

Metallic Material With Organic Composite Coating Excellent
In Corrosion Resistance And Coatability And Reduced In Finger
Mark Adhesion And Process For Producing The Same

5

Technical Field

This invention relates to a metallic material showing a surface that is highly corrosion-resistant, excellent coatability with paints and reduced in fingermark adhesion and adapted to be used for
10 home use electric appliances and building materials.

Background Art

Generally, metallic materials such as galvanized steel sheets and aluminium sheets are used for a wide variety of applications
15 including automobiles, building materials and electric appliances for home use. However, both zinc and aluminium have a drawback that they can easily be corroded in air to produce a corrosion product (so-called white rust). They further have insufficient coatability with paints and easily to be stained its surface by being adhered
20 finger marks of the operators.

In view of this problem, metallic materials whose surface is firstly treated by a treatment solution containing chromic acid, dichromic acid or a salt of either of them and subsequently coated with an upper layer of polyolefin type resin containing carboxyl
25 groups and colloidal silica has been widely used in order to improve the corrosion resistance, the coatability with paints and to reduce the finger mark adhesion of the surface of the metal.

However, in the trend of environment protection in recent years, the chromate treatment has become unpopular mainly because

hexavalent chromium contained in the treatment solution may hurt the human body. Additionally, waste water containing hexavalent chromium arising in chromate treatment is required to be subjected to a specific treatment process conforming to the Provision of Water Pollution Control Law, which raises the overall manufacturing cost. Furthermore, chromate-treated metal are classified as chromium-contaminated industrial waste after use and not easy to be recycled. Thus the chromate treatment is now arising a significant social issue.

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

However, protective coats of metallic material 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 metal 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 trialkoxy silane compound to the surface of a metallic material in order to improve the corrosion-resistance of the material.

Further, JP A 57-44751 and 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 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 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, there has not been realized any non-chromium type surface treatment agent nor surface treatment method to date that provides metallic material with a remarkable level of corrosion-resistance.

10 Disclosure Of The Invention

It is therefore the object of the present invention to provide a metallic material having organic coating of non-chromium type and showing a surface of excellent in corrosion resistance, coatability with paints and reduced fingermark.

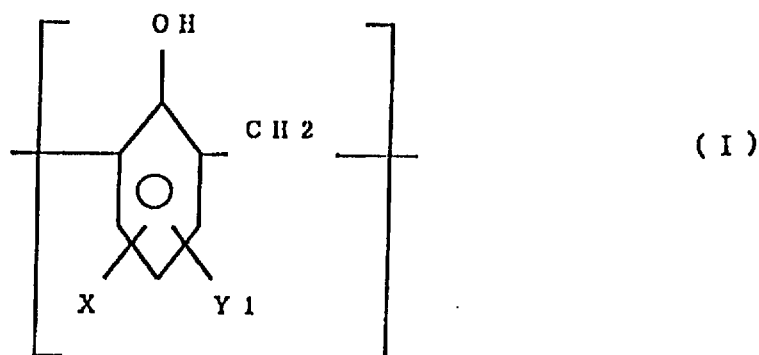
15 As a result of intensive efforts for solving the problems of the prior art, the inventors of the present invention came to find that a metallic material that has excellent in corrosion resistance, coatability with paints and reduced fingermark can be manufactured by coating the surface of the metallic material with a first coating
20 layer of a composition containing a silane coupling agent and a polymer of specific chemical structure and a second coating layer of a silica-containing resin composition on the first layer. The present invention is based on this finding.

Thus, according to the invention, there is provided a metallic
25 material with organic composite coating comprising a first coating layer being formed on the surface of the said metallic material comprising:

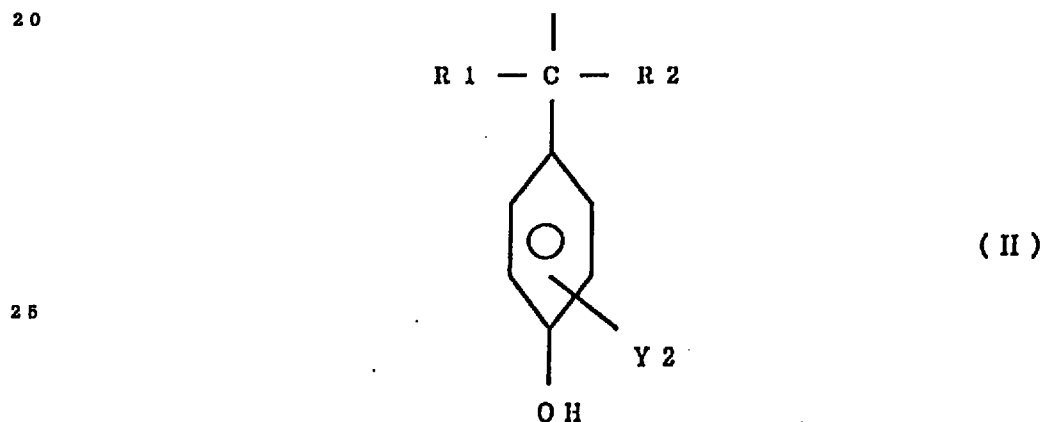
(A) a silane coupling agent containing one or more than one silane coupling compounds having at least a reactive functional

group selected from an active-hydrogen-containing amino group, an epoxy group, a vinyl group, a mercapto group and a methacryloxy group, and

