subsequently, the surface is washed with tap water to remove the residual alkaline solution to completely clean the surface of the metallic material.

20 3. Composition of Surface Treatment Solution

<Treatment Solution A>

3-mercaptopropoyltrimethoxysilane was used for the component (A) of silane coupling agent, and water-soluble polymers with $n = 5$, $X = \text{hydrogen}$ and $Y1 = Z = -\text{CH}_2\text{N}(\text{CH}_3)_2$ and the average
25 number of substitutions of Z group = 1 were used for the component (B), while colloidal silica was used for the component (C) of inorganic compound and the three components were adjusted to make (A) : (B) = 1 : 8 and (C) : [(A) + (B)] = 1 : 5. Then, the pH value was adjusted to 5.0 by using H_2SiF_6 and subsequently the

composition was diluted with deionised water to make it contain 10% of composition counted in solid weight.

<Treatment Solution B>

N-(2-aminoethyl)-3-aminopropyltrimethoxysilane was used for
 5 the component (A) of silane coupling agent, and water-soluble
 polymers with $n = 5$, $X = -CH_2-C_6H_4-OH$ and $Y1 = Z = -CH_2N(CH_3)_2$ and
 the average number of substitutions of Z group = 0.75 were used
 for the component (B), while alumina sol was used for the
 component (C) of inorganic compound and the three components were
 10 adjusted to make (A) : (B) = 5 : 1 and (C) : [(A) + (B)] = 1 : 1.
 Then, the pH value was adjusted to 4.0 by using HF and
 subsequently the composition was diluted with deionised water to
 make it contain 10% of composition counted in solid weight.

<Treatment Solution C>

15 3-aminopropyltriethoxysilane + 3-
 glycidoxypropylmethyldimethoxysilane (the equivalent ratio of the
 active hydrogen in the amino group : the epoxy group = 1 : 2) were
 used for the component (A) of silane coupling agent, and water-
 soluble polymers with $n = 5$, $X = -CH_2-C_6H_4-OH$ and $Y1=Z = -CH_2N(CH_3)_2$
 20 and the average number of substitutions of Z group = 0.75 were
 used for the component (B), while barium sulfate was used for the
 component (C) of inorganic compound and the three components were
 adjusted to make (A) : (B) = 1 : 1 and (C) : [(A) + (B)] = 1 : 2.
 Then, the pH value was adjusted to 4.0 by using H_2TiF_6 and
 25 subsequently the composition was diluted with deionised water to
 make it contain 10% of composition counted in solid weight.

<Treatment Solution D>

3-aminopropyltriethoxysilane + 3-
 glycidoxypropylmethyldimethoxysilane (the equivalent ratio of the

active hydrogen in the amino group : the epoxy group = 1 : 3) were used for the component (A) of silane coupling agent, and water-soluble polymers with $n = 5$, $X = -CH_2-C_6H_4-OH$ and $Y1=Z- -CH_2N(CH_3)_2$ and the average number of substitutions of Z group = 0.75 were used for the component (B), while colloidal silica was used for the component (C) of inorganic compound and the three components were adjusted to make (A) : (B) = 1 : 1 and (C) : [(A) + (B)] = 4 : 1. Then, the pH value was adjusted to 3.0 by using phosphoric acid and subsequently the composition was diluted with deionised water to make it contain 10% of composition counted in solid weight.

<Treatment Solution E>

N-(2-aminoethyl)-3-aminopropyltrimethoxysilane + 3-glycidoxypropylmethyldimethoxysilane (the equivalent ratio of the active hydrogen in the amino group : the epoxy group = 1 : 1) were used for the component (A) of silane coupling agent, and water-soluble polymers with $n = 5$, $X = \text{hydrogen}$ and $Y1 = Z = -CH_2N(CH_3)_2$ and the average number of substitutions of Z group = 1 were used for the component (B), while colloidal silica was used for the component (C) of inorganic compound and the three components were adjusted to make (A) : (B) = 1 : 1 and (C) : [(A) + (B)] = 1 : 1. Then, the pH value was adjusted to 4.0 by using H_2TiF_6 and phosphoric acid and subsequently the composition was diluted with deionised water to make it contain 10% of composition counted in solid weight.

