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(54) Title: CORROSION PROTECTION PRETREATMENT AGENT, TREATING METHOD USING THE SAME AND ARTICLE THEREOF

(57) Abstract: A corrosion protection pretreatment agent,comprising a solvent, at least one inorganic inhibitor, at least one silane compound, and a bi-functional epoxy resin precursor (C), the bi-functional epoxy resin precursor (C) being represented by the formulas of R_1-Y- [CH_2-CH (OH) -R_3-CH (OH) -CH_2-X-R_4-X]$_n$-R_2. A method for treating metallic surface by using the corrosion protection pretreatment agent and an article having at least one portion that comprises side treated surface by the corrosion protection pretreatment agent. The article demonstrates improved corrosion resistance, adhesion properties and impact resistance.

CORROSION PROTECTION PRETREATMENT AGENT, TREATING METHOD USING THE SAME AND ARTICLE THEREOF

Technical field

This invention relates to a corrosion protection pretreatment agent and a method for treating metallic substrate surfaces that are coated with zinc or zinc alloys, with aluminum or aluminum alloys or with magnesium or a zinc-magnesium alloy. It is particularly suitable for the surface treatment in coil coating for the application of these substrates in appliance and architectural segments as well as in the automobile industry. An article comprising such metallic substrate surfaces treated by the corrosion protection pretreatment agent demonstrates good corrosion resistance property and improved adhesion on treated surface.

Background of the invention

Among the practically used metal materials, light metal materials such as zinc, aluminium and magnesium materials are the lightest ones and also have high specific strength and therefore, they have been applied in various fields such as interior and exterior parts for motor cars and two-wheeled vehicles, parts for appliance appliances, containers for storage such as bags and suitcases, goods for sports, parts for optical machinery and tools, sticks and further new fields in electronic industries such as computers and acoustics. However, the light metal materials, especially the magnesium materials are the most active metal materials and accordingly, it has been difficult to use them per se without any treatment because of their low corrosion resistance.

According to the prior art, the coil coating method substantially consists of three sub-steps. In a first step, the sheet metal is cleaned and provided with an inorganic pretreatment layer, in the second step the primer is applied, and in the final third method step the topcoat is applied. In some applications, clear coats or protective film coverings may additionally be applied. Attempts have been made to provide just with the pretreatment step those functions which facilitate use in the manner of the above-stated pre-applied coating.

In case where the surface of a metal substrate is subjected to electrodeposition coating or a coating by paint application, for example, aqueous coating, solvent coating, powder coating or the like, the surface of the metal substrate is, before forming a coat, chemically treated to forma chemical conversion film for the purpose of improving the performance, such as corrosion resistance, adhesion to a coating film and the like. For example, a suitable organic polymer is added to the inorganic conversion treatment for this purpose, which polymer is capable of forming a surface film exhibiting the functional properties required of a pre-applied coating.

DE19923118A1 discloses a polymerizable composition for the organic coating of metallic substrates and a method for protecting a steel substrate by a thin film of an organic/inorganic hybrid polymer based on an alkoxysilane, a further condensable organometallic compound of the formula $M(OR)_4$ and (meth)acrylic acid, water and a polymerization initiator. Coating is cured by thermal or photopolymerization. Zirconium and titanium are mentioned as metals for the organometallic compound. It is stated that such a film protects steel substrates from corrosion and oxidation and this coating is moreover intended to protect the substrate from impact and other mechanical effects.

DE19751153A discloses polymerizable compositions containing titanium, manganese and/or zirconium salts of olefinically unsaturated, polymerizable carboxylic acids and other olefinically unsaturated comonomers and a radical polymerization initiator are suitable for the organic coil coating of metallic materials. These non-aqueous metal coatings are suitable for the chromium-free pretreatment of steel with excellent corrosion control.

DE19754108A1 describes a chromium-free aqueous corrosion protection composition for the treatment of galvanized or alloy galvanized steel surfaces as well as aluminum surfaces. The agent is particularly suitable for treating metal strips in order to protect them against corrosion, with or without subsequent painting, and is preferably applied in such a way as to produce a dry layer coating on the surface.

Despite the wide-ranging prior art, a need still remains for improved anticorrosion agents and coating methods for metal surfaces which permit chromium-free pretreatment of the metallic substrates with good corrosion protection while avoiding strong acids, large amounts of organic solvent and elevated fluoride concentrations.

Various metal substrates, such as aluminum, aluminum alloy, zinc, zinc alloy, magnesium, zinc-magnesium alloy, have been widely used in color coated steel field. Due to the different properties of substrates, it is hard to treat these substrates by the same pretreatment agent on the production line, especially on the same color coil line.

Accordingly, it is an object of the present invention to provide a pretreatment agent for light metallic material, especially aluminium or its alloy, zinc or its alloy, magnesium or zinc-magnesium alloy, which can eliminate the problems associated with the conventional surface treatment composition.

Summary of the invention

The present invention relates to a corrosion protection pretreatment agent which is alkaline or acid. The agent is organic solvent-free. The corrosion protection pretreatment agent can react with metallic substrate directly. The corrosion protection pretreatment agent is cured by thermal curing and forms a corrosion protection pretreatment on the metallic substrate, the corrosion protection pretreatment shows good corrosion protection property and connect the substrate and primer tightly.

The present invention also relates to a corrosion protection pretreatment agent comprising: a) a solvent, b) at least one inorganic inhibitor, c) at least one silane compound, d) a bi-functional epoxy resin precursor (C), the bi-functional epoxy resin precursor (C) being represented by the following formulas: $R_1\text{-}Y\text{-}[CH_2\text{-}CH(OH)\text{-}R_3\text{-}CH(OH)\text{-}CH_2\text{-}X\text{-}R_4\text{-}X]_n\text{-}R_2$, wherein, independently, X= -COO-, sulphur moiety，-NR(H)-, $-P(OR)_2-O-$, -P (OR)(OH)-O-, -PO-O-; Y= -COO-, sulphur moiety，-NR(H)-, $-P(OR)_2-O-$, -P (OR)(OH)-O-, -PO-O-; R_2 being aromatic chain or aliphatic chain having from 1 to 20 carbon atoms or H; R_4 being aromatic chain or aliphatic chain having from 1 to 20 carbon atoms; R_1

being aromatic chain or aliphatic chain having from 1 to 20 carbon atoms, -XH or -X-R_4; R_3 being any types of chain as far as it connects two hydroxyl α-carbon atoms; n being an integer of 1~10.

The present invention also relates to a method The present invention also relates to a method for treating a metallic surface by using the corrosion protection pretreatment agent according to present invention, comprising steps of: a) bringing the corrosion protection pretreatment agent according to any one of preceding embodiments into contact with a metallic surface at a process temperature of at least 40°C, but no higher than 200°C, thereby creating a film on the metallic surface; b) optionally removing excess quantities of the corrosion protection pretreatment agent from the surface; and c) curing the coating located on the surface by means of thermal methods at a process temperature of 50-90 °C, or high-energy irradiation for a period of at least 10−5 seconds to form a cured coating.

The present invention also relates to an article which has at least one portion that comprises the treated surface of present invention. The article which is surface treated by the corrosion protection pretreatment agent of the present invention, or by the treating method of the present invention. The surface treated article has excellent corrosion resistance properties and improved adhesion property (before and after aging) in appliance application and architecture application.

Detailed description of the invention

In the following passages the present invention is described in more detail. Each aspect so described may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particularly, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

In the context of the present invention, the terms used are to be construed in accordance with the following definitions, unless a context dictates otherwise.

As used herein, the singular forms “a”, “an” and “the” include both singular and plural referents unless the context clearly dictates otherwise. As used in this specification and the appended claims, the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

The terms “comprising”, “comprises” and “comprised of” as used herein are synonymous with “including”, “includes” or “containing”, “contains”, and are inclusive or open-ended and do not exclude additional, non-recited members, elements or process steps.

The recitation of numerical end points includes all numbers and fractions subsumed within the respective ranges, as well as the recited end points.

Unless otherwise defined, all terms used in the disclosing the invention, including technical and scientific terms, have the meaning as commonly understood by one of the ordinary skills in the art to which this invention belongs to. By means of further guidance, term definitions are included to better appreciate the teaching of the present invention.

In the context of this disclosure, several terms shall be utilized.

The terms “polymer” is used herein consistent with its common usage in chemistry. Polymers are composed of many repeated subunits. The term “polymer” is used to describe the resultant material formed from a polymerization reaction.

The terms aluminum or zinc is used herein includes both the pure metal and alloys are designated hereinafter simply as "aluminum" or “zinc”, unless the context requires otherwise.

The terms "mass" and "weight" are used synonymously herein. Thus "percent by weight" (% by weight) means the percentage by mass content, based on the mass (by weight) of the entire composition or on the basis of all molecules, unless otherwise stated.

The term “chromium-free” as used herein in connection with the described compositions denotes that the composition comprises less than 100 ppm, preferably less than 10 ppm, particularly preferably less than 1 ppm, based on the total composition of compounds of the element that is chromium, in each case calculated as Cr_2O_3.

The term “water-based” or “aqueous” as used herein in connection with the described compositions denotes that the composition is liquid and comprises water as the primary solvent. In different embodiments, based on the total weight of the composition, at least 50 wt.%, or at least 60 wt.%, preferably at least 70 wt.%, still more preferably at least 90 wt.% of the solvent of the compositions is water.

Either a freshly produced or a freshly cleaned metal surface that has not been subjected to any corrosion protection measure is brought into contact with the corrosion protection pretreatment agent according to the invention, and the corrosion protection pretreatment agent is cured, and a corrosion protection pretreatment is formed on a metal sheet surface. In this way a treated metal surface is obtained that has a corrosion resistance property. The metal sheet can be stored and/or shipped in this form. In addition, it can be cut into pieces and optionally shaped and joined together with further pieces into structural units. Metal surfaces that have been coated with the corrosion protection pretreatment agent according to the invention can also be coated by further additional decorative/functional coatings, such as primer and top coating.

Alternatively, the metal sheet surface coated with the corrosion protection pretreatment agent according to the invention or metal sheets cut out of it can be over coated with at least one additional decorative coating or functional coating such as for example with a top coating or a primer, before these metal sheets are commercialized and/or further processed into sub-assemblies. In this case the corrosion protection pretreatment according to the invention functions as a corrosion protector and a connector of “substrate” and “additional coating”. The corrosion protection coating also provides good adhesion between the “additional coating” and the metal substrate, for color-coated sheet, such good adhesion property could meet the molding requirement in the latter operation. Thus, it can reduce some failure conditions such as paint film pulverization, foaming, breakage etc.

Corrosion protection pretreatment agent

The present invention relates to a corrosion protection pretreatment agent comprising: a solvent, a bi-functional epoxy resin precursor (C), at least an inorganic inhibitor, at least a silane compound. In some embodiments, the corrosion protection pretreatment agent is an acid aqueous dispersion. In some embodiments, the corrosion protection pretreatment agent is an alkaline aqueous dispersion. In some embodiments, the corrosion protection pretreatment agent further comprises one or more resin being selected from a group consisting of polyurethane resin (A), polyurethane-acrylic resin(B) and polyacrylic-epoxy resin (D).

Bi-functional epoxy resin precursor (C)

The bi-functional epoxy resin precursor (C) of present invention can be commercially available or be prepared by known methods, such as reacting a bi-functional epoxy compound and a nucleophilic or electrophilic compound having active hydrogen atom.

In some embodiments of present invention, the bi-functional epoxy resin can react with polymer having hydroxyl group (-OH), polymer having ester group (-COOR), organic/inorganic acid containing heteroatoms (N, S, P), or amino compound to produce the bi-functional epoxy resin precursor (C).

The epoxy compound used in production is not particularly limited in type as far as it contains has at least two epoxy groups in the molecule.

Two epoxy groups could produce the two hydroxyl groups of the bi-functional epoxy resin precursor (C).

The bi-functional epoxy compound includes bisphenol A epoxy, bisphenol F epoxy, acryl modified epoxy, epoxy ester obtained by a reaction of epoxy and unsaturated fatty acid, urethane modified epoxy, silane modified epoxy, halogenated epoxy alkane such as epihalohydrin, phosphoric acid-modified epoxy resin and an epoxy compound having two or more glycidyl groups. The above epoxy resins may be used alone or may be used in combination of two or more. The epoxy resin of present invention has an epoxide equivalent weight of from about 100 grams/equivalent to about 2,000 grams/equivalent.

The rigidity and suitable flexibility derived from the polyhydroxyl and heteroatom structure units in the bi-functional epoxy resin precursor (C), which could improve the adhesion of the pretreatment coating. Further, such structures are difficult to hydrolyze, and it can improve the adhesive ability, it can further improve the corrosion resistance of the pretreatment coating. The hydroxyl groups in the bi hydroxyl functional epoxy resin precursor, due to their polarity, could strongly bond with metal substrate and help to improve the adhesion with the metallic substrate. Further, the heteroatom structure (O-C, N-C, S-C, P-C) can help to build strong bond with the metallic substrate, too. In the treating process of the pretreatment coating, the hydroxyl groups in the epoxy resin precursor (C) cross-link with the zirconium compound and silanol group-containing compound whereby the chemical resistance and corrosion resistance of the coating are improved.

The epoxy resin precursor (C) is preferably used in the form of an aqueous dispersion thereof. The aqueous dispersion of the bi-functional epoxy resin precursor (C) may also contain a dispersant such as a surfactant, if required.

The weight molecular (ave.) of the bi-functional epoxy resin precursor (C) is preferably 200 to 10,000.

The pH value of the bi-functional epoxy resin precursor (C) is not particularly limited.

The content ratio of the bi-functional epoxy resin precursor (C) to the total mass of solid contents is preferably from 20.0 wt.% to 85 wt.%, or 21 wt.% to 80 wt.%, or 25 wt.% to 70 wt.%. If the content ratio is less than 20 wt.%, or less than 25 wt.% the T-bend test can't be passed; while if over 70 wt.%, or over 80 wt.% the chemical resistance will be impacted negatively.

In some embodiments, the epoxy resin can react with polymer having functional groups, organic/inorganic acid with heteroatoms (N, S, P) and amino to produce the bi-functional epoxy resin precursor.

In some embodiments, bisphenol A epoxy react with orthophosphoric acid and propylene glycol monomethyl ether to produce a phosphoric acid-modified epoxy resin.

In some embodiments, bisphenol A epoxy react with citric acid and propylene glycol monomethyl ether to produce a carboxyl group-modified epoxy resin.