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

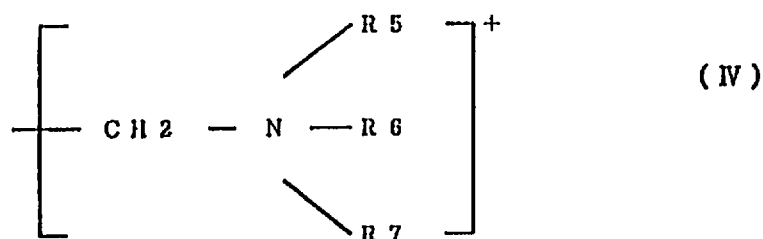
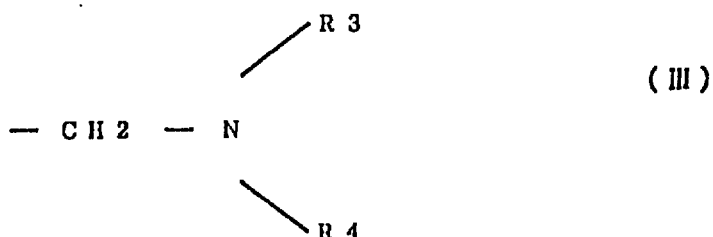


where X bonded to the benzene ring represents a hydrogen atom, a hydroxyl group, an alkyl group with any of C1 through C5, a hydroxyalkyl group with any of C1 through C5, an aryl group with any of C6 through C12, a benzyl group, a benzal group, an unsaturated hydrocarbon group to be condensed with said 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, and each of Y1 and Y2 bonded to the benzene rings in formulas (I) and (II) representing a Z group expressed 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 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 a second coating layer formed on said first coating layer by using a resin composition containing silica by 5 to 70 weight portions relative to 100 weight portions of resin.

In the metallic material with organic composite coating according to the invention, preferably, the ratio by weight of said component (A) to said component (B) namely (A) / (B), is between 1/10 and 10/1.

In the metallic material with organic composite coating according to the invention, preferably, said component (A) 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 group and (b) : a silane coupling agent containing

one or more than one silane coupling compounds having one or more than one epoxy group.

In the metallic material with organic composite coating according to the invention, preferably, the equivalent ratio of the active hydrogen containing amino group contained in said silane coupling agent (a) to the epoxy group contained in said silane coupling agent (b) is between 3:1 and 1:3.

In the metallic material with organic composite coating according to the invention, preferably, the ratio by weight of the sum of said silane coupling agent (a) and said silane coupling agent (b) to said polymer component (B), namely $[(a) + (b)] / (B)$ is between 1/5 and 5/1.

Best Mode For Carrying Out The Invention

In the metallic material with organic coating according to the invention, the first coating layer contains component (A) which is a silane coupling agent containing one or more than one silane coupling compounds having a specific reactive functional group and component (B) which is one or more than one phenol resin type polymers having a specific amino group.

The silane coupling compounds contained in the component (A) are not subjected to any limitations so long as it contains 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. And for example, silane coupling compounds as listed in ① through 5 below can be used for the purpose of the invention.

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-glycidoxypropyltrimethoxysilane,

5 3-glycidoxypropylmethyldimethoxysilane and

2-(3, 4epoxycyclohexyl)ethyltrimethoxysilane.

③ compounds having a vinyl group:

vinyltriethoxysilane.

④ compounds having a mercapto group:

10 3-mercaptopropyltrimethoxysilane.

⑤ compounds having a methacryloxy group:

3-methacryloxypropyltrimethoxysilane and

3-methacryloxypropylmethyldimethoxysilane.

The component (A) to be used for the invention may contain (a) a
15 silane coupling agent containing one or more than one silane
coupling compounds having one or more than one active-hydrogen-
containing amino group and (b) a silane coupling agent containing
one or more than one silane coupling compounds having one or more
than one epoxy group.

20 When the component (A) to be used for the invention 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 group and (b) a silane coupling agent containing
one or more than one silane coupling compounds having one or more
25 than one epoxy group, preferably, the equivalent ratio of the active
-hydrogen-containing amino group to the epoxy group contained in
said silane coupling agent is preferably between 3:1 and 1:3.