<Treatment Solution F -Comparative Example>

Water-soluble polymers with $n = 5$, $X = \text{hydrogen}$ and $Y1 = Z = -CH_2N(CH_3)_2$ and the average number of substitutions of Z group = 1 were used for the component (B), while colloidal silica was used

for the component (C) of inorganic compound and the components were adjusted to make (C) : (B) = 1 : 1. Then, the pH value of the composition was adjusted to 4.0 by using H_2TiF_6 and phosphoric acid and subsequently the composition was diluted with deionised water to make it contain 10% of composition counted in solid weight.

<Treatment Solution G -Comparative Example>

N-(2-aminoethyl)-3-aminopropyltrimethoxysilane + 3-glycidoxypropylmethyldimethoxysilane (the equivalent ratio of the active hydrogen in the amino group : the epoxy group = 1 : 1) were used for the component (A) of silane coupling agent, while water-soluble polymers with $n = 5$, $X = \text{hydrogen}$ and $\text{Y1} = \text{Z} = -\text{CH}_2\text{N}(\text{CH}_3)_2$ and the average number of substitutions of Z group = 1 were used for the component (B) and the components were adjusted to make (A) : (B) = 1 : 1. Then, the pH value of the composition was adjusted to 3.0 by using phosphoric acid and subsequently the composition was diluted with deionised water to make it contain 10% of composition counted in solid weight.

<Treatment Solution H -Comparative example>

3-mercaptopropyltrimethoxysilane was used for the component (A) of silane coupling agent, and water-soluble polymers with $n = 5$, $X = \text{hydrogen}$ and $\text{Y1} = \text{Z} = -\text{CH}_2\text{N}(\text{CH}_3)_2$ and the average number of substitutions of Z group = 1 were used for the component (B), while barium sulfate was used for the component (C) of inorganic compound and the three components were adjusted to make (A) : (B) = 1 : 8 and (C) : [(A) + (B)] = 1 : 20. Then, the pH value of the composition was adjusted to 4.5 by using HF and subsequently the composition was diluted with deionised water to make it contain 10% of composition counted in solid weight.

<Treatment Solution I -Comparative example>

3-aminopropyltriethoxysilane + 3-glycidioxypropylmethyldimethoxysilane (the equivalent ratio of the active hydrogen in the amino group : the epoxy group = 1 : 3) were used for the component (A) of silane coupling agent, and water-soluble polymers with $n = 5$, $X = -CH_2-C_6H_4-OH$ and $Y1 = Z = -CH_2N(CH_3)_2$ and the average number of substitutions of Z group = 0.75 were used for the component (B), while colloidal silica was used for the component (C) of inorganic compound and the three components were adjusted to make (A) : (B) = 1 : 1 and (C) : [(A) + (B)] = 1 : 2. Then, the pH value of the composition was adjusted to 1.0 by using phosphoric acid and subsequently the composition was diluted with deionised water to make it contain 10% of composition counted in solid weight.

15 <Treatment Solution J -Comparative example>

Conventional chromate solution of application type (Zinchrom-1 300AN : Product by Nihon Parkerizing Co., LTD)

4. Application of Treatment Solution to Metallic Materials.

20 <Example 1>

The treatment solution A was applied by roll-coating at 25°C to a hot dip galvanized steel sheet (GI) at a rate of 0.3g/m² after drying. Then, the solution was dried by heating to 80°C.

<Example 2>

25 The treatment solution B was applied by roll-coating at 15°C to an aluminium sheet (AL) at a rate of 0.1g/m² after drying. Then, the solution was dried by heating to 150°C.

<Example 3>

The treatment solution C was applied by roll-coating at 30°C

to a hot dip galvanized steel sheet (GI) at a rate of 1.0g/m^2 after drying. Then, the solution was dried by heating to 100°C .

<Example 4>

The treatment solution D was applied by roll-coating at 20°C
5 to a electric galvanized steel sheet (EG) at a rate of 0.05g/m^2 after drying. Then, the solution was dried by heating to 180°C .

<Example 5>

Nickel plating layer of 20 mg/m^2 was previously formed on the surface of hot dip galvanized steel sheet (GI) by treating it in
10 the nickel plating solution (Preparen 4015 : Product of Nihon Parkerizing Co., LTD) and then the treatment solution E was further applied by roll coating at 20°C at a rate of 1.5 g/m^2 after drying. And then the solution was dried by heating to 150°C .

<Example 6>

15 Nickel plating layer of 20 mg/m^2 was previously formed on the surface of hot dip galvanized steel sheet (GI) by treating it in the nickel plating solution (Preparen 4015), and then the treatment solution C was further applied by roll coating at 20°C at a rate of 0.1 g/m^2 after drying. And then the solution was
20 dried by heating to 100°C .