In some embodiments, the bi-functional epoxy resin precursors have a formula as below:

R_1-Y-[CH_2-CH(OH)-R_3-CH(OH)-CH_2-X-R_4-X] $_n$-R_2

wherein, independently,

X= -COO-, sulphur moiety，-NR(H)-, -P(OR)$_2$-O-, -P (OR)(OH)-O-, -PO-O-; preferably being -COO-, -P (OR)(OH)-O-; the R group in -NR(H)-, -P(OR)$_2$-O-, -P (OR)(OH)-O- includes aliphatic chain having from 1 to 5 carbon atoms;

Y= -COO-, sulphur moiety，-NR(H)-, -P(OR)$_2$-O-, -P (OR)(OH)-O-, -PO-O-; preferably being -COO-, -P (OR)(OH)-O-; the R group in -NR(H)-, -P(OR)$_2$-O-, -P (OR)(OH)-O- includes aliphatic chain having from 1 to 5 carbon atoms;

R_2 being aromatic chain or aliphatic chain having from 1 to 20 carbon atoms or H; preferably being 1 to 10 carbon atoms or H;

R_4 being aromatic chain or aliphatic chain having from 1 to 20 carbon atoms; preferably being 1 to 10 carbon atoms;

R_1 being aromatic chain or aliphatic chain having from 1 to 20 carbon atoms, -XH or -X-R_4; preferably being 1 to 10 carbon atoms;

R_3 being any types of chain as far as it connects two hydroxyl α-carbon atoms; preferably R_3 being one selected from the group consisting of aromatic or aliphatic moiety having from 1 to 20 carbon atoms, polyurethane moiety, aliphatic or aromatic alkane having from 2 to 20 carbon atoms, acrylates containing polymer moiety.

n being an integer of 1~10, preferably being an integer of 2~8.

In some embodiments, the bi-functional epoxy resin precursors have a formula as below:

HX-R_4-X-[CH_2-CH(OH)-R_3-CH(OH)-CH_2-X-R_4-X]$_n$-H,

wherein, independently,

X= -COO-, -P (OR)(OH)-O-;

R_4 being aromatic chain or aliphatic chain having from 1 to 10 carbon atoms;

R_3 being any types of chain as far as it connects two hydroxyl α-carbon atoms;

n being an integer of 2~8.

Solvent

The corrosion protection pretreatment agent of the present invention comprises a solvent, such as water, to dissolve all components to form the coating dispersion. In some of the embodiments, water is used to dilute the surface treatment composition of the invention, and it provides relatively long-term stability to the composition. For example, a composition that contains less than about 40% by weight of water is more likely to polymerize or "gel" compared to a surface treatment composition with about 60%or greater by weight water under identical storage conditions. Although the corrosion protection pretreatment agents of the invention typically applied to the substrate will contain about 70 wt.% water or greater, such as 85 wt.%, it is to be understood that a corrosion protection pretreatment agent of the invention also includes a concentrated formulation composition with 50 wt.% to 85 wt.% water. The end-user simply dilutes the concentrated formulation with additional water to obtain an optimal corrosion protection pretreatment agent concentration for a particular surface treatment application.

In some embodiments of the present invention, it is preferably to use deionized water as solvent. In some embodiments of present invention, the solvent content of the corrosion protection pretreatment agent is 50 wt.% to 85 wt.%, or 60% wt.% to 85 wt.%, or 65% wt.% to 75 wt.%, based on the total weight of the corrosion protection pretreatment agent.

The corrosion protection pretreatment agent of the invention can be provided as a ready-to-use corrosion protection pretreatment agent, as a concentrated corrosion protection pretreatment agent that is diluted with water prior to use, as a replenishing composition, or as a multi-component coating system.

As used therein, “aqueous solution” refers to a corrosion protection pretreatment agent containing at least 50 wt.%, or at least 60 wt.%, or at least 65 wt.% of water, based on the total weight of the composition. In addition to water, other suitable solvents include those that have found particular utility in water borne coating technologies. Examples of other suitable solvents include, but are not limited to, water-compatible solvent, such as alcohols or ethers, more detailly, methanol and ethanol, glycols, such as dipropylene glycol, and other glycol ethers, such as propylene glycol monobutyl ether and dipropylene glycol monobutyl ether.

pH value of the corrosion protection pretreatment agent

In some embodiments, the corrosion protection pretreatment agent is an acid aqueous dispersion.

The pH value of the corrosion protection pretreatment agent is greater than 2.7 to less than 7, or 2.9 to 6.5, or 3.0 to 6.0, or 3.5 to 5.5, or 4.0 to 5.0. The lower limit of pH value is 2.7, 2.8, 2.9, 3.0, or 3.5, or 4.0, or 4.5, or 5.0; the upper limit of pH value is less than 7, or 6.5, or 6.0, or 5.5, or 5.2, or 5.0. One or more optional pH-adjusting agents, including minor amounts of mineral acids, alkali components, and organic acids may be used to adjust the pH value to above desired operating pH value if needed. The corrosion protection pretreatment agent with a basic operating pH value will lead to a better anti corrosion result.

The pH value of the aqueous corrosion protection pretreatment agent is in the range of 3.0 to 6.0, preferably 4.0 to 5.0 and in other words, the aqueous corrosion protection pretreatment agent according to the present invention is an acid solution or an acid dispersion.

In some embodiments, the corrosion protection pretreatment agent is an alkaline aqueous dispersion.

The pH value of the corrosion protection pretreatment agent is greater than 7 to 12, or 7.5 to 12, or 8 to 12, or 8.1 to 11.5. The lower limit of pH value is 7.1, 7.5, 8.0, 8.1, or 8.2; the upper limit of pH value is 12, or 11.8, or 11.6, or 11.5, or 11.2, or 11.0, or 10.0, 9.5, or 9.2, or 9.0, or 8.8, or 8.5. One or more optional pH-adjusting agents, including minor amounts of mineral acids, alkali components, and organic acids may be used to adjust the pH value to above desired operating pH value if needed. The corrosion protection pretreatment agent with a basic operating pH value will lead to a better anti corrosion result.

The pH value of the aqueous corrosion protection pretreatment agent is in the range of 7.1 to 12, preferably 8 to 12 and in other words, the aqueous corrosion protection pretreatment agent according to the present invention is an alkaline solution or an alkaline dispersion.

< Inorganic inhibitor>

The inorganic inhibitor of present invention can be selected by known methods based on the pH value of the corrosion protection pretreatment agent.

In some alkaline embodiments, the zirconium compound is used as the coating-forming component to form a coating of a three-dimensionally cross-linked zirconium oxide by hydrolysis and condensation accompanied with desorption of volatile acids in the aqueous system during the curing process and can provide positive effect on the corrosion resistance and the force with the substrate. The zirconium compound selected should stabilized in the alkali aqueous solution. The zirconium compound is not particularly limited in type as long as it contains a zirconium atom, and examples thereof include basic zirconium carbonate, zirconium carbonate salts such as sodium zirconium carbonate, potassium zirconium carbonate, lithium zirconium carbonate, and ammonium zirconium carbonate, zirconium hydroxide, zirconium lactate, zirconium acetate, zirconium nitrate, zirconium sulfate, zirconium chloride, calcium zirconate, zirconium ethoxide, and zirconium hexafluoroacetylacetonato. Of these, zirconium ammonium carbonate and zirconium sodium carbonate are preferred in terms of excellent corrosion resistance. The zirconium compound is selected form ammonium zirconium carbonate, potassium zirconium carbonate, basic zirconium oxide and zirconium acetate.

In some alkaline embodiments, wherein the inorganic inhibitor is metal compound like vanadium compound. The metallic material may have a three-dimensional shape as in constructs made of sheet metal. The metal compound including the metal atom is not particularly limited in type as long as it contains the metal, and examples thereof include metal oxides and/or metal alkoxides containing metal atoms mentioned above. The supply source of metal ions may be at least one metal compound selected from, for instance, ammonium salts and acetonates of Mo, W, Y, Bi, Mn, La, Ce, Sm, Zn, AL, Si, Ni, Co, Zr, Mg, Ti and V. Of these, compounds that dissolve in an alkali solution are preferred. Such as Vanadium compound, for example, vanadium pentaoxide, vanadium trioxide, vanadium oxyacetyl acetonate, vanadium acetyl acetonate and so on.

In some alkaline embodiments, the content mass ratio [M/silane] of the metallic material and organic silane is 1 to 5, preferably 2 to 4. If the solid content mass ration is less than 1, the effect on the corrosion resistance does not appear, while if the ration is higher than 5, the system is hard to keep stability and the chemical resistance will be impacted negatively.

In the alkaline aqueous corrosion protection pretreatment agent, the inorganic inhibitors present in an amount of from 0.3 wt.% to 7.0 wt.%, or from 0.5 wt.% to 6.5 wt.%, or from 1.5 wt.% to 6.3 wt.%, or from 1.7 wt.% to 6.1 wt.%, or from 2.0 wt.% to 4.0 wt.%, or from 3.0 wt.% to 4.0 wt.%, based on the weight of the solid contents in the corrosion protection pretreatment agent.

In some acid embodiments, inorganic inhibitor includes at least one water-soluble or water-dispersible fluorinated acid or salt thereof, wherein the fluorinated acid is defined by the following general empirical formula: $H_mT_qF_pO_n$,

wherein:

q and p each represent an integer from 1 to 10;

m and n each represent an integer from 0 to 10; and,

T is an element selected from Ti, Zr, Hf, Si, Sn, Al, Ge, and B.

In some acid embodiments, inorganic inhibitor includes at least one fluoro acid selected from fluotitanic acid (H_2TiF_6), fluozirconic acid (H_2ZrF_6), fluosilicic acid (H_2SiF_6), fluoboric acid (HBF_4), fluostanoic acid (H_2SnF_6), fluogermanic acid (H_2GeF_6), hafnium fluoride Acid (H_2HfF_6) and fluoroaluminate (H_3AlF_6). In some preferred embodiments, inorganic inhibitor includes at least one fluorinated acid is selected from fluotitanic acid (H_2TiF_6), fluozirconic acid (H_2ZrF_6) and fluosilicic acid (H_2SiF_6).

Under the condition that the salt is water-soluble or water-dispersible, one or more H atoms of the above-mentioned fluorinated acid may be replaced by a suitable cation such as ammonium, alkaline earth metal cation or alkali metal cation.

It is not ruled out that there are free fluoride ions that are not combined in a complex form in the passivation composition, because fluoride anions can act as a promoter in the formation of the coating and exist at the interface between the coating and the metal substrate. Such free fluoride can be included by adding, for example, hydrofluoric acid; alkali metal fluoride such as sodium fluoride; alkali metal fluoride such as sodium fluoride; ammonium fluoride; and ammonium fluoride to the passivation composition anion.

In some embodiments of present invention, the acid corrosion protection pretreatment agent should include a fluorinated acid or its salt, so that the molar concentration of the metal (T) in the aqueous composition is usually 0.1-1.0 mol/L, but it is more preferably 0.2-0.8 mol/L.

< Silane Compound>

The corrosion protection pretreatment agent in the present invention also comprises a silane compound as coupling agent. The silane coupling agent of present invention can be selected based on the pH value of the corrosion protection pretreatment agent.

While exact composition of the silane coupling agent is not crucial to the invention, silane coupling agents that conform to the following general chemical formula are preferred: $Y_yR_rSiX_x$, wherein R represents an alkyl group; X represents a group selected from methoxy and ethoxy groups; Y represents a group selected from a vinyl group, a mercapto group, a glycidoxyalkyl group, or a methacryloxyalkyl group; and each of r, x, and y is an integer independently selectable from 1 to 3, except that r may also be zero and the sum $r+x+y = 4$.

More preferably, the silane coupling agent component is selected from the group consisting of vinyltrimethoxysilane, vinyltriethoxysilane, gamma-mercaptopropyltrimethoxysilane, gamma-glycidoxypropyltrimethoxysilane, gamma-glycidoxypropylmethyldimethoxysilane, gamma-methacryloxypropyltrimethoxysilane, gamma-methacryloxypropylmethyldimethoxysilane, and mixtures of any two or more of these.

Silane coupling agents with the above general formula are preferred in acid corrosion protection pretreatment agents, because they have good solubilities in the aqueous solution used to contact metallic surfaces in a process according to present invention and make a relatively large contribution to improving the corrosion resistance of the pretreatment coating formed on the metallic surface.

In some alkaline embodiments, the silane coupling agent in the present invention comprises silanol group-containing compounds, which are hydrolysis of an organic silicone compound having a glycidoxyl group. The hydrolysis of the organic silicone can be processed at pH value a range of 8 to 10. As the hydrolysis aid, prefer is alkaline materials, such as aqueous ammonia and organic amine since it evaporates in the coating forming process and is difficult to remain in the pretreatment coating.

There is no limitation to the silane coupling agents to be used in the alkaline pretreatment agent, as long as the silane coupling agents are compatible to the rare earth element containing compound, such as the water-soluble zirconium salts and other components contained.

The silane coupling agents may have an amino functional group or epoxy functional group. The amino or epoxy functional silane may comprise C2 -C10 alkoxy groups.

In some embodiments of present invention, the silane coupling agent may have the general structure $XY(Z)_nSi(OH)_{3-n}$, wherein independently, X being a glycidoxyl group or functional group derived from a glycidoxy group, Y being a C1 to C10 alkylene group, Z being a methoxy group, ethoxy group or methyl group, and n being an integer of 0 to 2.

Some exemplary epoxy functional silanes include 3-glycidyloxypropyltrimethoxysilane, 3-glycidyloxypropyltriethoxysilane or beta- (3, 4-epoxycyclohexyl) ethyltrimethoxysilane.

A suitable amine functional silane coupling agent for use in the surface treatment composition of the present invention has the structure: $(R_2\text{-}O)_3\text{-}Si\text{-}R_3\text{-}NH_2$, wherein R_2 is an alkyl group containing 1 to 10 carbon atoms, preferably 1 to 6 carbon atoms and most preferably is a methyl group, R_3 is an alkylene moiety containing 1 to 10 carbon atoms optionally substituted with an amine group. Examples of amine functional silane coupling agent are aminomethylaminopropyltrimethoxylsilane ($(MeO)_3\text{-}Si\text{-} (CH_2)_3 \text{-}NH\text{-} (CH_2) \text{-}NH_2$), aminopropyltrimethoxysilane ($(MeO)_3\text{-}Si\text{-}(CH_2)_3\text{-}NH_2$), and/or aminopropyltriethoxysilane ($(EtO)_3\text{-}Si\text{-}(CH_2)_3\text{-}NH_2$).