The coating obtained from the surface treatment composition
performs only poorly in terms of corrosion-resistance and

coatability with paints if the equivalent ratio of the active-hydrogen-containing amino group to the epoxy group exceeds 3 : 1, whereas the corrosion-resistance and the coatability with paints of the produced coating can be saturated if the equivalent ratio of the active-hydrogen-containing amino group to the epoxy group is lower than 1:3.

Then, component (B) to be used for the invention is either an oligomer or a polymer and the average degree of polymerisation of each unit of polymerisation of the formula (I) is preferably 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 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 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 in formula (II) represents independently a hydrogen atom, a hydroxyl group, 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 C10 such as hydroxymethyl group, hydroxyethyl group or hydroxypropyl group.

Each of Y1 and Y2 bonded to the benzene rings in the formulas (I) and (II) represents a hydrogen atom and a Z group expressed independently by the 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.

5 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 as X, Y1 or Y2 in another benzene ring, and may be different from X, Y1 or Y2 in another benzene ring. The average number of substitutions of Z group in each of the benzene rings of said polymer molecule is
10 between 0.2 and 1.0.

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. If, for example, $n=10$ in the formula (I) and X represents a benzene-
15 ring-containing group as in 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, the average number of substitutions of Z group of the polymer molecule will be $[(1 \times 10) + (0 \times 10)] / 20 = 0.5$.

20 The obtained polymer shows insufficient adhesive strength with the metallic material and decreases the coatability when 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 coating will not be satisfactorily corrosion-resistant when the
25 average number of substitutions of Z group exceeds 1.0.

Each of R3 through R7 in the Z group as expressed in 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 coating performs only poorly in corrosion-resistance and coatability

with paints if the number of carbon atoms is greater than 11.

The second coating layer of a metallic material according to the invention contains silica preferably by 5 to 70 weight portions, more preferably by 10 to 50 weight portions to 100 weight portions of resin. The organic composite coating does not operate enough for improving the corrosion-resistance and reducing of fingermark of the metallic material if the silica content is less than 5 weight portions, whereas the second coating layer is stiffened and the corrosion-resistance of the metal material falls if the silica contains exceeds 70 weight portions. The silica contained in the second coating layer may be colloidal silica, organo-silica-sol, gas phase silica or powdery silica, which are all commercially available.

Further, silica products of SNOWTEX O, C, OS, N (Products of Nissan Chemical Industries, Ltd.) and AEROZIL 100, 200, 300 (Products of Nippon Aerosil Co.) may also be available. And the particle size of silica are not subjected to any particular limitations.

The resin used for the second coating layer preferably has hydroxyl and/or carboxyl groups. Commercially available resins that can be used include epoxy resin, alkyd resin, acryl resin, urethane resin, acryl modified polyester resin, phenol modified alkyd resin, polyvinyl butyral resin, phenol resin, melamine resin and ethylene acrylic resin. While there are no specific limitations to the structure and the molecular weight of the resin to be used, it has to be able to contain silica in a uniformly dispersed state.

The amount of the second coating layer should preferable to be 0.1 to 5.0g/m². The corrosion-resistance and the reducing of fingermark will be insufficient if the amount of the second coating layer is less than 0.1g/m² whereas the coatability with paints and the adhesiveness will be unsatisfactory if the amount of the second

coating layer exceeds 5.0g/m^2 .

If necessary, the second coating layer may contain wax in order to give a lubricative property thereto.

The corrosion-resistance of the product may further be improved in some case when an ordinary anti-rust pigment such as molybdcic acid type pigment or phosphate type pigment or a rust preventive agent (e.g., phenol type carboxylic acid such as tannic acid or gallic acid) is added.

In a surface treatment composition to be used for the purpose of the invention, the ratio by weight of said component (A) to said component (B), namely (A) / (B) is preferably between 1/10 and 10/1 and more preferably between 1/5 and 5/1. The adhesion strength of the composition to the underlying metallic material is reduced to make unsatisfactorily in terms of corrosion-resistance and coatability with paints if the ratio by weight is less than 1/10. The produced metallic material may perform only poorly in terms of corrosion-resistance and coatability with paints if the ratio by weight exceeds 10/1.

Now, a process for producing the metallic material with organic-composite-coating according to the invention will be described. In the invention, first coating layer is formed on the surface of the metallic material by applying an aqueous composition being adjusted its pH value between 2.0 and 6.5 at a rate of $10\sim 500\text{ mg/m}^2$, more preferably at a rate of $50\sim 500\text{ mg/m}^2$ being measued at dry state, and dry the aqueous composition preferably at $10\sim 60^\circ\text{C}$ and for $0.1\sim 30$ sec.