<Example 7>

Zinc phosphate layer of 2 g/m^2 was previously formed on the surface of hot dip galvanized steel sheet (GI) by treating it conventionally in the phosphating solution (Palbond-L 3300 :
25 Product of Nihon Parkerizing Co., LTD.) and then the treatment solution E was further applied by roll coating at 20°C at a rate of 0.3 g/m^2 after drying. And then the solution was dried by heating to 100°C .

<Example 8>

Zinc phosphate layer of 2 g/m^2 was previously formed on the surface of cold rolled steel sheet (SPC) by treating it conventionally in the phosphating solution (Palbond-L3020 :Product of Nihon Parkerizing Co., LTD.) and then the treatment solution E
5 was further applied by roll coating at 20°C at a rate of 0.1 g/m^2 after drying. And then the solution was dried by heating to 100°C .

<Comparative Example 1>

The treatment solution F was applied by roll-coating at 30°C to a hot dip galvanized steel sheet (GI) at a rate of 1.0 g/m^2
10 after drying. Then, the applied solution was dried by heating to 100°C .

<Comparative Example 2>

The treatment solution G was applied by roll-coating at 30°C to an aluminium sheet (AL) at a rate of 0.3 g/m^2 after drying.
15 Then, the applied solution was dried by heating to 200°C .

<Comparative Example 3>

Nickel plating layer of 20 mg/m^2 was previously formed on the surface of hot dip galvanized steel sheet (GI) by treating it in nickel plating solution (Preparen 4015), and then the treatment
20 solution H was further applied by roll coating at 20°C at a rate of 0.3 g/m^2 after drying. And then the solution was dried by heating to 80°C .

<Comparative Example 4>

Nickel plating layer of 20 mg/m^2 was previously formed on the
25 surface of hot dip galvanized steel sheet (GI) by treating it in nickel plating solution (Preparen 4015), and then the treatment solution I was further applied by roll coating at 20°C at a rate of 0.3 g/m^2 after drying. And then the solution was dried by heating to 150°C .

<Comparative Example 5>

Nickel plating layer of 20 mg/m^2 was previously formed on the surface of hot dip galvanized steel sheet (GI) by treating it in nickel plating solution (Preparen 4015), and then the treatment solution J was further applied by roll coating at a rate of 40 mg/m^2 of chromium. And then the solution was dried by heating to 80°C .

5. Method of Preparing Test Specimen

To the metallic materials of <Example 1> ~ <Comparative Example 5>, a commercially available undercoat paint (V-Knit #200: Product by Dainihon Paint Co., Ltd) was applied to a thickness of $5.5\mu\text{m}$, baked at 200°C , and then a commercially available finish coat paint (V-Knit # 500 : Product by Dainihon Paint Co., LTD) was applied further to a thickness of $17\mu\text{m}$ and baked it again at 220°C .

6. Test and Evaluation

6-1. Corrosion-Resistant

Cutting scratches having the depth reaching to the metallic material are formed by cutter knife on the surface of each test specimens, and a salt water spray test conforming to JIS-Z 2371 were conducted for 480 hours. The specimens were evaluated by observing the width (mm) of the rust produced in the scratch area and using the following rating system.

◎: less than 3mm

○: not less than 3mm and less than 5mm

△: not less than 5mm and less than 10mm

×: not less than 10mm

6-2. Bend Adhesion Test

• Primary Bend Adhesion Test

Test specimens were subjected to the bending at 20°C and peeling off area of coating were measured conforming to JIS-G 3312.

• Secondary Bend Adhesion Test

- 5 Test specimens were immersed in boiling water for 2 hours and exposed to air for 1 day. Then bend adhesion test were carried out in the same way as primary bend adhesion test.

• Evaluation of Bend Adhesion Test

- 5 : no peeling off
 10 4 : peeling off area is less than 10 %
 3 : peeling off area is 10~50 %
 2 : peeling off area is 51~80 %
 1 : peeling off area is more than 80 %

6-3. Coin-Scratch Test

- 15 A 10 yen coin was held with an angle of 45° to the test specimen and the coated surface was scratched by it under a load of 3kg at a constant rate. After the test, the scars on the coated surface were examined. The specimens were evaluated by using the following rating.