Other examples of silane coupling agents suitable for the present invention include but not limited to 3-aminopropylmethyldiethoxysilane, 3-aminopropyltriethoxysilane, 4-aminobutyltriethoxysilane, 3-

[2- (2-aminoethylamino) ethylamino] propyltrimethoxysilane, N- (2-aminoethyl) -3-aminoisobutylmethyldimethoxysilane, (aminoethylaminomethyl) phenethyltrimethoxysilane, N- (2-aminoethyl) -3-aminopropylmethyldimethoxysilane, N- (2-aminoethyl) -3-aminopropyltrimethoxysilane, N- (2-aminoethyl) -3-aminopropyltris (2-ethylhexoxy) silane, N- (6-aminohexyl) aminopropyltrimethoxysilane, m-aminophenyltrimethoxysilane, p-aminophenyltrimethoxysilane, o-aminophenyltrimethoxysilane, 3-aminopropyltrimethoxysilane, N-2-aminoethyl-3-aminopropyltrimethoxysilane, aminopropyltrimethoxysilane, aminopropylmethyldimethoxysilane, aminopropyltriethoxysilane, aminopropylmethyldiethoxysilane, aminophenyltrimethoxysilane, 4-amino-3-dimethylbutyltrimethoxysilane, 4-amino-3-dimethylbutylmethyldimethoxysilane, 4-amino-3-dimethylbutyltriethoxysilane, 4-amino-3-dimethylbutylmethyldiethoxysilane, N-phenyl-aminopropyltrimethoxysilane, N-naphthyl-aminopropyltrimethoxysilane, N-phenyl-aminopropylmethyldimethoxysilane, N-naphthyl-aminopropylmethyldimethoxysilane, N- (n-butyl) aminopropyltrimethoxysilane, N- (n-butyl) aminopropylmethyldimethoxysilane, N-ethyl-aminopropyltrimethoxysilane, N-ethyl-aminopropylmethyldimethoxysilane, N-methyl-aminopropyltrimethoxysilane, N-methyl-gamma aminopropylmethyldimethoxysilane, N-beta- (aminoethyl) -aminopropyltrimethoxysilane, N-beta- (aminoethyl) -aminopropyltriethoxysilane, N-beta (aminoethyl) aminopropylmethyldimethoxysilane, N-beta- (aminoethyl) aminopropylmethyldiethoxysilane, N-3- [amino (dipropyleneoxy)] aminopropyltrimethoxysilane, (aminoethylaminomethyl) phenethyltrimethoxysilane, N- (6-aminohexyl) aminopropyltrimethoxysilane, N- (2-aminoethyl) -11-aminoundecyltrimethoxysilane, bis (trimethoxysilylpropyl) amine, (3-trimethoxysilylpropyl) diethylenetriamine, (aminoethylamino) -3-isobutyldimethylmethoxysilane, (cyclohexylaminomethyl) triethoxysilane, (N, N-diethyl-3-aminopropyl) trimethoxysilane, (phenylaminomethyl) methyldimethoxysilane, 11-aminoundecyltriethoxysilane, 2- (2-pyridylethyl) thiopropyltrimethoxysilane, 2- (4-pyridylethyl) triethoxysilane, 2- (trimethoxysilylethyl) pyridine, 3- (1, 3-dimethylbutylidene) aminopropyltriethoxysilane, 3- (2-imidazolin-1-yl) propyltriethoxysilane, 3- (m-aminophenoxy) propyltrimethoxyaminopropylsilanetriol, 3- (m-aminophenoxy) propyltrimethoxysilane, 3- (N, N-dimethylaminopropyl) trimethoxysilane, 3- (N-allylamino) propyltrimethoxysilane, 3-

aminopropyldiisopropylethoxysilane, 3-aminopropyldimethylethoxysilane, 3-aminopropylmethyldiethoxysilane, 3-aminopropyltriethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyltris (methoxyethoxyethoxy) silane, 4-aminobutyltriethoxysilane, acetamidopropyltrimethoxysilane, aminopropylsilanetriol, bis (2-hydroxyethyl) -3-aminopropyltriethoxysilane, bis (methyldiethoxysilylpropyl) amine, bis (methyldimethoxysilylpropyl) n-methylamine, bis (triethoxysilylpropyl) amine, bis (trimethoxysilylpropyl) urea, bis [(3-trimethoxysilyl) propyl] ethylenediamine, bis [3- (triethoxysilyl) propyl] urea, diethylaminomethyltriethoxysilane, N- (2-aminoethyl) -3-aminoisobutylmethyldimethoxysilane, N- (2-aminoethyl) -3-aminopropylmethyldimethoxysilane, N- (2-aminoethyl) -3-aminopropylsilanetriol, n-(2-aminoethyl) -3-aminopropyltriethoxysilane, N- (2-aminoethyl) -3-aminopropyltrimethoxysilane, N-(3-aminopropyldimethylsila) aza-2, 2-dimethyl-2-silacyclopentane, N- (3-triethoxysilylpropyl) 4, 5-dihydroimidazole, N- (3-trimethoxysilylpropyl) pyrrole, N- (6-aminohexyl) aminomethyltriethoxysilane, N- (6-aminohexyl) aminomethyltrimethoxysilane, N, N, N-trimethyl-3- (trimethoxysilyl) -1-propanaminium, N, N-dioctyl-N'-triethoxysilylpropylurea, N- [5- (trimethoxysilyl) -2-aza-1-oxopentyl] caprolactam, N-3- [(amino (polypropylenoxy)] aminopropyltrimethoxysilane, N-butylaminopropyltrimethoxysilane, N-cyclohexylaminopropyltrimethoxysilane, N-ethylaminoisobutylmethyldiethoxysilane, N-ethylaminoisobutyltrimethoxysilane, N-phenylaminomethyltriethoxysilane, n-trimethoxysilylpropylcarbamoylcaprolactam, ureidopropyltriethoxysilane, ureidopropyltrimethoxysilane, and mixture thereof, and preferably is selected from N-2-aminoethyl-3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-aminopropyltrimethoxysilane, bis [3- (trimethoxysilyl) propyl] amine.

The amine functional silane coupling agent and/or epoxy functional silane coupling agent can be used alone or may be used in combination of two or more in alkaline pretreatment agent.

In some embodiments of present invention, the silane coupling agent, based on the total weight of solid contents, the silanol group containing resin being represented by the following formulas $Y\text{-}[Si(Y)_2\text{-}O]_n\text{-}R$,

wherein, independently, n being an integer of 1 to 3,

R being a moiety of C1 to C6 alkyl groups and preferably C1 to C3 alkyl groups, Y being a moiety selected from alkyl groups with not more than 10 carbon atoms carrying at least one epoxy, amino, hydroxyl, vinyl and/or thiol group, wherein the Y being selected mutually independent from each other.

In some especially preferred embodiments, the agent of this invention comprises silane compounds that are selected from vinyltriacetoxysilane, bis-trialkoxysilypropylamines, aminoethylaminopropyltrialkoxylsiane, aminoethylaminopropyltrialkoxysilanes, mercaptopropyltrialkoxysilanes, bis-trialkoxysilylpropyl-tetrasulfide, 3-glycidoxypropyltrialkoxysilane, wherein the alkoxy groups have not more than 3 carbon atoms.

In some alkaline pretreatment agents of present invention, the silane coupling agent is present in an amount of from 2.0 wt.% to 4.5 wt.%, or from 2.5 wt.% to 4.5 wt.%, or from 2.0 wt.% to 4.2 wt.%, or from 2.5 wt.% to 4.0 wt.%, or from 2.5 wt.% to 3.8 wt.%, based on the total weight of the solid contents of the pretreatment agent.

In some acid pretreatment agent of present invention, the silane coupling agent is present in an amount of from 40.0 wt.% to 60.0 wt.%, or from 42.0 wt.% to 58.0% wt.%, or from 45.0% wt.% to 55.0 wt.%, or from 46.0 wt.% to 53.0 wt.%, based on the total weight of the solid contents of the pretreatment agent.

Resin(s)

The corrosion protection pretreatment agent further comprises one or more resin being selected from a group consisting of polyurethane resin (A), polyurethane-acrylic resin(B) and polyacrylic-epoxy resin (D).

<Polyurethane resin (A)>

The polyurethane resin (A) used in the present invention may be produced by subjecting an organic compound containing two or more hydroxyl groups in a molecule thereof (polyol) and a polyisocyanate to polyaddition reaction, further chain-extending with diamine or the like, and dispersing it in water or the like.

The polyol is not particularly limited as long as it contains two or more hydroxyl groups in a molecule thereof. As the polyol, preferred are a polycarbonate polyol, a polyester polyol. More specifically, the polyurethane resin (A) is preferably in the form of a polycarbonate-based polyurethane or a polyester-based polyurethane.

The polycarbonate polyol may be produced by reacting a carbonate compound with a diol. Examples of the carbonate compound include dimethyl carbonate, diethyl carbonate, diphenyl carbonate, ethylene carbonate, diethylene carbonate and the like. Examples of the diol include an aliphatic diol that may be substituted with a lower alcohol; an alicyclic diol such as cyclohexanediol, a hydrogenated xylene glycol, etc.; and an aromatic diol such as xylylene glycol, etc. Among these diols, preferred is an aliphatic diol, and more preferred is an aliphatic diol having a carbon chain length of not less than 4 and not more than 9, such as 1,4-butanediol, 3-methyl-1,5-pentanediol, 1,6-hexanediol, heptanediol, octanediol, nonanediol, etc.

The polyester polyol may be produced by subjecting a low-molecular diol and a dicarboxylic acid to condensation reaction. Examples of the low-molecular diol include diols having not less than 2 and not more than 6 carbon atoms, such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,4-butanediol, etc. Among these low-molecular diols, preferred are ethylene glycol, propylene glycol, 1,4-butanediol and the like. Examples of the dicarboxylic acid include aliphatic dibasic acids such as succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, brassylic acid, etc.; and aromatic dibasic acids such as isophthalic acid, terephthalic acid, naphthalenedicarboxylic acid, etc. Among these dicarboxylic acids, preferred are aliphatic dibasic acids, and more preferred are dibasic acids having a methylene chain length of not less than 4 and not more than 8, such as adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, etc.

Examples of the polyisocyanate include a chain-like aliphatic diisocyanate such as tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, dodecamethylene diisocyanate, trimethyl hexamethylene diisocyanate, lysine diisocyanate, etc.; an aliphatic diisocyanate having a cyclic structure such as isophorone diisocyanate, a hydrogenated xylylene diisocyanate, dicyclohexylmethane 4,4′-diisocyanate, etc.; an aromatic ring-containing aliphatic diisocyanate such as xylylene diisocyanate, tetramethyl xylylene diisocyanate, etc.; an aromatic diisocyanate such as tolylene diisocyanate, diphenylmethane diisocyanate, etc.; and modified products of these diisocyanates (such as carbodiimide-, uretdione- and uretimine-containing modified products, etc.), and the like. Among these polyisocyanates, preferred are an aliphatic diisocyanate and an aromatic diisocyanate.

The polyurethane resin (A) is preferably used in the form of an aqueous dispersion thereof. The aqueous dispersion of the polyurethane resin (A) may also contain a dispersant such as a surfactant, if required.

In some embodiments, the polyurethane resin (A) is an aqueous anionic dispersion. In some embodiments, the polyurethane resin (A) preferably contains acid groups from the viewpoint of improving dispersion stability thereof in an aqueous medium as well as from the viewpoint of improving storage stability of the aqueous dispersion as well as adhesion properties and optical density of the aqueous dispersion. As the acid groups of the polyurethane resin (A), from the viewpoint of improving storage stability of the water-based pigment dispersion as well as adhesion properties and optical density of the water-based ink, preferred is a carboxyl group.

The carboxy group-containing polyurethane resin (A) may be produced by subjecting the polyol, the polyisocyanate and a dialkanol carboxylic acid to polyaddition reaction. Examples of the dialkanol carboxylic acid include dimethylol butanoic acid, dimethylol propionic acid and salts of these acids, and the like. Examples of the reaction solvent used in the aforementioned polyaddition reaction include acetone, methyl ethyl ketone, tetrahydrofuran, dioxane, ethyl acetate, toluene, xylene and the like. In the aforementioned polyaddition reaction, a chain extender or a reaction terminator may also be used in combination with the aforementioned components, if required. By using the chain extender, it is possible to increase a molecular weight of the resulting resin. As the chain extender, there may be a polyol and a polyamine. Also, as the reaction terminator, there may be a monoalcohol and a monoamine.

In some alkaline embodiments, most or even all of the polyurethane resins included in the corrosion protection pretreatment agent preferably have carboxyl groups. The carboxyl groups, which are optionally neutralized and reacted, in particular by ammonia, amines (in particular alkanolamines) or/and alkali metal compounds, to form an aqueous solution with a polyurethane synthetic resin which can be dispersed easily with water, are optionally not water-soluble before the reaction under standard conditions. The neutralization of the -COOH groups is an anionic stabilization. It may additionally be necessary to additionally add at least one emulsifier or/and at least one protective colloid (as additives within the scope of the present application) to stabilize the dispersion of the polyurethane synthetic resin and the corrosion protection pretreatment agent.

In some acid embodiments, the polyurethane resin (A) having a cationic group, the polyol, polyisocyanate and polymerization method which are the monomer components to be constituted are not particularly limited. For example, the polyurethane resin (A) can be obtained by selecting the respective raw materials from above-mentioned anionic type polyurethane resin to polycondensation in an inert organic solvent such as methyl ethyl ketone, and reacting the resultant urethane prepolymer with an acid such as formic acid or acetic acid, or a cationizing agent such as dimethyl sulfate, and thereby quaternizing a part of the tertiary amino group, for a polyol such as a polyester polyol, a polyether polyol, or a polycarbonate polyol, a diisocyanate such as an aliphatic, alicyclic, or aromatic diisocyanate, and a compound having 2 or more hydroxyl groups or amino groups and 1 or more tertiary amine and/or quaternary ammonium groups, which are generally used for producing the urethane resin.

The amount of the cationic group and the total amine number contribute to the water dispersion stability of the cationic polyurethane resin (A) and the miscibility with other components. Further, the cationic group and the total amine is possible to improve the acid resistance and alkali resistance of the formed pretreatment layer while ensuring the storage stability, and as a result, excellent corrosion resistance is exhibited.

In the preparation process of the present invention, the pH of the aqueous pretreatment agent without the addition of further compounds may preferably be from greater than 7 to 12, particularly preferably from greater than 7 to 11, from 7.5 to 10.5 or from 8 to 9.5. It should be noted that the polyurethane resin has typically been neutralized by the manufacturer, e.g., during polymerization. The aqueous pretreatment agent preferably has a pH of 1 to 12 in an aqueous formulation without the addition of other compounds. If during the preparation of the aqueous composition the pH of the aqueous composition shifts to a value outside the range of greater than 7 to 11, it is advisable to bring it back to the pH range of greater than 7 to 11 or even to a narrower working range within this range by means of a suitable addition, but preferably only at least one basic substance is added, since undesirable salt formation may occur upon addition of acid or/and acidic substance. If the pH drops as a result of storage of the synthetic resin or/and mixture, it may be helpful to bring the pH (in particular the pH of the aqueous pretreatment agent otherwise ready for use) back into the more alkaline range by adding, for example, aqueous sodium hydroxide solution.

In some embodiments of the present invention, the polyurethane resins have a glass transition temperature (Tg) of -100 °C to -50 °C, or -100 °C to -70 °C, and an elongation of 300% or more, or 500% or more.

In some embodiments of the present invention, the weight average molecular weight of the polyurethane resin may be at least 2,000, preferably 5,000-250,000, particularly preferably 20,000-200,000.