In the invention, preferably, the pH value of the aqueous composition for the first coating layer is regulated to between 2.0 and 6.5 by using phosphoric acid, an acidic phosphate, a fluoride, a

fluoride complex sulphuric acid, nitric acid and organic acid. 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 metallic material react each other excessively to produce a defective coating that is only insufficiently corrosion-resistant and coatability with paints if the pH value is less than 2.0, whereas the service life of the aqueous composition is curtailed because the component (B) that is water-soluble polymers is apt to precipitate and deposit out of the aqueous composition if the pH value exceeds 6.5.

Application method of the aqueous composition in the invention are not particularly limited. And usual application methods of immersion, spraying and roll-coating can be used. While the application temperature and the application time are not subjected to particular limitations. And the temperature is preferably between 10 and 60°C and the time is preferably between 0.1 and 20 seconds. The treated metallic material is preferably heated and dried. The heating temperature is preferably between 50 and 280°C.

It should be noted that, when the treatment composition is brought into contact with the metallic material, some of the metal ions eluted from the metallic material and mixed with the treatment composition, and the metal ions and the component (B) that is water-soluble polymers may react each other to form a complex compound, which eventually 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 this purpose include EDTA, Cy-DTA, triethanolamine, gluconic acid, heptgluconic acid, oxalic acid, tartaric acid and malic acid.

While in the aqueous resin composition to be used for the second

coating layer, application method, application temperature and time of treatment are not subjected to any limitations, and preferably it is held in contact at temperature between 10 and 60°C for 0.1 to 10 seconds.

5 The metallic material to be used for the purpose of the invention may be selected from an steel sheet, a galvanized steel sheet, an aluminium sheet, an aluminium alloy sheet and a stainless steel sheet.

10 Embodiment Examples And Comparative Examples

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

1. Metallic Materials Used in the Examples

- 15 ① cold rolled steel sheet (SPC)
commercially available grade of JIS G 3141, 0.6mm thickness.
- ② galvanized steel sheet
commercially available hot dip galvanized steel sheet, 0.6mm thickness, (GI)
- 20 commercially available electric galvanized steel sheet, 0.6mm thickness, (EG)
- ③ aluminium sheet
commercially available JIS A 5052, 0.6mm thickness, (AL)

2. Method of Pre-Cleaning of Metallic Materials.

25 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 Parkerizing Co.,Ltd.) onto the surface of the metallic material at temperature of 60 °C for 20 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.

3. Composition of Surface Treatment Solution for First Coating Layer

<Treatment Solution A>

3-mercaptopropyltrimethoxysilane was used for the component (A) of silane coupling agent, and water-soluble polymers with $n = 5$, $X =$ hydrogen, $Y1 = Z = -CH_2N(CH_3)_2$ and the average number of
 10 substitutions of z group = 1 were used for the component (B), and were adjusted to make (A) : (B) = 1 : 8. Then, the pH value was adjusted to 3.0 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.

15 <Treatment Solution B>

N-(2-aminoethyl)-3-aminopropyltrimethoxysilane was used for the component (A) of silane coupling agent, and water-soluble polymers with $n = 5$, $X = -CH_2-C_6H_4-OH$, $Y1 = Z = -CH_2N(CH_3)_2$ and the average
 20 number of substitutions of Z group = 0.50 were used for the component (B), and were adjusted to make (A) : (B) = 5 : 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>

25 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 $n = 5$, $X = -CH_2-C_6H_4-OH$, $Y1 = Z = -CH_2N(CH_3)_2$

and the average number of substitutions of Z group = 0.75 were used for the component (B), and were adjusted to make (A) : (B) = 1 : 1. Then, the pH Value was adjusted to 4.0 by using H_2TiF_6 and subsequently the composition was diluted with deionised water to make it contain 10% of composition counted in solid weight.

<Treatment Solution D>

N-(2-aminoethyl)-3-aminopropyltrimethoxysilane + 3-glycidoxypropylmethyldimethoxysilane (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 $n = 5$, $X = -CH_2-C_6H_4-OH$, $Y1 = Z = -CH_2N(CH_3)_2$ and the average number of substitutions of Z group = 0.75 were used for the component (B), and were adjusted to make (A) : (B) = 1 : 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, while water-soluble polymers with $n = 5$, $X = \text{hydrogen}$, $Y1 = Z = -CH_2N(CH_3)_2$ and the average number of substitutions of Z group = 0.3 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 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.

4. Application of Treatment Solution to Metallic Materials.

<Embodiment 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 at dried state. Then, the applied solution was dried by heating to 80 °C. Thereafter, an aqueous resin composition containing powdery silica (AEROZIL 200 : Products of Nippon Aerosil Co.) by 30 weight portions to 100 weight portions of acryl modified alkyd resin was applied thereto by roll-coating at a rate of 2g/m² at dried state. Then, was dried by heating to 100°C.