- 20 5: no exposed metal surface (only the primer was exposed)
 4: exposed metal surface less than 10%
 3: exposed metal surface not less than 10% and less than 50%
 2: exposed metal surface not less than 50% and less than 80%
 25 1: exposed metal surface area not less than 80%

Test results are summerized in Table 1. Comparative example 5 in Table 1 shows excellent corrosion-resistance and paintability. However, it is produced using the liquid containing chromate, and

it is not suitable since it arises contaminated industrial wastes. In Example 1~8 of Table 1, a surface treatment composition of the present invention were used and harmful industrial wastes were not arisen. An excellent corrosion-resistance and paintability as good as that of comparative example 5 were obtained. Comparative example 1 is not containing silane coupling agent. Also in comparative example 2, 3 and 4, different solution other than the surface treatment composition of the present invention were used, and showing unsatisfactory results in corrosion-resistance and / or paintability.

Table 1

	No	Metallic Material	Pre treatment Layer	Corrosio resistant	Bend Adhesion test		Coin Scratch Test
					Primary	Scondary	
Example	1	GI	—	◎	4	4	5
	2	AL	—	◎	4	4	5
	3	GI	—	◎	4	4	4
	4	EG	—	◎	4	4	5
	5	GI	Ni	○	5	5	5
	6	GI	Ni	○	5	5	5
	7	GI	Zinc phosphate	○	5	5	5
	8	SPC	Zinc phosphate	◎	5	5	5
Comparative Example	1	GI	—	×	1	1	4
	2	AL	—	△	4	5	1
	3	GI	Ni	×	5	5	2
	4	GI	Ni	×	2	2	3
	5	GI	Ni	◎	5	5	5

Advantages of the Invention

Since a surface treatment agent according to the invention provides corrosion-resistance and paintability to a satisfactory level without using any chromate, it can make the industry

adaptable in future when the use of chromate is more rigorously prohibited. Additionally, since a surface treatment composition according to the invention is not selective to a sort of metallic material to be used, it can enhance the corrosion-resistance and
5 the paintability of many sort of metallic material so that the advantageous properties of each metallic material may be fully exploited.

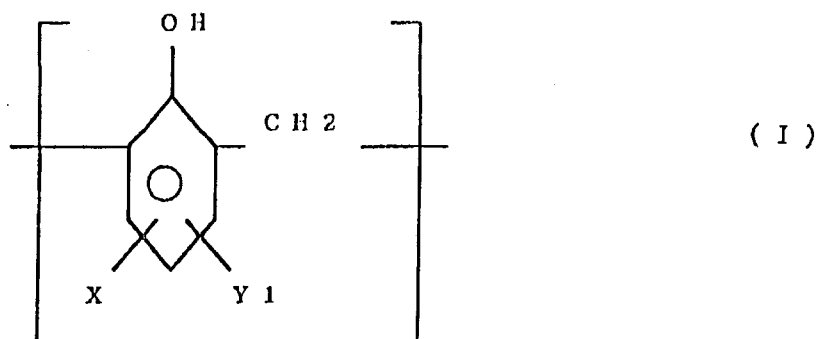
Therefore, a surface treatment composition according to the invention is highly feasible to practical applications
10 particularly in terms of environment protection and recycling of resources.

CLAIMS

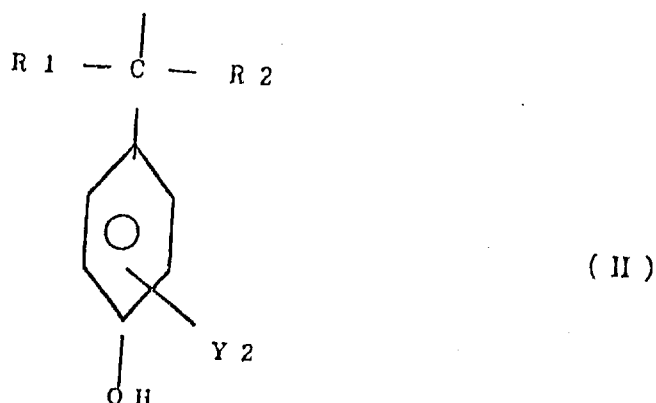
1. A surface treatment aqueous composition to be used for a metallic material comprising (A), (B) and (C) being dissolved and / or dispersed in the aqueous composition.