As used herein, "M_w" refers to the weight average molecular weight and means the theoretical value as determined by Gel Permeation Chromatography (GPC) relative to linear polystyrene standards of 1.1 M to 580 Da and may be performed using Waters 2695 separation module with a Waters 2414 differential refractometer (RI detector).

In some embodiments, the polyurethane resin (A) is an aqueous anionic dispersion, and the polyurethane resins include polyether based polyurethane resins and polyester based polyurethane resins.

Examples of commercially available polyurethane resins are, for example, Leasys 3900 or Leasys 5531 from Wanhua Chemical, K200 polyurethane resin from Anhui Andahuatai materials.

The above polyurethane resin can be used alone or in any combinations.

In some embodiments, the polyurethane resin (A) is an aqueous anionic dispersion, and the polyurethane resins include polycarbonate based polyurethane resins.

Examples of commercially available polycarbonate resins are, for example, Hauthane L-3528 and L-3529 from Hauthaway, Esacote PU A32D and ESACOTE PU 6419 from Lamberti.

The above polycarbonate polyurethane resins can be used alone or in any combinations.

In some embodiments, the polyurethane resin (A) is an aqueous cationic dispersion, and the polyurethane resins include polyether based polyurethane resins and polyester based polyurethane resins.

Examples of commercially available polyurethane resins are, for example, AH-1730 and AH-1610Y from Anhui Andahuatai materials, PU7305 polyurethane resin from Shanghai Beite New Material Technology and Wantipro 0380 and Wantipro 0312N from Wanhua Chemical.

<Polyurethane-acrylic resin (B)>

In some embodiments, the polyurethane-acrylic resin (B) is an aqueous dispersion of polyurethane-acrylic resin.

The polyurethane-acrylic resin can be directly synthesized according to a known method, or be commercially available. For example, the acrylic urethane dispersion can be prepared by reacting polyols, acids, isocyanates, and acrylates. The polyols may be one or more selected from the group comprising polybutylene glycol (PTMG), 1,6-hexanediol, ethylene glycol, propylene glycol, diethylene glycol, butylene glycol, neopentyl glycol, trimethylolpropane, butanediol, 1,4-hexanediol and 3-methylpentanediol. The acids may be one or more selected from the group comprising dimethylolpropionic acid (DMPA), acrylic acid, and adipic acid, phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, adipic acid, fumaric acid, maleic acid, trimellitic acid, malic acid and aconitic acid. In addition, the isocyanates may be one or more of selected from the group comprising isophorone diisocyanate (IPDI), trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, propylene diisocyanate, ethylene diisocyanate, 2,3-dimethylethylene diisocyanate, 1-methyl trimethylene diisocyanate, 1,3-cyclopentene diisocyanate, 1,4-cyclopentene diisocyanate, 1,2-ring pentene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, oligomeric isocyanate, isophorone diisocyanate, 4,4-diphenylpropane diisocyanate, xylene diisocyanate, and 1,1,6,6-tetramethylhexamethylene diisocyanate. The acrylates may include monounsaturated esters of (meth)acrylic acid with an unsubstituted alkyl radical that are suitable with particular preference are methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, amyl (meth)acrylate, hexyl (meth)acrylate, ethylhexyl (meth)acrylate, 3,3,5-trimethylhexyl (meth)acrylate, stearyl (meth)acrylate, lauryl (meth)acrylate, cycloalkyl (meth)acrylates. Suitable monounsaturated esters of (meth)acrylic acid with a substituted alkyl radical may be substituted preferably by one or more hydroxyl groups, such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate and 4-hydroxybutyl (meth)acrylate, with 2-hydroxyethyl (meth)acrylate. The total mass of the (meth) acrylates preferably has a content of 5.0 wt.% to 70.0 wt.%, more preferably 30.0 wt.% to 50.0 wt.%, based on the total weight of the polyurethane-acrylic resin (B). And the (meth)acrylates selected such that the resulting polyurethane-acrylic resin (B) has a glass transition temperature Tg of from 5 °C to 45 °C and preferably from 10 °C to 40 °C.

In some embodiments, the polyurethane-acrylic resin (B) preferably contains a mixed or crosslinked (meth)acrylic resin and the polyurethane resin.

It is more preferred that the acid groups contained in each of the (meth)acrylic resin and the polyurethane resin are partially crosslinked with the crosslinking agent.

In some embodiments of present invention, the aqueous dispersion of polyurethane-acrylic resin includes a polyester-polyurethane-poly (meth) acrylate, polyester-polycarbonate-polyurethane-poly(meth)acrylate, and corresponding derivatives.

Examples of commercially available polyurethane-acrylic resins are, for example, BS PUAW TT-10 and SGR-0215W from Shanghai Xinyang Chemical, or SGR-3002W from Changle Chemical, or Neopac E-123 and Neopac E-129 from DSM.

The above polyurethane-acrylic resins can be used alone or in any combinations.

In some embodiments of present invention, the above polyurethane-acrylic resin (B) and polyurethane resin (A) can be used alone or in any combinations.

In some embodiments, the polyurethane-acrylic resin (B) is a cationic aqueous dispersion of polyurethane-acrylic resin, the cationic acrylic urethane dispersion can be prepared by reacting polyols, cationizing agent (hydrophilic chain extender), isocyanates, and acrylates. The hydrophilic chain extender is selected based on the pH value of the corrosion protection pretreatment agent. In some acid embodiments, cationizing agent is preferred to form a cationic aqueous dispersion; in some alkaline embodiments, anionizing agent is preferred to form a anionic aqueous dispersion.

<Polyacrylic-epoxy resin (D)

The corrosion protection pretreatment agent of present invention further comprises a polyacrylic-epoxy resin (D).

In some embodiments of present invention, the polyacrylic-epoxy resin (D) is an aqueous dispersion.

In some embodiments of present invention, the polyacrylic-epoxy resin (D) of the present invention including a carboxyl group-containing polymer containing a repeating unit derived from a carboxyl group-containing vinyl monomer. In other words, the polyacrylic-epoxy resin (D) contains the carboxyl group-containing polymer chain as a part of the structure.

The glass transition temperature (Tg) of the aqueous polyacrylic-epoxy resin (D) is not particularly limited and is preferably from 50 °C to 100 °C. The method of producing the aqueous polyacrylic-epoxy resin (D) is not particularly limited, and any known method is applicable.

For example, epoxy resin is at least reacted with glycidyl group-containing vinyl monomers or amido group-containing vinyl monomers or amino group-containing vinyl monomers, and glycidyl ethers of polyalkylene glycols, here amine was added as the catalyst to obtain the carboxyl group containing vinyl monomer. And then polymerize the monomer and carboxyl group-containing vinyl monomer. For the glycidyl group-containing vinyl monomer may be used without limitation as long as it contains glycidyl group and polymerizable vinyl group in the molecule including glycidyl (meth) acylate, 3-methyl glycidyl (meth)acrylate and (meth)allyl glycidyl ether. For the amido group-containing vinyl monomer may be used without limitation as long as it contains amido group and polymerizable vinyl group in the molecule. including acrylamide, N-butoxymethyl(meth)acrylamide, N-methyl (meth)acrylamide, N,N-dimethyl(meth)acrylamide, N-isopropyl(meth)acrylamide, diacetone(meth)acrylamide and N-vinylformamide. For the amino group-containing vinyl monomer, it contains amino group and polymerizable vinyl group in the molecule, including 20 N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate and N,N-dimethylaminopropyl (meth)acrylate.

The above polyacrylic-epoxy resins can be used alone or in any combinations.

Examples of commercially available polyurethane-acrylic resins are, for example, aqueous polyurethane-epoxy resins MR1487W from KDD functional material; GS-5000B; GS-500D from Guangshu Chemical. And ACUST 3958 from Wuxi Honghui New Materials Technology.

In some embodiments of the present invention, the above polyacrylic-epoxy resin (D), polyurethane-acrylic resin (B) and polyurethane resin (A) can be used alone or in any combinations.

In some acid aqueous corrosion protection pretreatment agents of present invention, the content ratio of the resin(s) is from 0 wt.% to 48% wt.%, or 0 wt.% to 45 wt.%, or 0 wt.% to 42 wt.%, or 20 wt.% to 42 wt.%, based on the total weight of resins and bi-functional epoxy resin precursor (C) in the corrosion protection pretreatment agent. The lower limit concentration of the resin(s) is 0 wt.%, or 15 wt.%, or 20 wt.%, or 25 wt.%, based on the total weight of resins and bi-functional epoxy resin precursor (C) in the corrosion protection pretreatment agent. The upper limit concentration of the resin(s) is 48 wt.%, 45 wt.%, or 42 wt.%, or 40 wt.%, or 38 wt.%, based on the total weight of resins and bi-functional epoxy resin precursor (C) in the corrosion protection pretreatment agent.

In some alkaline aqueous corrosion protection pretreatment agents, the content ratio of the resin(s) is from or 25 wt.% to 55 wt.%, or 28 wt.% to 53 wt.%, based on the total weight of resins and bi-functional epoxy resin precursor (C) in the corrosion protection pretreatment agent. The lower limit concentration of the resin(s) is 25 wt.%, or 27 wt.%, or 28 wt.%, or 30 wt.%, or 33 wt.%, based on the total weight of resins and bi-functional epoxy resin precursor (C) in the corrosion protection pretreatment agent. The upper limit concentration of the resin(s) is 55 wt.%, or 54 wt.%, or 53 wt.%, or 50 wt.%, based on the total weight of resins and bi-functional epoxy resin precursor (C) in the corrosion protection pretreatment agent.

Optional additives

The corrosion protection pretreatment agent of the present invention may further comprise optional additives.

The corrosion protection pretreatment agent/solution can optionally comprise conventional additives known to a person skilled in the adhesive art. Conventional additives which are compatible with the disclosed surface treatment composition/solution may simply be determined by combining a potential additive with the composition and determining if they remain homogenous. Non-limiting examples of suitable additives include, without limitation, solvents, corrosion inhibitors, defoamers, surfactants, UV-stabilizers, extenders, plasticizers, as are known in the art.

The total level of additives will vary depending on amount of each particular additive needed to provide the corrosion protection pretreatment agent/solution for light metallic material with desired properties. The level of additives can be from 0 to about 10 wt.%, and preferably from about 0.1 to about 5 wt.% of the total weight of the corrosion protection pretreatment agent.

Preparing Method of the bi-functional epoxy resin precursor

The bi-functional epoxy resin precursor might be prepared by repeating an addition reaction and condensation reaction of a bi-functional epoxy. The epoxy of present invention comprises used is not particularly limited in type as long as it contains two epoxy groups in the molecule, including bisphenol A, bisphenol F, and epichlorohydrin such as epihalohydrin and an epoxy compound having two or more glycidyl groups.

In some embodiments of the present invention, the bi-functional epoxy resin precursor is preferably prepared by steps of:

Reacting bi-functional epoxy with a nucleophilic or electrophilic compound having active hydrogen atom; adding a pH adjustor and water to the solution to obtain 5 wt.% to 32 wt.% solid content of the neutralized bi-functional epoxy resin precursor.

In some embodiments of the invention, the bi-functional epoxy resin precursor is presented by a formula as below:

R_1-Y-[CH_2-CH(OH)-R_3-CH(OH)-CH_2-X-R_4-X] $_n$-R_2

wherein, independently,

R_1 being aromatic chain or aliphatic chain having from 1 to 20 carbon atoms, preferred from 1 to 10 carbon atoms;

R_2 being aromatic chain or aliphatic chain having from 1 to 20 carbon atoms, preferred from 1 to 10 carbon atoms or H;

R_4 being aromatic chain or aliphatic chain having from 1 to 20 carbon atoms, preferred from 1 to 10 carbon atoms;

X= -COO-, sulphur moiety，-NR(H)-, -P(OR)$_2$-O-, -P (OR)(OH) -O-, -PO-O-, preferred being -COO-, -NR(H)-, -P(OR)$_2$-O-, -P (OR)(OH) -O-, -PO-O-; the R group in -NR(H)-, -P(OR)$_2$-O-, -P (OR)(OH)-O- includes aliphatic chain having from 1 to 5 carbon atoms;

Y= -COO-, sulphur moiety，-NR(H)-, -P(OR)$_2$-O-, -P (OR)(OH) -O-, -PO-O-, preferably being -COO-, -NR(H)-, -P(OR)$_2$-O-, -P (OR)(OH) -O-, -PO-O-; the R group in -NR(H)-, -P(OR)$_2$-O-, -P (OR)(OH)-O- includes aliphatic chain having from 1 to 5 carbon atoms;

R_3 being any types of chain as far as it connects two hydroxyl α-carbon atoms; preferred R_3 being one selected from the group consisting of aromatic or aliphatic moiety having from 1 to 20 carbon atoms, polyurethane moiety, aliphatic or aromatic alkane having from 2 to 20 carbon atoms, acrylates containing polymer moiety.

n being an integer of 1~10, preferred being an integer of 2~8.

Preparing method of the corrosion protection pretreatment agent

The corrosion protection pretreatment agent may be prepared by dispersing all resin materials, metallic compounds, silane coupling agent and other raw materials if needed in water or in a water-soluble solvent to prepare the corrosion protection pretreatment agent. The solid content is adjusted by removing the solvent and volatile components. The solvent is usually water, some water-based solvent (such as alcohol, ketone, and cello solve-based water-soluble organic solvent) with a small amount can be used in combination to reduce film forming time. The solid content concentration of the aqueous corrosion protection pretreatment agent is not particularly limited, but it is preferably in range of 15 wt.% to 50 wt.%, or 15 wt.% to 40 wt.%, or 25 wt.% to 35 wt.%.

The method for forming the intermediate layer is not particularly limited. For example, roll coater, dipping and spray, then dried by hot air oven, induction heating furnace and IR heater. The peak steel sheet temperature is 40~150 °C, but preferably in range of 50 to 80 °C.

In some embodiments of the present invention, the corrosion protection pretreatment agent is preferably prepared by steps of:

a) dissolving resin compounds and other compounds in water with stirring so as to obtain a solution,

b) adjusting to the solution obtained in step a) to achieve a proper pH value for the solution by ammonia solution. The solution preferably has a pH from 8 to 12, preferably from greater than 9 to 12, or more preferably from 9 to 10.

c) adding the silane coupling agent with stirring to achieve the equilibrium of hydrolysis and condensation.

d) adding other additives if needed with stirring uniform solution without delamination.

Method for coating and curing on a metallic surface

The method according to the invention is particularly suitable for coating metal sheets that are selected from sheets of zinc or zinc alloys, aluminum or aluminum alloys as well as steel strips that are coated with zinc or zinc alloys, or with aluminum or aluminum alloys. Here, “zinc alloys” or “aluminum alloys” are understood to mean those alloys that consist of more than 50 atoms% zinc or aluminum.