10 <Embodiment Example 2>

The treatment solution B was applied by roll-coating at 15°C to an aluminium sheet (AL) at a rate of 0.1g/m² at dried state. Then, the applied solution was dried by heating to 150°C. Thereafter, an aqueous resin composition containing powdery silica (AEROZIL 300 : Product of Nippon Aerosil Co.) by 70 weight portions to 100 weight portions of phenol modified alkyd resin was applied thereto by roll-coating at a rate of 1g/m² at dried state. Then, was dried by heating to 150°C.

<Embodiment Example 3>

20 The treatment solution B was applied by roll coating at 30°C to a hot dip galvanized steel sheet (GI) at a rate of 0.05g/m² at dried state. Then, the applied solution was dried by heating to 100°C. Thereafter, an aqueous resin composition containing powdery silica (AEROZIL 200: Products of Nippon Aerosil Co.) by 50 weight portions to 100 weight portions of acryl resin was applied thereto by roll-coating at a rate of 3g/m² as dried state. Then, was dried by heating to 100°C.

<Embodiment Example 4>

The treatment solution C was applied by roll coating at 20°C to

a electric galvanized steel sheet (EG) at a rate of 0.05g/m^2 at dried state. Then, the applied solution was dried by heating to 180°C . Thereafter, an aqueous resin composition containing colloidal silica (SNOWTEX N: Products of Nissan Chemical Industries Co.) by 70 weight portions to 100 weight portions of ethylene acrylic resin was applied thereto by roll-coating at a rate of 1g/m^2 at dried state. Then, was dried by heating to 100°C .

<Embodiment Example 5>

The treatment solution D was applied by roll coating at 20°C to a hot dip galvanized steel sheet (GI) at a rate of 0.1g/m^2 at dried state. Then, the applied solution was dried by heating to 80°C . Thereafter, an aqueous resin composition containing colloidal silica (SNOWTEX N) by 20 weight portions to 100 weight portions of ethylene acrylic resin was applied thereto by roll-coating at a rate of 2g/m^2 at dried state. Then, the applied composition was dried by heating to 100°C .

<Embodiment Example 6>

The treatment solution E was applied by roll coating at 20°C to a hot dip galvanized steel sheet (GI) at a rate of 0.03g/m^2 at dried state. Then, the applied solution was dried by heating to 80°C . Thereafter, an aqueous resin composition containing colloidal silica (SNOWTEX 0: Products of Nissan Chemical Industries Co.) by 20 weight portions to 100 weight portions of ethylene acrylic resin was applied thereto by roll-coating at a rate of 1g/m^2 at dried state. Then, the applied composition was dried by heating to 80°C .

<Embodiment Example 7>

The treatment solution E was applied by roll coating at 20°C to a hot dip galvanized steel sheet (GI) at a rate of 0.5g/m^2 at dried state. Then, the applied solution was dried by heating to 80°C .

°C. Thereafter, an aqueous resin composition containing colloidal silica (SNOWTEX 0) by 70 weight portions to 100 weight portions of urethane modified epoxy resin was applied thereto by roll-coating at a rate of 0.3g/m^2 at dried state. Then, the applied composition
5 was dried by heating to 180°C .

<Embodiment Example 8>

The treatment solution E was applied by roll coating at 20°C to a cold rolled steel sheet (SPC) at a rate of 0.5g/m^2 at dried state. Then, the applied solution was dried by heating to 80°C . Thereafter,
10 an aqueous resin composition containing colloidal silica (SNOWTEX N) by 70 weight portions to 100 weight portions of urethane modified epoxy resin was applied thereto by roll-coating at a rate of 4g/m^2 at dried state. Then, the applied composition was dried by heating to 180°C .

15 <Comparative Example 1>

The treatment solution C was applied by roll coating at 20°C to a hot dip galvanized steel sheet (GI) at a rate of 0.3g/m^2 at dried state. Then, the applied solution was dried by heating to 180°C .

<Comparative Example 2>

20 The treatment solution A was applied by roll coating at 20°C to a electric galvanized steel sheet (EG) at a rate of 0.05g/m^2 at dried state. Then, the applied solution was dried by heating to 80°C . Thereafter, an aqueous resin composition containing only urethane resin was applied thereto by roll-coating at a rate of 1g/
25 m^2 at dried state. Then, the applied composition was dried by heating to 100°C .

<Comparative Example 3>

The treatment solution B was applied by roll coating at 30°C to an aluminium sheet (AL) at a rate of 0.1g/m^2 at dried state. Then,

the applied solution was dried by heating to 180°C. Thereafter, an aqueous resin composition containing colloidal silica (SNOWTEX N) by 90 weight portions to 100 weight portions of ethylene acrylic resin was applied thereto by roll-coating at a rate of 1g/m² at dried state. Then, the applied composition was dried by heating to 100°C.