(A) a silane coupling agent containing one or more than one silane coupling compounds having at least a reactive functional group selected from an active-hydrogen-containing amino group, an epoxy group, a vinyl group, a mercapto group and a methacryloxy group;

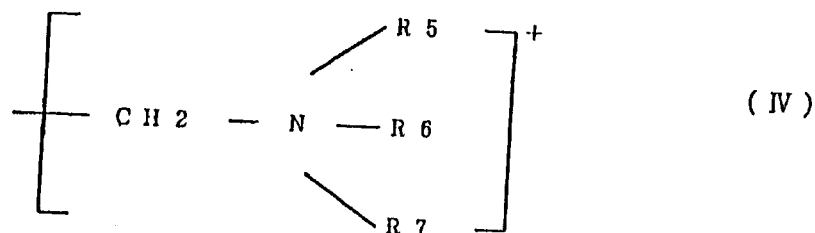
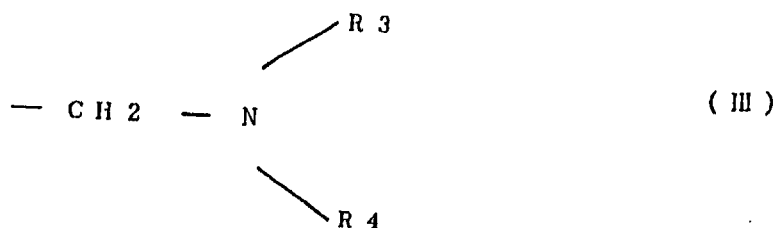
(B) one or more than one water-soluble polymers being expressed by general formula (I) below and showing average degree of polymerisation between 2 and 50:



where X bonded to the benzene ring represents a hydrogen atom, a hydroxyl group, an alkyl group with any of C1 through C5, a hydroxyalkyl group with any of C1 through C5, an aryl group with any of C6 through C12, a benzyl group, a benzal group, an unsaturated hydrocarbon group adapted to be condensed with said benzene ring and form a naphthalene ring or a group expressed by formula (II) below:



where each of R₁ and R₂ represents a hydrogen atom, a hydroxyl group, an alkyl group with any of C₁ through C₅ or a hydroxyalkyl group with any of C₁ through C₁₀, each of Y₁ and Y₂ bonded to the respective benzene rings in formulas (I) and (II) representing a Z group expressed independently by formula (III) or (IV) below:



where each of R₃, R₄, R₅, R₆ and R₇ represents a hydrogen atom, an alkyl group with any of C₁ through C₁₀ or a hydroxyalkyl group with any of C₁ through C₁₀ independently relative to each other and the average number of substitutions of Z group in each of the benzene rings of said polymer molecule is between 0.2 and 1.0; and

(C) one or more than one inorganic compound selected from a group of silica, silicates, compounds of metal salts and a mixture

of any of them, each are being dispersed in said aqueous medium in a colloidal state.

2. A surface treatment composition to be used for a metallic material according to claim 1, wherein the ratio of said component (A) that is silane coupling agent to said component (B) that is water-soluble polymers, namely (A) : (B) is between 1:10 and 10:1 and the ratio by weight of said component (C) that is inorganic compound to [(A) + (B)], namely C : [(A) + (B)] is between 1:5 and 5:1.

3. A surface treatment composition to be used for a metallic material according to claim 1, wherein said component (A) that is silane coupling agent contains (a) a silane coupling agent containing one or more than one silane coupling compounds having one or more than one active-hydrogen-containing amino groups and (b) a silane coupling agent containing one or more than one silane coupling compounds having one ore more than one epoxysilane groups.

4. A surface treatment composition to be used for a metallic material according to claim 3, wherein the equivalent ratio of the active-hydrogen-containing amino groups contained in said silane coupling agent (a) to the epoxysilane groups contained in said silane coupling agent (b) is between 3:1 and 1:3.

5. A surface treatment composition to be used for a metallic material according to claim 3 or 4, wherein weight ratio of the sum of said silane coupling agent (a) and said silane coupling agent (b) to said water-soluble polymer component (B), namely

$[(a) + (b)] : (B)$ is between 1:1 and 5:1.

6. A surface treatment method to be used for a metallic material comprising:

using a surface treatment aqueous composition according to any of claim 1~ claim 5 with the pH value regulated to between 2.0 and 6.5 to adhere to the surface of the metallic material and drying it to form a coat having a dried weight of between 0.01 and 2.0g/m².

7. A surface treatment method to be used for a metallic material according to claim 6, wherein the surface of the metallic material to be treated is preliminarily treated by means of a phosphate layer forming process or a plating layer forming process before using a surface treatment aqueous solution.