For test plates, the materials of (i) to (V) were used as below.

i. Cold-rolled steel sheet (SPCC): sheet thickness, 0.8 mm

ii. Electrogalvanized steel sheet (EG): sheet thickness, 0.8 mm;

iii. Galvanized steel sheet (HDG): sheet thickness, 0.6 mm;

iv. Galvalume steel sheet (GL): sheet thickness 0.6 mm

v. Zinc-magnesium-Aluminum alloy (ZAM): sheet thickness 0.5mm,

Test plates were treated according to steps (1) to (5) as below.

1) degreasing the metal surface of plate,

2) rinsing with tap water,

3) drying the metal surface by compressed air,

4) roller coating the pretreatment agent on the surface of plate,

5) the pretreatment agent by hot air or in an oven,

wherein, during the step (5), the temperature is preferably at least 75 °C, but not more than 240 °C, preferably not more than 150 °C.

In some embodiments of present invention, the pretreatment agent for treating the metallic plate was applied with a bar coater on the fresh surface of the metallic plate, dried the test plate in a hot air dryer so that the test plate had peak metal temperatures (PMT) of 95 °C.

Measurement of Coating Thickness

In the measurement of coating thickness, cross-section samples were first produced using X-ray spectrometer (ZSX Primus Ⅲ+; Rigaku Corporation from Japan). Three spots of the panel are chosen to test the coating thickness. The minimum value is the lower limit, and the maximum is the upper limit.

The dry film thickness is 0.05~1.0 μm. Preferred film thickness is 0.1~0.4 μm.

Formation of top coating layer

After forming the pretreatment coating layer (the cured corrosion protection pretreatment agent), the top coating material and primer was coated by a bar coater to a dried thickness of 15μm, then the sample was heated to dry in a hot air-drying furnace to a peak plate temperature of 230 °C. The top coating is selected the polyurethane paint for appliance applications from Nippon.

Listing of Embodiments

1. A corrosion protection pretreatment agent comprises:
    a) a solvent,
    b) at least one inorganic inhibitor,
    c) at least one silane compound,
    d) a bi-functional epoxy resin precursor (C), the bi-functional epoxy resin precursor (C) being represented by the following formulas:

R_1-Y-[CH_2-CH(OH)-R_3-CH(OH)-CH_2-X-R_4-X]$_n$-R_2

wherein, independently,

X= -COO-, sulphur moiety, -NR(H)-, -P$(OR)_2$-O-, -P (OR)(OH)-O-, -PO-O-;

Y= -COO-, sulphur moiety, -NR(H)-, -P$(OR)_2$-O-, -P (OR)(OH)-O-, -PO-O-;

R_2 being aromatic chain or aliphatic chain having from 1 to 20 carbon atoms or H;

R_4 being aromatic chain or aliphatic chain having from 1 to 20 carbon atoms;

R_1 being aromatic chain or aliphatic chain having from 1 to 20 carbon atoms, -XH or -X-R_4;

R_3 being any types of chain as far as it connects two hydroxyl α-carbon atoms;

n being an integer of 1~10.

2. The corrosion protection pretreatment agent according to embodiment 1, wherein, independently, R_2 being aromatic chain or aliphatic chain having from 1 to 10 carbon atoms or H, R_4 being aromatic chain or aliphatic chain having from 1 to 10 carbon atoms, R_1 being aromatic chain or aliphatic chain having from 1 to 10 carbon atoms, -XH or -X-R_4.
3. The corrosion protection pretreatment agent according to any one of preceding embodiments, wherein R_3 being selected from the group consisting of aromatic or aliphatic moiety having from 1 to 20 carbon atoms, polyurethane moiety, aliphatic or aromatic alkane having from 2 to 20 carbon atoms, acrylates containing polymer moiety.
4. The corrosion protection pretreatment agent according to any one of preceding embodiments, wherein X being selected from -COO-, -P (OR)(OH)-O-; and n being an integer of 2~8.
5. The corrosion protection pretreatment agent according to any one of preceding embodiments, wherein, the bi-functional epoxy resin precursor (C) being represented by the following formulas:

   $(H)X\text{-}R_4\text{-}X\text{-}[CH_2\text{-}CH(OH)\text{-}R_3\text{-}CH(OH)\text{-}CH_2\text{-}X\text{-}R_4\text{-}X]_n\text{-}H$

   wherein, independently,

   X= -COO-, -P (OR)(OH)-O-;

   R_4 being aromatic chain or aliphatic chain having from 1 to 10 carbon atoms;

   R_3 being any types of chain as far as it connects two hydroxyl α-carbon atoms;

   n being an integer of 2~8.
6. The corrosion protection pretreatment agent according to any one of preceding embodiments, wherein the corrosion protection pretreatment agent further comprises at least a resin, the resin being selected from a group consisting of polyurethane resin (A), polyurethane-acrylic resin(B), polyacrylic-epoxy resin (D).
7. The corrosion protection pretreatment agent according to any one of preceding embodiments, wherein the pH value of the corrosion protection pretreatment agent is from greater than 7 to 12.
8. The corrosion protection pretreatment agent according to any one of preceding embodiments, wherein the pH value of the corrosion protection pretreatment agent is from 3 to less than 7.
9. The corrosion protection pretreatment agent according to embodiments 7, wherein the bi-functional epoxy resin precursor (C) is present in proportions by weight of 45%-75%, based on

the total weight of the bi-functional epoxy resin precursor (C) and the resin(s).

10. The corrosion protection pretreatment agent according to embodiments 8, wherein the bi-functional epoxy resin precursor (C) is present in proportions by weight of 52%-100%, based on the total weight of the bi-functional epoxy resin precursor (C) and the resin(s).
11. The corrosion protection pretreatment agent according to any embodiments of 7 or 9, wherein the corrosion protection pretreatment agent comprises 2.0 wt.% to 4.5 wt.% of the silane coupling agent, based on the total weight of solid contents, the silanol group containing resin being represented by the following formulas $XY(Z)_nSi(OH)_{3-n}$,

    wherein, independently, X being a glycidoxy group or functional group derived from a glycidoxy group, Y being a C1 to C10 alkylene group, Z being a methoxy group, ethoxy group or methyl group, and n being an integer of 0 to 2.
12. The corrosion protection pretreatment agent according to any embodiments of 8 or 10, wherein the corrosion protection pretreatment agent comprises 40.0 wt.% to 60.0 wt.% of the silane coupling agent, based on the total weight of solid contents, the silanol group containing resin being represented by the following formulas $Y\text{-}[Si(Y)_2\text{-}O]_n\text{-}R$,

    wherein, independently, n being an integer of 1 to 3,

    R being a moiety of C1 to C6 alkyl groups and preferably C1 to C3 alkyl groups,

    Y being a moiety selected from alkyl groups with not more than 10 carbon atoms carrying at least one epoxy, amino, hydroxyl, vinyl and/or thiol group,

    wherein the Y being selected mutually independent from each other.
13. The corrosion protection pretreatment agent according to any embodiments of 7 or 9 or 11, wherein the corrosion protection pretreatment agent comprises, 0.3 to 7 wt.% of an inorganic inhibitor, based on the total weight of solid contents in the composition, the inorganic inhibitor comprising a zirconium compound and/or a vanadium compound.
14. The corrosion protection pretreatment agent according to embodiments 13, wherein the zirconium compound being selected from a group consisting of ammonium zirconium carbonate, potassium zirconium carbonate, basic zirconium carbonate, zirconium acetate, and combination.
15. The corrosion protection pretreatment agent according to any embodiments of 8 or 10 or 12,

wherein the corrosion protection pretreatment agent comprises, 0.1 to 1.0 mol/L wt.% of a inorganic inhibitor, the inorganic inhibitor comprising at least one water-soluble or water-dispersible fluorinated acid or salt thereof, wherein the fluorinated acid is defined by the following general empirical formula: $H_mT_qF_pO_n$, wherein: q and p each represent an integer from 1 to 10; m and n each represent an integer from 0 to 10; and, T is an element selected from Ti, Zr, Hf, Si, Sn, Al, Ge, and B.

16. The corrosion protection pretreatment agent according to any one of preceding embodiments, wherein the solid content of the corrosion protection pretreatment agent is 15 wt.% to 50 wt.%, based on the total weight of the corrosion protection pretreatment agent.
17. A method for providing anticorrosion protection and enhanced coating adhesion on a metallic surface, comprising steps of:

    a) bringing the corrosion protection pretreatment agent according to any one of preceding embodiments into contact with a metallic surface at a process temperature of at least 40°C, but no higher than 200°C, thereby creating a film on the metallic surface;

    b) optionally removing excess quantities of the corrosion protection pretreatment agent from the surface; and

    c) curing the coating located on the surface by means of thermal methods at a process temperature of 50-90 °C, or high-energy irradiation for a period of at least 10−5 seconds to form a cured coating.

18. The method according to embodiment 17, wherein the cured coating exhibits a layer thickness of at least 0.1 μm, but of no more than 0.5 μm.

19. An article having at least one portion that comprises the treated metallic surface of embodiment 17.

20. The article of embodiments 19, wherein protection coating exhibits a layer thickness of at least 0.1 μm, but of no more than 0.5 μm.

21. The article of any one of embodiments 19 to 20, wherein the article is used for appliance application, said treated metallic surface having a T-bend (fresh) of equal to or less than 1T

when subjected to GB/T13448-2006, a T-bend (aged, after 24 hours aging at a temperature of 50±2℃ and a humidity of 95%) of equal to or less than 2T when subject to GB/T13448-2006.

22. The article of any one of embodiments 19 to 20, wherein the article is used for architecture application, said treated metallic surface has a T-bend (fresh) of equal to or less than 3T when subjected to GB/T13448-2006, a T-bend (aged, after 24 hours aging at a temperature of 50±2℃ and a humidity of 95%) of equal to or less than 4T when subject to GB/T13448-2006.

23. An article having at least one portion that comprises a pretreatment coating, wherein the protection coating is a cured product of the corrosion protection pretreatment agent according to any one of embodiments 1 to 16.

Examples:

The present invention will be further described and illustrated in detail with reference to the following examples. The examples are intended to assist one skilled in the art to better understand and practice the present invention, however, are not intended to restrict the scope of the present invention. All numbers in the examples are based on weight unless otherwise stated.

Raw Materials

Description/function	Product name	Source
Polyurethane resin (A) / polycarbonate-based aliphatic PU	Hauthane L-3528	C.L. Hauthaway & Sons Corporation；US
Polyurethane resin (A) / polycarbonate-based aliphatic PU	Hauthane L-3529	C.L. Hauthaway & Sons Corporation；US
Polyurethane resin (A) / polycarbonate-based aliphatic PU	Esacote PU A32D	LAMBERTI S.p.A.；Italy
Polyurethane resin (A)	AH-1730	ANHUI ANDAHUATAI NEW MATERIALS
Polyurethane resin (A)	AH-1610Y	ANHUI ANDAHUATAI NEW MATERIALS
Polyurethane resin (A)	Wantipro 0380	Wanhua Chemical
Polyurethane-acrylic resin (B)	BS PUAW TT-10	Shanghai Xinyang Chemical
Polyurethane-acrylic resin (B)	SGR-0215W	Shanghai Xinyang Chemical,
Polyacrylic-epoxy resin (D)	MR1487W	KDD functional material (local company)

Polyacrylic-epoxy resin (D)	ACUST 3958	Wuxi Honghui New Materials Technology Co., Ltd.
Epoxy resin	YD-128A	KUKDO Chemical (kunshan) CO.,Ltd
Orthophosphoric acid	≥85 wt. % in H_2O	Sigma-Aldrich (Shanghai) Trading Co.Ltd.
Adipic acid	99%	Sigma-Aldrich (Shanghai) Trading Co.Ltd.
Propylene glycol monomethyl ether	PROGLYD DMM Glycol Diether	DOW CHEMICAL (SHANGHAI) COMPANY LIMITED
28% aqueous ammonia	GR level	Sinopharm chemical reagent Co., Ltd
3-glycidoxypropyltriethoxysilane	JH-O1871	HUBEI JIANGHAN NEW MATERIALS
3-(Trimethoxysilyl)propan-1-amine	JH A 111	HUBEI JIANGHAN NEW MATERIALS
3-glycidoxypropylmethyldiethoxysilane	Dynasylan GLYEO	EVONIK
Methyltriethoxysilane	Dynasylan A	EVONIK
Ammonium zirconium carbonate	Zircosol AC 20	Daiichi Kigenso Kagaku Kogyo
Zirconium acetate	Zirconium (IV) acetate	Sinopharm chemical reagent Co., Ltd
Vanadium pentaoxide	Vanadium (V) oxide	Sinopharm chemical reagent Co., Ltd
Vanadium acetyl acetonate	Vanadium (3) acetylacetonate	Sigma Aldrich
Hexafluorotitanic acid	Hexafluorotitanic acid solution, 60 wt.% in H_2O	Shanghai Aladdin Bio-Chem Technology Co., LTD
Hexafluorozirconic acid	Hexafluorozirconic acid solution, 45 wt.% in H_2O	Shanghai Aladdin Bio-Chem Technology Co., LTD

* All raw materials are directly used without any special treatment.

Example 1

<Preparation of bi-functional epoxy resin precursor >

Bi-functional epoxy resin precursor C1 (C1) was synthesized by steps of:

Loaded Adipic acid and 40 g propylene glycol monomethyl ether into a 100 ml round bottom fournecks flask and heated at 90 °C. Then added 260 g A-type epoxy liquid resin YD-128A (from Guodu) having 190 epoxy equivalent slowly and kept the temperature at 95 °C for 2 hours. After the reaction, added 28 wt.% aqueous ammonia solution 180 g slowly at 40 °C, then added water to obtain a 5%~32% solid content of the ammonia neutralized bi-functional epoxy resin precursor C1. Bi-functional epoxy resin precursor C1 had a weight-average molecular weight of 13,000.

Bi-functional epoxy resin precursor C2 (C2) was synthesized by steps of:
The orthophosphoric acid and 100 g propylene glycol monomethyl ether was slowly added into the 1250 g A-type epoxy resin having 500 epoxy equivalent and kept at 95 °C for 2 hours. After the reaction, 28% aqueous ammonia solution 40 g was added slowly at 140 °C, water was then added to obtain a 5%~32% solid content of the ammonia neutralized phosphoric acid-modified bi-functional epoxy resin precursor C2. The Bi-functional epoxy resin precursor (C2) had a weight-average molecular weight of 20,000.

<Preparation of corrosion protection pretreatment agent>

Corrosion protection pretreatment agent was prepared by steps of:

a) Charged 6.7 g of AH-730 (liquid, from Anhui Andahuatai New Materials), 11.7 g of bi-functional epoxy resin precursor C1 (produced as above), 2 g of Dynasylan GLYEO (liquid, from Evonik), 2 g Dynasylan A (liquid, from Evonik), 2 g JH A 111 (liquid, from Hubei Jianghan New Material) mixed them for 6hrs to form an aqueous dispersion.

b) Charged 1.6 g Hexafluorotitanic acid solution, 60 wt.% in H_2O (liquid, from Shanghai Aladdin Bio-Chem Technology Co., LTD) in the aqueous dispersion made in step a).