<Comparative Example 4>

The treatment solution D was applied by roll coating at 20°C to a electric galvanized steel sheet (EG) at a rate of 0.05g/m² at dried state. Then, the applied solution was dried by heating to 180 °C. Thereafter, an aqueous resin composition containing powdery silica (AEROZIL 200) by 50 weight portions to 100 weight portions of ethylene acrylic resin was applied thereto by roll-coating at a rate of 0.05g/m² at dried state. Then, the applied composition was dried by heating to 100°C.

<Comparative Example 5>

An aqueous resin composition containing colloidal silica (SNOWTEX N) by 50 weight portions to 100 weight portions of ethylene acrylic resin was applied by roll-coating to an electric galvanized steel sheet (EG) at a rate of 1g/m² at dried state. Then, the applied composition was dried by heating to 100°C.

Test/Evaluation Method

The prepared test specimen plates were tested and evaluated by means of the rating systems described below.

5. Test and Evaluation

5-1. Corrosion-Resistance

Each specimen was subjected to a salt water spray test conforming to JIS-Z2371 for 240 hours, and the white rust formed thereon was visually observed. The specimens were evaluated by using the following rating system.

- ◎ : white rust less than 5%
- : white rust not less than 5% and less than 10%
- △ : white rust not less than 10% and less than 50%
- × : white rust not less than 50%

5 5-2. Coatability with Paints

Each specimen was coated with the paint listed below and the adhesive property was tested.

Paint : AMILACK #1000 White (Product of Kansai Paint Co.)

Painting Method : Bar Coat Method

10 Baking : 140°C, 20 minutes

Film thickness : 25 μ m

5-2-1 Primary Adhesion Test

100 sections of 1mm squares were formed on the coated specimen by scratching the paint film with an NT cutter. Then the specimen
15 were projected by using a Ericksen test machine. The projected portion of the specimen were covered tightly by adhesive tape. After that, adhesive tape were peeled off from the specimen. In this peeling off, paint at some section(spot) square were peeled off with the adhesive tape, and were exfoliated from the specimen. Primary
20 adhesion test was evaluated by using the rating system shown below.

- ◎ : no peeled spot
- : peeled spots - more than one and less than 10
- △ : peeled spots - not less than 10 and less than 50
- × : peeled spot - not less than 50 and less than 100

25 5-2-2. Secondary Adhesion Test

Each specimen was immersed in boiling water for two hours and then a test as same as the primary adhesion test was conducted.

5-2-3. Post-Painting Corrosion-Resistance

The paint film of each specimen was scratched by means of an

acryl cutter until the scratch get to the underlying metallic surface and the specimen was subjected to a salt water spray test conforming to JIS-Z2371 for 240 hours. After the test, the scratched area was covered and peeled off by means of an adhesive tape and the
 5 width (mm) of the exfoliated paint was observed for evaluation. The specimens were rated by using the following rating system.

- ◎ : less than 3 mm
- : not less than 3 mm and less than 5 mm
- △ : not less than 5mm and less than 10 mm
- 10 × : not less than 10 mm

5-3. Finger mark printing

A finger was pressed against each specimen and the finger mark printed on the surface was visually observed for evaluation. The following rating system was used.

- 15 ◎ : no finger mark observable
- : finger mark slightly observable
- △ : finger mark insignificantly observable
- × : finger mark clearly observable

6. Test Result

20 The results are summerized in Table 1. As clearly seen from Table 1, Embodiment Examples 1 through 8, where a surface treatment composition according to the invention was properly used, evidenced excellent corrosion resistance, coatability with paints and excellent reducing of finger mark. However, Comparative Example 1,
 25 where no second coating layer was formed, produced a poor product in terms of corrosion-resistance and fingermark-printing. Comparative Example 2, where the second coating layer contained no silica, produced a poor product also in terms of corrosion-resistance and fingermark-printing. Comparative Example 3, where the second coating

Table 1

	No.	Metallic Material	Corrosion Resistance	Coatability with Paints			Fingermark Printing
				Primary Adhesion Test	Secondary Adhesion Test	Post-Painting Corrosion Resistance	
Embodiment Example	1	GI	○	◎	◎	◎	◎
	2	AL	◎	◎	◎	◎	◎
	3	GI	◎	◎	◎	○	◎
	4	EG	○	◎	◎	○	◎
	5	GI	◎	◎	◎	◎	◎
	6	GI	○	◎	◎	○	◎
	7	GI	○	◎	◎	◎	◎
	8	SPC	○	◎	◎	○	◎
Comparative Example	1	GI	×	◎	◎	△	△
	2	EG	×	○	△	×	×
	3	AL	○	△	△	△	◎
	4	EG	×	○	○	×	○
	5	EG	×	×	×	×	◎

layer contained silica to an amount beyond the range of the present invention, produced a poor product in terms of coatability with paint. Comparative Example 4, where the amount of second coating layer is beyond the range of the invention produced a poor product in terms of corrosion-resistance. Comparative Example 5, where no first coating layer was formed, produced a product that was

considerably poor in terms of corrosion-resistance and adhesion.

Advantages Of The Invention

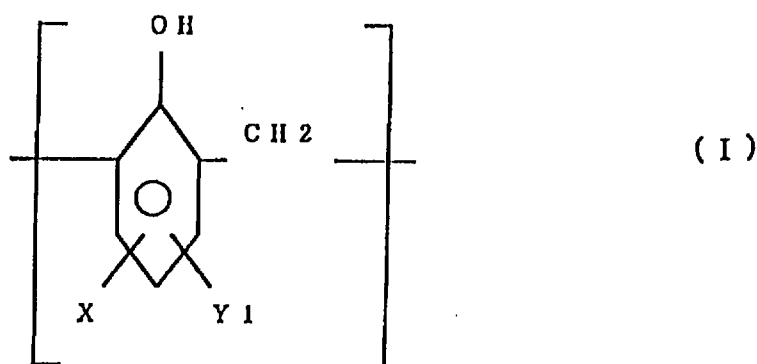
5 Metallic material of the invention are prepared by a method of not using any chromate compound, and are excellent in corrosion resistance, coatability with paints and reducing of finger mark adhesion. Additionally, the surface treatment composition of the invention is applicable to many sorts of metallic materials. Thus the present invention are suitable for recent industries where
10 environment are rigorously controlled and excellent properties of metallic materials are required. Further the invention makes a recycle of the metallic material easy since the harmful chromium are not contained in the metallic material.

C L A I M S

1. A metallic material with organic composite coating comprising a first coating layer being formed on the surface of the said metallic material containing :

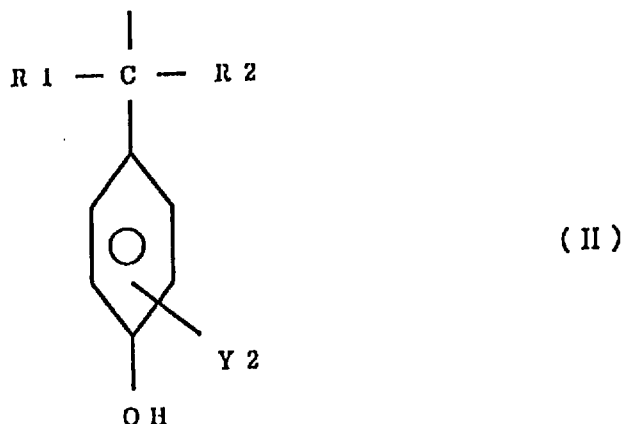
(A) a silane coupling agent containing one or more than one silane coupling compounds having at least a reactive functional group selected from an active-hydrogen-containing amino group, an epoxy group, a vinyl group, a mercapto group and a methacryloxy group, and

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

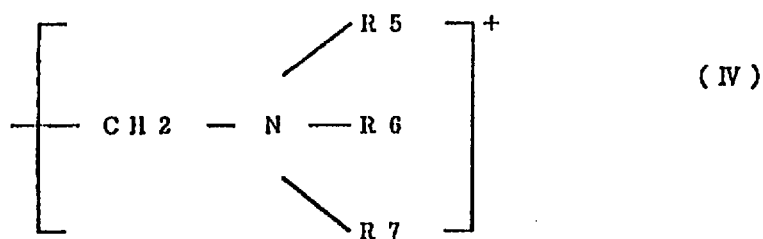
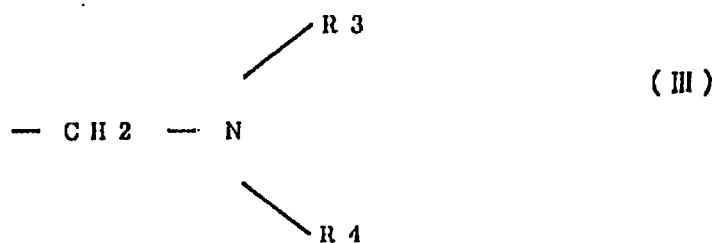


where X bonded to the benzene ring represents a hydrogen atom, a hydroxyl group, an alkyl group with any of C1 through C5, a hydroxyalkyl group with any of C1 through C5, an aryl group with any of C6 through C12, a benzyl group, a benzal group, an unsaturated hydrocarbon group to be condensed with said 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, and each of Y1 and Y2 bonded to the benzene rings in formulas (I) and (II) representing a Z group expressed 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 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 a second coating layer formed on said first coating layer by



using a resin composition containing silica by 5 to 70 weight portions relative to 100 weight portions of resin.

2. A metallic material with organic composite coating according to claim 1, wherein

the ratio by weight of said component (A), to said component (B), namely (A) / (B) is between 1/10 and 10/1

3. A metallic material with organic composite coating according to claim 1, wherein

said component (A) 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 group and (b) : a silane coupling agent containing one or more than one silane coupling compounds having one or more than one epoxy group.