<Coating & curing of metallic surface>

Test Material

Galvanized steel sheet (GA): sheet thickness, 0.8mm; coating weight, 90/45 g/m^2,

Galvalume steel sheet (GL): sheet thickness 0.6 mm, Zinc-magnesium-Aluminum alloy (ZAM): sheet thickness 0.5mm.

The process of metallic surface treatment preferably comprises the following subsequent steps (1)-(5):

1) degreased the metal surface with RIDOLINE1559 degreasant from Henkel.
2) rinsed with tap water.
3) dried the metal surface by compressed air.
4) roller coated primer/pretreatment on the substrate.
5) cured by hot air/oven.

wherein, during the step (5), the temperature is about 85 °C.

The corrosion protection pretreatment agent was applied with a bar coater on the fresh substrate, dried in a hot air dryer so that the test plates had peak metal temperatures (PMT) 95 °C.

In the measurement of coating thickness, cross-section samples were first produced using X-ray spectrometer (ZSX Primus Ⅲ+; Rigaku Corporation from Japan.). Three spots of the panel are cut/choose to test/detect the coating thickness. The minimum value is the lower limit, and the maximum is the upper limit.

The dry film thickness range is from 0.1 μm to 0.4 μm.

The primer layer was coated by a bar coater to a dried thickness of 5 μm, the sample was heated to dry in a hot air-drying furnace to a peak plate temperature of 230 °C. The primer is a non-chrome polyester-based primer from Nippon for appliance application, and the primer is NPEP 750 from Nippon for architecture application.

The top coating material was coated by a bar coater to a dried thickness of 15 μm, next, the sample was heated to dry in a hot air-drying furnace to a peak plate temperature of 230 °C. The top coating is a polyester paint from Nippon for appliance application, and the top coating is PCM500 from Nippon for architecture application.

Example 2-23, and CE1-CE26

The retreatment agents of E2 to E23 and CE1 to CE26 were prepared in reference to Example 1. The metallic surface of E2 to E23 and CE1 to CE26 were treated in reference to Example 1. More details are listed in below result part.

The prepared samples were subjected to various of tests.

Test Methods

Adhesion ability

<T-bend (fresh)> and < T-bend (aged)>

A T-bend tester is adopted to perform 180-degree bending tests according to the requirements of a bending test method in GB/T13448-2006 color coated steel plate and steel strip test method. Meanwhile, the samples were put into a test chamber, set temperature at 50±2 °C and humidity of 95% for 24 hours of accelerated aging test, and after the samples were taken out, a T-bend test (aged T-bend) was performed. The equipment for T-bend test is WZJ-II T-bend form Shanghai Xiandai Environment Engineering Technique Co., Ltd.

Appliance application T-bend (fresh) results are recorded and ranked as follows:

- Not pass: greater than 1T.
- Pass: lower than or equal to 1T.
- Good: equal to 0T.

Architecture application T-bend (fresh) results are recorded and ranked as follows:

- Not pass: greater than 3T.
- Pass: lower than or equal to 3T.
- Good: equal to 1T.
- Excellent: equal to 0T.

House application T-bend (aged) results are recorded and ranked as follows:

- Not pass: greater than 2T.
- Pass: lower than or equal to 2T.
- Good: lower than or equal to 1T.
- Excellent: equal to 0T.

Architecture application T-bend (aged) results are recorded and ranked as follows:

- Not pass: greater than 4T.
- Pass: lower than or equal to 4T.
- Good: equal to 2T.
- Excellent: equal to 1T.

< cross-cupping test >

The cross-cupping tests were carried out by a cup bursting test machine according to the requirements of the bending test in GB/T13448-2006 color coated steel plate and steel strip test method. The equipment is Electrohydraulic cupping tester Cat. No.5400 from BYK- Gardner GmbH. Cross-cupping testing method and ranking criteria are the same for appliance and architecture application.

Cross-cupping test results are recorded and ranked as follows:

Not pass (F): peeled area is greater than 5%.

Pass (P): peeled area is lower than or equal to 5%.

Good (G): peeled area is lower than or equal to 2%.

Very Good (VG): peeled area is equal to 0%.

<Reverse Impact test >

Reverse impact test is dropped onto the strip from a height that is 3 times the metal thickness. The deformed surface is examined for cracks or breaks in the coating. Then tape is applied to the deformed area, then removed. If any coating is removed from the surface of the strip, the sample has failed the test. The energy impact test instrument is Elcometer 1615. The weight of heavy hammer is 1 Kg and height is 90cm, the impact energy is 9J. Reverse impact testing method and ranking criteria are the same for appliance and architecture application.

Evaluation criteria：

Good (G): no painting peels off and no crack.

Not pass (F): has crack or has painting peel off.

Anti-Corrosion ability

<Cross Neutral salt spray test 240 hrs and 1000 hrs>

Each test plate (150mm X 70mm) with cross"X" cutting was tested by Neutral salt spray test (GBT10125-1997), 240 hours for appliance and 1000 hours for architecture. The cutting line is longer than 50 mm. The swelling width of cross (maximum value) was measured and evaluated in accordance with the following criteria. The equipment for the corrosion test is Q-fog SSP salt spray chamber form Q-Lab Corporation. Trimming guard: stage 10 specified in GB/T6461. Evaluation criteria is the same for appliance and architecture application

Very good (VG): lower than or equal to 1 mm.

Good (G): lower than or equal to 2mm.

Pass (P): lower than or equal to 3 mm.

No pass (F): greater than 3mm.

<Plate Neutral salt spray test 500hrs and 1000hrs>

Each test plates (150mm X 70mm) were tested by Neutral salt spray test (GBT10125-1997) for 500hrs (appliance) or 1000hrs and examined by the naked eye and evaluated by the following. Evaluation criteria is the same for appliance and architecture application

Evaluation criteria:

Very good (VG): No blisters.

Good (G): single blister size of less than 1.0 mm and generation number is less than 5.

Pass (P): single blister size of less than 1.0 mm and generation number is equal to or greater than 5 and less than 10.

No pass (F): single blister size is equal to or greater than 1.0 mm and generation number is equal to or greater than 10 and less than 20.

<Scrap edge Neutral salt spray test 240hrs (appliance application)>

Each test plate (150mm X 70mm) with scrap edge were tested by Neutral salt spray test (GBT10125-1997) for 240 hours (appliance) and examined by the naked eye and evaluated by the following.

Evaluation criteria:

Very good (VG): less than or equal to 3 mm.

Good (G): less than or equal to 6 mm.

Pass (P): greater than 6 mm and less than 10 mm.

Not pass (F): equal to or greater than 10 mm.

<Scrap edge Neutral salt spray test 1000hrs (architecture application)>

Each test plate (150mm X 70mm) with scrap edge were tested by Neutral salt spray test (GBT10125-1997) for 1000 hours (architecture) and examined by the naked eye and evaluated by the following.

Evaluation criteria:

Very good (VG): less than or equal to 5 mm.

Good (G): less than or equal to 8 mm.

Pass (P): greater than 8 mm and less than 12 mm.

Not pass (F): equal to or greater than 12 mm.

Solvent Resistance

<Surface resistance (MEK) solvent wipe>:

The equipment is DJH MEK Rub Test Machine from DJH Designs Inc. Set the speed of 1 to-fro per second with the 0.1±0.02 MPa and the test length not less than 150mm. Apply 100 round-trip wipes for color-coated panels for architectural application and apply 50 round-trip wipes for color-coated panels for appliance application.

Evaluation criteria:

Good (G): no mark or have wipe mark and no paint peel.

No pass (P): has top paint peel.

Chemical Resistance

<Alkali resistance >

Each test plate was immersed in a 5 wt.% NaOH aqueous solution at RT for 24hrs. Then the size and the generation density of the blisters generated were examined by the naked eye and evaluated for alkali resistance by the following.

Evaluation criteria:

Very good (VG): No blisters.

Good (G): single blister size of less than 1.0 mm and generation number is less than 5.

Pass (P): single blister size of 1.0 mm and generation number is equal to or greater than 5 and less than 10.

No pass (F): single blister size of 1.0 mm or more or generation number is greater than 10.

<Sulfuric acid resistance test> and <Hydrochloric acid resistance test>

Each test plate was immersed in a 5 wt.% sulfuric acid aqueous solution at room temperature for 24 hrs, then the size and generation density of the blisters generated were examined by the naked eye and evaluated by criteria similar to the alkali resistance.

Each test plate was immersed in a 5 mass% hydrochloric acid aqueous solution at room temperature for 24 hrs, then the size and generation density of the blisters generated were examined by the naked eye and evaluated by criteria similar to the alkali resistance.

Very good (VG): No blisters

Good (G): single blister size of less than 1.0 mm and generation number is less than 5.

Pass (P): single blister size of 1.0 mm and generation number is equal to or greater than 5 and less than 10.

No pass (F): single blister size of 1.0 mm or more or generation number is greater than 10.

Results

Table 1.

	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11
AH-1730	2								2.5		
AH-1610Y		2									
Wantipro 0380			2							1	1
SGR-0215W;				2	2						
C1	3.5	3.5	3.5	3.5		3.5	5.5				
C2					3.5			5.5	3.5	3	4
ACUST 3958						2				1	
Dynasylan A	2	2	2	2	2	2	2	2	2	2	2
JH A 111	2	2	2	2	2	2	2	2	2	2	2
Dynasylan GLYEO	2	2	2	2	2	2	2	2	2	2	2
H_2TiF_6	1		1	1	1	1	1	1		1	1
H_2ZrF_6		1							1		
solid content total	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	13	12	12
agent total	87.5	87.5	87.5	87.5	87.5	87.5	87.5	87.5	87	88	88
C: (total resin(s)+C)	63%	63%	63%	63%	63%	100%	100%	100%	58%	60%	80%
pH	5.5	5.5	6	6	6	6	6	6	5.5	6	6
film thickness (μm)	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4

Table 1 shows compositions of the corrosion protection pretreatment agents of E1-E11.

Table 2.

		E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11
Anti-corrosion (HDG)	Cross Neutral salt spray test 240hrs (appliance)	VG	VG	VG	VG	VG	G	P	P	VG	VG	VG
	Plate Neutral salt spray test 240hrs (appliance)	VG	VG	VG	VG	VG	G	P	P	VG	VG	VG
	Scrap Edge Neutral salt spray test 240hrs (appliance)	VG	VG	VG	VG	VG	G	P	P	VG	VG	VG
	Cross Neutral salt spray test 1000hrs (architecture)	P	G	G	G	G	G	G	P	G	G	G
	Plate Neutral salt spray test 1000hrs (architecture)	G	G	G	G	G	G	F	F	G	G	G
	Scrap Edge Neutral salt spray test 1000hrs (architecture)	P	G	G	G	G	G	G	P	G	G	G
	T-bend test (appliance-fresh)	0T	1T	0T	0T	0T	1T	0T	0T	1T	0T	0T
	T-bend test (appliance-aged)	0T	1T	0T	1T	1T	1T	1T	1T	2T	1T	1T

Adhesion ability (HDG)	T-bend test (architecture-fresh)	2T	2T	1T	2T	1T	2T	1T	2T	2T	2T	1T
	T-bend test (architecture -aged)	3T	3T	3T	4T	3T	3T	3T	3T	3T	3T	3T
	Cross-hatch and cupping test (appliance)	VG	G	VG	VG	VG	G	VG	G	G	VG	VG
	Cross-hatch and cupping test (architecture)	VG	P	VG	VG	VG	P	VG	G	P	VG	VG
	Reverse Impact Testing (appliance)	VG	G	VG	VG	VG	G	VG	G	G	VG	VG
	Reverse Impact Testing (architecture)	VG	G	VG	VG	VG	G	VG	G	G	VG	VG
Solvent Resistance (HDG)	MEK rub test (appliance)	G	G	G	G	G	G	G	G	G	G	G
	MEK rub test (architecture)	G	G	G	G	G	G	G	G	G	G	G
Chemical resistance (HDG)	Alkali resistance	VG	G	P	VG	P	P	P	P	G	P	P
	Sulfuric acid resistance test	VG	G	G	P	G	G	G	P	G	G	G
	Hydrochloric acid resistance test	VG	G	G	VG	G	G	G	P	G	G	G
Anti-corrosion (ZAM)	Cross Neutral salt spray test 1000hrs (architecture)	G	G	G	G	G	G	G	G	G	G	G
	Plate Neutral salt spray test 1000hrs (architecture)	G	G	G	G	G	G	G	G	G	G	G
	Scrap Edge Neutral salt spray test 1000hrs (architecture)	G	G	G	G	G	G	F	F	G	G	G
Adhesion ability (ZAM)	T-bend test (architecture-fresh)	2T	3T	1T	1T	1T	3T	3T	3T	1T	2T	1T
	T-bend test (architecture-aged)	2T	3T	2T	2T	2T	3T	3T	3T	2T	2T	2T
	Cross-hatch and cupping test (architecture)	G	P	VG	VG	VG	P	P	P	VG	VG	VG
	Reverse Impact Testing (architecture)	VG	G	VG	VG	VG	G	VG	G	VG	VG	VG
Chemical resistance (ZAM)	MEK rub test (architecture)	G	G	G	G	G	G	G	G	G	G	G
	Alkali resistance	VG	G	P	G	P	P	P	G	P	G	P
	Sulfuric acid resistance test	VG	G	G	G	G	G	P	P	G	G	G
	Hydrochloric acid resistance test	VG	G	G	G	G	G	P	P	G	G	G
Anti-corrosion (GL)	Cross Neutral salt spray test 1000hrs (architecture)	G	G	G	G	G	G	G	G	G	G	G
	Plate Neutral salt spray test 1000hrs (architecture)	G	G	G	G	G	G	G	G	G	G	G
	Scrap Edge Neutral salt spray test 1000hrs (architecture)	G	G	G	G	G	G	G	G	G	G	G
Adhesion ability (GL)	T-bend test (architecture-fresh)	2T	3T	2T	2T	2T	3T	3T	3T	2T	3T	2T
	T-bend test (architecture-aged)	3T	3T	3T	3T	3T	3T	3T	3T	3T	3T	3T
	Cross-hatch and cupping test (architecture)	G	P	G	VG	VG	P	P	P	G	VG	VG

	Reverse Impact Testing (architecture)	VG	G	VG	VG	VG	VG	VG	VG	VG	VG	VG
Chemical resistance (GL)	MEK rub test (architecture)	G	G	G	G	G	G	G	G	G	G	G
	Alkali resistance	VG	G	P	G	P	P	P	G	P	P	P
	Sulfuric acid resistance test	VG	G	G	G	G	G	G	P	G	G	G
	Hydrochloric acid resistance test	VG	G	G	G	G	G	G	P	G	G	G

Table 2 shows testing results of the corrosion protection pretreatment agents E1-E11.