4. A metallic material with organic composite coating according to claim 3, wherein the equivalent ratio of the active-hydrogen-containing amino group contained in said silane coupling agent (a) to the epoxy group contained in said silane coupling agent (b) is between 3:1 and 1:3.

5. A metallic material with organic composite coating according to any of claim 3 and 4, wherein

the ratio by weight of the sum of said silane coupling agent (a) and said silane coupling agent (b) to said polymer component (B), namely [(a) + (b)] / (B), is between 1/5 and 5/1.

6. A metallic material with organic composite coating



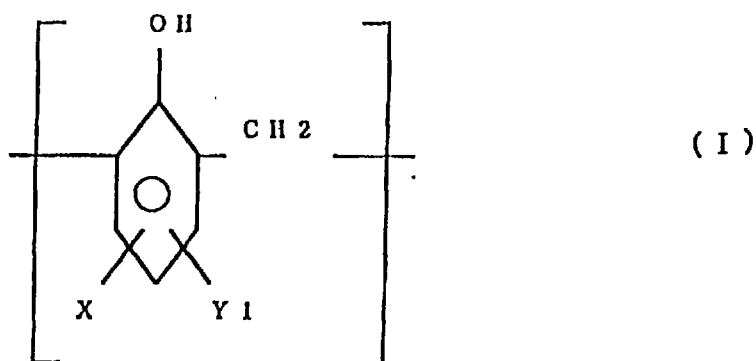
according to claim 1, wherein

said resin of the second layer has a structure having hydroxy group and/or carboxyl group.

7. A process for producing a metallic material with organic composite coating comprising a formation of a first coating layer on the surface of the metallic material by applying an aqueous composition having pH value of between 2.0 and 6.5 at a rate of 10~500 mg/m² at dried state and drying the aqueous composition to form the first coating layer, wherein the said aqueous composition is containing;

(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, and

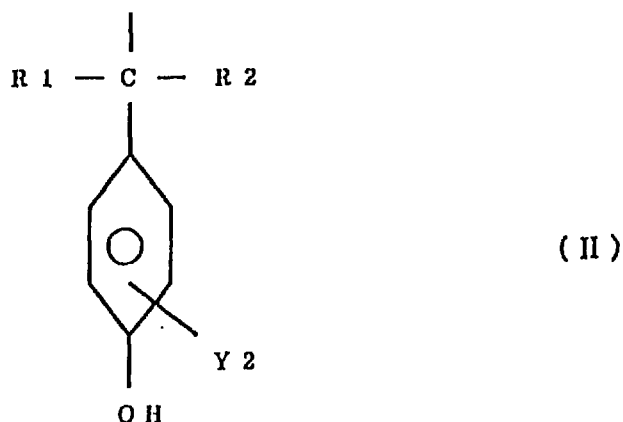
(B) one or more than one water-soluble polymers, each being expressed by general formula (I) below and showing an average degree of polymerisation between 2 and 50:



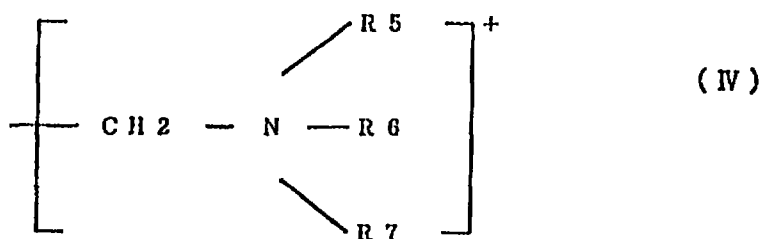
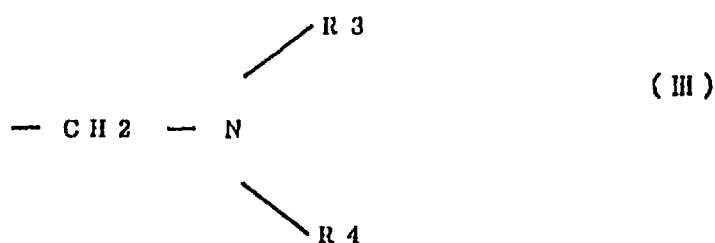
where X bonded to the benzene ring represents a hydrogen atom, a hydroxyl group, an alkyl group with any of C1 through C5, a hydroxyalkyl group with any of C1 through C5, an aryl group with any



of C6 through C12, a benzyl group, a benzal group, an unsaturated hydrocarbon group 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, and each of Y1 and Y2 bonded to the benzene rings in formulas (I) and (II) representing a Z group expressed 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 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 a formation of a second coating layer by applying on the said first coating layer using a resin composition containing silica by 5 to 70 weight portions relative to 100 weight portions of resin at a rate of 0.1 to 5.0 g/m² at dried state and drying it to form the second coating layer.