In Examples 1 to 11, the corrosion protection pretreatment agents were prepared according to the formulations provided by the present invention and have good adhesion properties, even after aging, the adhesion properties are still meet the requirements of architecture and appliance applications, on different substrates. In addition, E1-E11 have excellent anti-corrosion properties.

Table 3.

	CE1	CE2	CE3	CE4	CE5	CE6	CE7	CE8	CE9	CE10	CE11	CE12	CE13
AH-1730		3	5.5										
Wantipro 0380				5.5			4						
SGR-0215W;	2	3			5.5			5	3	2	2	2	2
C1							1.5	3.5	3	3.5	3.5	3.5	3.5
ACUST 3958	4					5.5							
Dynasylan A	2	2	2	2	2	2	2	2	2				
JH A 111	2	2	2	2	2	2	2	2	2				
3-Dynasylan GLYEO	2	2	2	2	2	2	2	2	2				
H_2TiF_6	1	1	1	1	1	1		1	1	2		1	
H_2ZrF_6							1				2		
solid content total	13	13	12.5	12.5	12.5	12.5	12.5	15.5	13	7.5	7.5	6.5	5.5
agent total	87	87	87.5	87.5	87.5	87.5	87.5	84.5	87	92.5	92.5	93.5	
C: total resin(s)+C	0%	0%	0%	0%	0%	0%	27.20%	41.10%	50.00%	63%	63%	63%	
pH	5.5	5.5	6	6	6	6	6	6	6	5.5	5.5	5.5	
film thickness(μm)	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4

Table 3 shows compositions of the corrosion protection pretreatment agents of CE1-CE13.

Table 4.

		CE 1	CE 2	CE 3	CE 4	CE 5	CE 6	CE 7	CE 8	CE 9	CE 10	CE 11	CE 12	CE 13
Anti-corrosion (HDG)	Cross Neutral salt spray test 240hrs (appliance)	VG	G	G	VG	G	/	VG	VG	VG	/	/	F	F
	Plate Neutral salt spray test 240hrs (appliance)	VG	G	G	VG	G	/	VG	VG	VG	/	/	F	F
	Scrap Edge Neutral salt spray test 240hrs (appliance)	VG	G	G	VG	G	/	VG	VG	VG	/	/	F	F
	Cross Neutral salt spray test 1000hrs (architecture)	G	F	P	P	G	/	G	G	G	/	/	P	F
	Plate Neutral salt spray test 1000hrs (architecture)	G	F	P	P	G	/	G	G	G	/	/	P	F
	Scrap Edge Neutral salt spray test 1000hrs (architecture)	G	F	P	P	G	/	G	G	G	/	/	P	F
Adhesion ability (HDG)	T-bend test (appliance-fresh)	3T	3T	3T	2T	3T	/	1T	1T	1T	/	/	0T	0T
	T-bend test (appliance-aged)	5T	5T	5T	4T	5T	/	2T	2T	2T	/	/	1T	1T
	T-bend test (architecture-fresh)	6T	4T	4T	3T	4T	/	3T	4T	3T	/	/	2T	3T
	T-bend test (architecture-aged)	>6T	6T	5T	6T	5T	/	4T	4T	4T	/	/	3T	4T
	Cross-hatch and cupping test (appliance)	P	G	F	F	F	/	G	VG	VG	/	/	VG	VG
	Cross-hatch and cupping test (architecture)	F	P	F	F	P	/	P	G	G	/	/	VG	VG
	Reverse Impact Testing (appliance)	P	G	G	G	G	/	G	VG	VG	/	/	VG	VG
	Reverse Impact Testing (architecture)	P	G	G	G	G	/	G	VG	VG	/	/	VG	VG
Solvent Resistance (HDG)	MEK rub test (appliance)	G	G	F	F	G	/	G	G	G	/	/	G	G
	MEK rub test (architecture)	G	G	G	G	G	/	G	G	G	/	/	G	G
Chemical resistance (HDG)	Alkali resistance	G	G	P	F	P	/	G	VG	VG	/	/	P	F
	Sulfuric acid resistance test	G	G	F	F	G	/	G	VG	VG	/	/	P	G
	Hydrochloric acid resistance test	G	G	F	F	G	/	G	VG	VG	/	/	P	G
Anti-corrosion (ZAM)	Cross Neutral salt spray test 1000hr(architecture)	P	G	F	F	G	/	G	G	G	/	/	F	F
	Plate Neutral salt spray test 1000hrs (architecture)	P	G	F	F	G	/	G	G	G	/	/	F	F
	Scrap Edge Neutral salt spray test 1000hrs (architecture)	P	G	F	F	G	/	G	G	G	/	/	F	F
	T-bend test (architecture-fresh)	5T	5T	4T	4T	4T	/	3T	4T	4T	/	/	2T	4T

Adhesion ability (ZAM)	T-bend test (architecture-aged)	6T	5T	6T	6T	5T	/	4T	5T	5T	/	/	3T	5T
	Cross-hatch and cupping test (architecture)	F	F	F	F	P	/	P	P	P	/	/	VG	G
	Reverse Impact Testing (architecture)	F	G	G	G	G	/	G	VG	VG	/	/	VG	VG
Chemical resistance (ZAM)	MEK rub test (architecture)	G	G	G	G	G	/	G	G	G	/	/	G	G
	Alkali resistance	G	G	P	F	P	/	G	F	F	/	/	P	F
	Sulfuric acid resistance test	G	G	F	F	G	/	G	G	G	/	/	P	G
	Hydrochloric acid resistance test	G	G	F	F	G	/	G	G	G	/	/	P	G
Anti-corrosion (GL)	Cross Neutral salt spray test 1000hrs (architecture)	P	G	P	P	G	/	G	G	G	/	/	F	F
	Plate Neutral salt spray test 1000hrs (architecture)	P	G	P	P	G	/	G	G	G	/	/	F	F
	Scrap Edge Neutral salt spray test 1000hrs (architecture)	P	G	P	P	G	/	G	G	G	/	/	F	F
Adhesion ability (GL)	T-bend test (architecture-fresh)	5T	4T	4T	4T	4T	/	4T	4T	4T	/	/	2T	3T
	T-bend test (architecture-aged)	>6T	5T	5T	5T	6T	/	5T	6T	5T	/	/	4T	4T
	Cross-hatch and cupping test (architecture)	F	F	F	F	P	/	F	G	G	/	/	VG	G
	Reverse Impact Testing (architecture)	F	G	F	F	G	/	G	VG	VG	/	/	VG	G
Chemical resistance (GL)	MEK rub test (architecture)	G	G	G	G	G	/	G	G	G	/	/	G	G
	Alkali resistance	G	G	F	P	P	/	G	P	P	/	/	F	G
	Sulfuric acid resistance test	G	G	P	P	G	/	G	G	G	/	/	F	G
	Hydrochloric acid resistance test	G	G	P	P	G	/	G	G	G	/	/	F	G

Table 4 shows testing results of the corrosion protection pretreatment agents CE1-CE13.

Table 5.

	E12	E13	E14	E15	E16	E17	E18	E19	E20	E21	E22	E23
Hauthane L-3528			4									
Hauthane L-3529						3			4			
Esacote PU A32D	4	4				3	4	4				3
BS PUAW TT-10;					4						4	
C1	8		8	8	8	5.5	8		8	8	8	8
C2		8						8				
MR1487W				4						4		
JH-O1871	0.5	0.5	0.5	0.5	0.5	0.5						0.5
Dynasylan GLYEO							0.5	0.5	0.5	0.5	0.5	
Zircosol AC 20	0.6	0.6	0.6	0.6	0.6	0.6						

Zirconium (IV) acetate							0.6	0.6	0.6	0.6	0.6	
Vanadium (V) oxide							0.2	0.2	0.2	0.2	0.2	0.2
Vanadium (3) acetylacetonate	0.2	0.2	0.2	0.2	0.2	0.2						
Solid content total	13.3	13.3	13.3	13.3	13.3	12.8	13.3	13.3	13.3	13.3	13.3	11.7
Agent total	86.7	86.7	86.7	86.7	86.7	87.2	86.7	86.7	86.7	86.7	86.7	88.3
C: total resin(s)+C	66%	66%	66%	66%	66%	47%	66%	66%	66%	66%	66%	72%
pH	8.0	7.5	8.0	7.5	8.0	7.5	7.5	8.0	7.5	8.0	8.0	8.0
Film thickness(μm)	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4

Table 5 shows compositions of the corrosion protection pretreatment agents of E12-E23.

Table 6.

		E12	E13	E14	E15	E16	E17	E18	E19	E20	E21	E22	E23
Anti-corrosion (HDG)	Cross Neutral salt spray test 240hrs (appliance)	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG
	Plate Neutral salt spray test 240hrs (appliance)	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG
	Scrap Edge Neutral salt spray test 240hrs (appliance)	VG	VG	VG	VG	VG	VG	G	G	G	G	G	VG
	Cross Neutral salt spray test 1000hrs (architecture)	G	G	G	G	G	G	VG	VG	VG	VG	VG	G
	Plate Neutral salt spray test 1000hrs (architecture)	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG
	Scrap Edge Neutral salt spray test 1000hrs (architecture)	G	G	G	G	G	G	G	G	G	G	G	G
Adhesion ability (HDG)	T-bend test (Appliance-fresh)	0T	0T	1T	1T	0T	0T	0T	0T	0T	0T	0T	1T
	T-bend test (Appliance-aged)	0T	0T	1T	2T	0T	0T	0T	0T	0T	1T	0T	1T
	T-bend test (Architecture-fresh)	1T	2T	1T	1T	2T	2T	1T	1T	1T	2T	1T	1T
	T-bend test (Architecture-aged)	2T	3T	2T	3T	3T	3T	2T	2T	2T	3T	2T	2T
	Cross-hatch and cupping test (appliance)	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG
	Cross-hatch and cupping test (architecture)	VG	VG	VG	G	VG	VG	VG	VG	VG	G	VG	G

	Reverse Impact Testing (appliance)	VG	VG	VG	VG	VG	VG	VG	VG	VG	G	VG	VG
	Reverse Impact Testing (architecture)	VG	VG	VG	VG	VG	VG	VG	VG	VG	G	VG	VG
Solvent Resistance (HDG)	MEK rub test (appliance)	G	G	G	G	G	G	G	G	G	G	G	G
	MEK rub test (architecture)	G	G	G	G	G	G	G	G	G	G	G	G
chemical resistance (HDG)	Alkali resistance	G	G	G	G	G	G	G	G	G	G	G	P
	Sulfuric acid resistance test	G	G	G	G	G	G	G	G	G	G	G	G
	Hydrochloric acid resistance test	G	G	G	G	G	G	G	G	G	G	G	G
Anti-corrosion (ZAM)	Cross Neutral salt spray test 1000hrs (architecture)	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG
	Plate Neutral salt spray test 1000hrs (architecture)	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG
	Scrap Edge Neutral salt spray test 1000hrs (architecture)	G	G	G	G	G	G	G	G	G	G	G	G
Adhesion ability (ZAM)	T-bend test (architecture-fresh)	2T	2T	2T	3T	2T	2T	2T	2T	2T	3T	2T	2T
	T-bend test (architecture-aged)	3T	3T	3T	3T	3T	2T	3T	2T	3T	3T	2T	2T
	Cross-hatch and cupping test (architecture)	VG	VG	VG	G	VG	VG	VG	VG	VG	P	VG	G
	Reverse Impact Testing (architecture)	VG	VG	VG	VG	VG	VG	VG	VG	VG	G	VG	VG
Chemical resistance (ZAM)	MEK rub test (architecture)	G	G	G	G	G	G	G	G	G	G	G	G
	Alkali resistance	G	G	G	G	G	G	G	G	G	G	G	G
	Sulfuric acid resistance test	G	G	G	G	G	G	G	G	G	G	G	G
	Hydrochloric acid resistance test	G	G	G	G	G	G	G	G	G	G	G	G
Anti-corrosion (GL)	Cross Neutral salt spray test 1000hrs (architecture)	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG
	Plate Neutral salt spray test 1000hrs (architecture)	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG	VG
	Scrap Edge Neutral salt spray test 1000hrs (architecture)	G	G	G	G	G	G	G	G	G	G	G	G

Adhesion ability (GL)	T-bend test (architecture-fresh)	2T	2T	2T	3T	2T	2T	2T	2T	2T	3T	2T	2T
	T-bend test (architecture-aged)	3T	3T	2T	3T	3T	3T	2T	3T	2T	3T	3T	2T
	Cross-hatch and cupping test (architecture)	VG	VG	VG	G	VG	VG	VG	VG	VG	P	VG	G
	Reverse Impact Testing (architecture)	VG	VG	VG	VG	VG	VG	VG	VG	VG	G	VG	VG
Chemical resistance (GL)	MEK rub test (architecture)	G	G	G	G	G	G	G	G	G	G	G	G
	Alkali resistance	G	G	G	G	G	G	G	G	G	G	G	G
	Sulfuric acid resistance test	G	G	G	G	G	G	G	G	G	G	G	G
	Hydrochloric acid resistance test	G	G	G	G	G	G	G	G	G	G	G	G

Table 6 shows testing results of the corrosion protection pretreatment agents E12-E23.

Table 7.

	CE 14	CE 15	CE 16	CE 17	CE 18	CE 19	CE 20	CE 21	CE 22	CE 23	CE 24	CE 25	CE 26
Hauthane L-3528													
Hauthane L-3529													
Esacote PU A32D		12		4	4	7	7	4	4	4	4	4	4
BS PUAW TT-10	12			4									
C1			12		4	5	5.5	8	13	8	8	8	8
C2													
MR1487W				4	4								
JH-O1871	0.5	0.5	0.5	0.5			0.5		0.5	0.5	0.1		
Dynasylan GLYEO					0.5	0.5						0.5	0.1
Zircosol AC 20	0.6	0.6	0.6	0.6			0.6		0.6	2	0.6		
Zirconium (IV) acetate					0.6	0.6						2	0.6
Vanadium (V) oxide					0.2	0.2						0.2	0.2
Vanadium (3) acetylacetonate	0.2	0.2	0.2	0.2			0.2		0.2	0.2	0.2		
solid content total	13.3	13.3	13.3	13.3	13.3	13.3	13.8	12	18.3	14.7	12.9	14.7	12.9
agent total	86.7	86.7	86.7	86.7	86.7	86.7	86.2	88	81.7	85.3	87.1	85.3	87.1
C: total resin(s)+C	0%	0%	100%	0%	33%	41%	44%	66%	76%	66%	66%	66%	66%
pH	7.5	7.5	7.5	7.5	8.0	8.0	8.0	7.5	8.0	8.0	8.0	8.0	8.0
Film thickness(μm)	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4

Table 7 shows compositions of the corrosion protection pretreatment agents of CE14-CE26.

Table 8.

		CE 14	CE 15	CE 16	CE 17	CE 18	CE 19	CE 20	CE 21	CE 22	CE 23	CE 24	CE 25	CE 26
Anti-corrosion (HDG)	Cross Neutral salt spray test 240hrs (appliance)	VG	VG	P	VG	G	G	VG	F	VG	VG	G	VG	G
	Plate Neutral salt spray test 240hrs (appliance)	VG	VG	G	VG	G	G	VG	P	VG	VG	G	VG	G
	Scrap Edge Neutral salt spray test 240hrs (appliance)	G	G	G	G	G	G	G	F	G	G	F	G	G
	Cross Neutral salt spray test 1000hrs (architecture)	G	VG	P	VG	G	G	VG	F	VG	G	G	VG	G
	Plate Neutral salt spray test 1000hrs (architecture)	VG	VG	G	VG	G	G	VG	P	VG	VG	G	VG	G
	Scrap Edge Neutral salt spray test 1000hrs (architecture)	G	G	F	G	G	G	G	F	G	G	F	G	P
Adhesion ability (HDG)	T-bend test (appliance-fresh)	2T	2T	1T	2T	2T	2T	2T	0T	0T	0T	0T	0T	0T
	T-bend test (appliance-aged)	3T	3T	1T	3T	3T	3T	3T	1T	1T	1T	0T	0T	0T
	T-bend test (architecture-fresh)	4T	4T	2T	4T	3T	3T	3T	2T	2T	2T	1T	2T	1T
	T-bend test (architecture-aged)	6T	6T	3T	6T	4T	5T	5T	2T	2T	3T	2T	3T	2T
	Cross-hatch and cupping test (appliance)	F	F	VG	F	F	F	F	VG	VG	G	G	VG	G
	Cross-hatch and cupping test (architecture)	F	F	VG	F	F	F	F	VG	VG	G	G	VG	G
	Reverse Impact Testing (appliance)	P	P	VG	P	P	P	P	VG	VG	VG	VG	VG	G
	Reverse Impact Testing (architecture)	P	P	VG	P	P	P	P	VG	VG	VG	VG	VG	G
Solvent Resistance (HDG)	MEK rub test (appliance)	G	F	F	F	G	G	F	F	F	G	G	G	G
	MEK rub test (architecture)	G	F	F	F	G	G	F	F	F	G	G	G	G
Chemical resistance (HDG)	Alkali resistance	G	G	F	G	G	G	G	G	F	G	G	G	G
	Sulfuric acid resistance test	G	G	F	G	G	G	G	G	F	F	G	F	G
	Hydrochloric acid resistance test	G	G	F	G	G	G	G	G	F	F	G	F	G
Anti-corrosion (ZAM)	Cross Neutral salt spray test 1000hrs (architecture)	G	VG	P	VG	G	G	VG	F	VG	G	P	VG	G
	Plate Neutral salt spray test 1000hrs (architecture)	G	VG	P	VG	G	G	VG	F	VG	G	P	VG	G
	Scrap Edge Neutral salt spray	G	G	F	G	G	G	G	F	G	G	F	G	P

	test 1000hrs (architecture)													
Adhesion ability (ZAM)	T-bend test (architecture-fresh)	4T	4T	2T	4T	4T	4T	4T	2T	3T	2T	2T	2T	2T
	T-bend test (architecture-aged)	6T	6T	3T	6T	5T	5T	5T	3T	3T	4T	3T	4T	3T
	Cross-hatch and cupping test (architecture)	F	F	VG	F	F	F	F	VG	VG	VG	VG	VG	VG
	Reverse Impact Testing (architecture)	P	P	VG	P	P	P	P	VG	VG	VG	VG	VG	G
Chemical resistance (ZAM)	MEK rub test (architecture)	G	F	F	F	G	G	F	F	F	G	G	G	G
	Alkali resistance	G	G	F	G	G	G	G	G	F	G	G	G	G
	Sulfuric acid resistance test	G	G	F	G	G	G	G	G	F	F	G	F	G
	Hydrochloric acid resistance test	G	G	F	G	G	G	G	G	F	F	G	F	G
Anti-corrosion (GL)	Cross Neutral salt spray test 1000hrs (architecture)	G	VG	P	VG	G	G	VG	F	VG	G	P	VG	G
	Plate Neutral salt spray test 1000hrs (architecture)	G	VG	P	VG	G	G	VG	F	VG	G	P	VG	G
	Scrap Edge Neutral salt spray test 1000hrs (architecture)	G	G	F	G	G	G	G	F	G	G	F	G	p
Adhesion ability (GL)	T-bend test (architecture-fresh)	4T	4T	2T	4T	4T	4T	4T	2T	3T	2T	2T	2T	2T
	T-bend test (architecture-aged)	6T	6T	3T	5T	5T	5T	5T	3T	4T	3T	3T	3T	3T
	Cross-hatch and cupping test (architecture)	F	F	VG	F	F	F	F	VG	VG	VG	VG	VG	VG
	Reverse Impact Testing (architecture)	P	P	VG	P	P	P	P	VG	VG	VG	VG	VG	G
Chemical resistance (GL)	MEK rub test (architecture)	G	F	F	F	G	G	F	F	F	G	G	G	G
	Alkali resistance	G	G	F	G	G	G	G	G	F	G	G	G	G
	Sulfuric acid resistance test	G	G	F	G	G	G	G	G	F	F	G	F	G
	Hydrochloric acid resistance test	G	G	F	G	G	G	G	G	F	F	G	F	G

Table 8 shows testing results of the corrosion protection pretreatment agents CE14-CE26.

What is claimed is:

1. A corrosion protection pretreatment agent comprises:

e) a solvent,

f) at least one inorganic inhibitor,

g) at least one silane compound,

h) a bi-functional epoxy resin precursor (C), the bi-functional epoxy resin precursor (C) being represented by the following formulas:

R_1-Y-[CH_2-CH(OH)-R_3-CH(OH)-CH_2-X-R_4-X]$_n$-R_2

wherein, independently,

X= -COO-, sulphur moiety, -NR(H)-, -P($OR)_2$-O-, -P (OR)(OH)-O-, -PO-O-;

Y= -COO-, sulphur moiety, -NR(H)-, -P($OR)_2$-O-, -P (OR)(OH)-O-, -PO-O-;

R_2 being aromatic chain or aliphatic chain having from 1 to 20 carbon atoms or H;

R_4 being aromatic chain or aliphatic chain having from 1 to 20 carbon atoms;

R_1 being aromatic chain or aliphatic chain having from 1 to 20 carbon atoms, -XH or -X-R_4;

R_3 being any types of chain as far as it connects two hydroxyl α-carbon atoms;

n being an integer of 1~10.

2. The corrosion protection pretreatment agent according to claim 1, wherein, independently, R_2 being aromatic chain or aliphatic chain having from 1 to 10 carbon atoms or H, R_4 being aromatic chain or aliphatic chain having from 1 to 10 carbon atoms, R_1 being aromatic chain or aliphatic chain having from 1 to 10 carbon atoms, -XH or -X-R_4.

3. The corrosion protection pretreatment agent according to claim 1, wherein R_3 being selected from the group consisting of aromatic or aliphatic moiety having from 1 to 20 carbon atoms, polyurethane moiety, aliphatic or aromatic alkane having from 2 to 20 carbon atoms, acrylates containing polymer moiety.

4. The corrosion protection pretreatment agent according to claim 1, wherein X being selected from -COO-, -P (OR)(OH)-O-; and n being an integer of 2~8.

5. The corrosion protection pretreatment agent according to claim 1, wherein, the bi-functional epoxy resin precursor (C) being represented by the following formulas:

$(H)X\text{-}R_4\text{-}X\text{-}[CH_2\text{-}CH(OH)\text{-}R_3\text{-}CH(OH)\text{-}CH_2\text{-}X\text{-}R_4\text{-}X]_n\text{-}H$

wherein, independently,

X= -COO-, -P (OR)(OH)-O-;

R_4 being aromatic chain or aliphatic chain having from 1 to 10 carbon atoms;

R_3 being any types of chain as far as it connects two hydroxyl α-carbon atoms;

n being an integer of 2~8.

6. The corrosion protection pretreatment agent according to claim 1, wherein the corrosion protection pretreatment agent further comprises at least a resin, the resin being selected from a group consisting of polyurethane resin (A), polyurethane-acrylic resin(B), polyacrylic-epoxy resin (D).
7. The corrosion protection pretreatment agent according to anyone of claim 1 to 6, wherein the pH value of the corrosion protection pretreatment agent is from greater than 7 to 12.
8. The corrosion protection pretreatment agent according to anyone of claim 1 to 6, wherein the pH value of the corrosion protection pretreatment agent is from 3 to less than 7.
9. The corrosion protection pretreatment agent according to claim 7, wherein the bi-functional epoxy resin precursor (C) is present in proportions by weight of 45%-75%, based on the total weight of the bi-functional epoxy resin precursor (C) and the resin(s).
10. The corrosion protection pretreatment agent according to claim 8, wherein the bi-functional epoxy resin precursor (C) is present in proportions by weight of 52%-100%, based on the total weight of the bi-functional epoxy resin precursor (C) and the resin(s).
11. The corrosion protection pretreatment agent according to claim 7, wherein the corrosion protection pretreatment agent comprises 2.0 wt.% to 4.5 wt.% of the silane coupling agent, based on the total weight of solid contents, the silanol group containing resin being represented by the following formulas $XY(Z)_nSi(OH)_{3-n}$,

    wherein, independently, X being a glycidoxy group or functional group derived from a glycidoxy group, Y being a C1 to C10 alkylene group, Z being a methoxy group, ethoxy group or methyl group, and n being an integer of 0 to 2.
12. The corrosion protection pretreatment agent according to claim 8, wherein the corrosion

protection pretreatment agent comprises 40.0 wt.% to 60.0 wt.% of the silane coupling agent, based on the total weight of solid contents, the silanol group containing resin being represented by the following formulas $Y-[Si(Y)_2-O]_n-R$,

wherein, independently, n being an integer of 1 to 3,

R being a moiety of C1 to C6 alkyl groups and preferably C1 to C3 alkyl groups,

Y being a moiety selected from alkyl groups with not more than 10 carbon atoms carrying at least one epoxy, amino, hydroxyl, vinyl and/or thiol group,

wherein the Y being selected mutually independent from each other.

13. The corrosion protection pretreatment agent according to claim 7, wherein the corrosion protection pretreatment agent comprises, 0.3 to 7 wt.% of an inorganic inhibitor, based on the total weight of solid contents in the composition, the inorganic inhibitor comprising a zirconium compound and/or a vanadium compound.
14. The corrosion protection pretreatment agent according to claim 13, wherein the zirconium compound being selected from a group consisting of ammonium zirconium carbonate, potassium zirconium carbonate, basic zirconium carbonate, zirconium acetate, and combination.
15. The corrosion protection pretreatment agent according to claim 8, wherein the corrosion protection pretreatment agent comprises, 0.1 to 1.0 mol/L wt.% of a inorganic inhibitor, the inorganic inhibitor comprising at least one water-soluble or water-dispersible fluorinated acid or salt thereof, wherein the fluorinated acid is defined by the following general empirical formula: $H_mT_qF_pO_n$, wherein: q and p each represent an integer from 1 to 10; m and n each represent an integer from 0 to 10; and, T is an element selected from Ti, Zr, Hf, Si, Sn, Al, Ge, and B.
16. The corrosion protection pretreatment agent according to claim 1, wherein the solid content of the corrosion protection pretreatment agent is 15 wt.% to 50 wt.%, based on the total weight of the corrosion protection pretreatment agent.
17. A method for providing anticorrosion protection and enhanced coating adhesion on a metallic surface, comprising steps of:

a) bringing the corrosion protection pretreatment agent according to any one of claims 1 to 16 into contact with a metallic surface at a process temperature of at least 40°C, but no higher than 200°C, thereby creating a film on the metallic surface;

b) optionally removing excess quantities of the corrosion protection pretreatment agent from the surface; and

c) curing the coating located on the surface by means of thermal methods at a process temperature of 50-90 °C, or high-energy irradiation for a period of at least 10−5 seconds to form a cured coating.

18. The method according to claim 17, wherein the cured coating exhibits a layer thickness of at least 0.1 μm, but of no more than 0.5 μm.

19. An article having at least one portion that comprises the treated metallic surface of claim 17.

20. The article of claim 19, wherein protection coating exhibits a layer thickness of at least 0.1 μm, but of no more than 0.5 μm.

21. The article of claim 20, wherein the article is used for appliance application, said treated metallic surface having a T-bend (fresh) of equal to or less than 1T when subjected to GB/T13448-2006, a T-bend (aged, after 24 hours aging at a temperature of 50±2℃ and a humidity of 95%) of equal to or less than 2T when subject to GB/T13448-2006.

22. The article of claim 20, wherein the article is used for architecture application, said treated metallic surface has a T-bend (fresh) of equal to or less than 3T when subjected to GB/T13448-2006, a T-bend (aged, after 24 hours aging at a temperature of 50±2℃ and a humidity of 95%) of equal to or less than 4T when subject to GB/T13448-2006.

23. An article having at least one portion that comprises a pretreatment coating, wherein the protection coating is a cured product of the corrosion protection pretreatment agent according to any one of claims 1 to 16.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2022/105722

A. CLASSIFICATION OF SUBJECT MATTER

C09D 5/08(2006.01)i； C09D 163/00(2006.01)i； C23C 28/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C; C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNABS;CNTXT;DWPI;SIPOABS;WOTXT;USTXT;EPTXT;CJFD;Web of Science:HENKEL AG,wu xiaomeng,zhu yakun,zhang xilin,zhang yi,corrosion,pretreatment,agent,epoxy resin,epoxy,precursor,metal+,surface,protect+,adhes+,hydroxyl,polyhydroxyl,bi-functional,silane,inhibitor,solvent,water,sulphur,carboxyl group, Amino+, phosphat+,zirconium,vanadium, fluoro+,aqueous dispersion

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2010156020 A (JFE STEEL CORP. et al.) 15 July 2010 (2010-07-15) see paragraphs 0004-0005，0032，0038，0045-0049 of the description	1-23
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A	EP 0687715 A2 (DAINIPPON TORYO K.K.) 20 December 1995 (1995-12-20) the whole document	1-23
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☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search **24 November 2022**	Date of mailing of the international search report **16 December 2022**
Name and mailing address of the ISA/CN **National Intellectual Property Administration, PRC** **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China** Facsimile No. **(86-10)62019451**	Authorized officer **YAN,Lei** Telephone No. **86-(10)-53962925**

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	CN 101292003 A (CHUGOKU MARINE PAINTS) 22 October 2008 (2008-10-22) the whole document	1-23

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2022/105722

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				IN	255477	B	01 March 2013
				KR	101011114	B1	25 January 2011
				JP	5367983	B2	11 December 2013
				EP	1947154	B1	13 January 2016