

SURFACE TREATED METAL SHEET

DETAILED DESCRIPTION OF THE INVENTION

Field of the Invention

The present invention relates to a surface-treated metal sheet, in particular, to a surface-treated metal sheet excellent in corrosion resistance, abrasion resistance, coating property (coated film adhesiveness), conductivity, and alkaline degreasing resistance for used in automobiles, electronic home appliances, building materials, and others.

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Prior Art

Galvanized steel plates such as electroplated galvanized steel plates, hot dipping galvanized steel sheet, and inorganic surface-treated steel sheets chemically treated with chromate, phosphoric acid salt, or the like for further improvement in corrosion resistance and film adhesiveness have been used widely as the materials for use in automobiles, electronic home appliances, and building materials. In addition, a resin-coated steel sheet with an organic resin film formed on a chromate-treated surface-of a steel sheet for further improvement in corrosion resistance, film adhesiveness, and processability were also proposed.

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However, for example, in the case of motor case parts for electronic home appliances that demand deep drawing for

production, often encountered is a blackening phenomenon that the resin film on the sliding face exfoliates due to the sliding friction with the mold and turns black, thus damaging the appearance of the product and leading to other problems in other facilities as the separated blackened film adhered thereto.

To solve the problems associated with these resin-coated steel sheets, a lubricant steel sheet in which a film containing an inorganic polymeric compound and a solid lubricant is formed as a resin film and a lubricant steel sheet which further contains an aqueous resin were proposed (for example, Japanese Patent Application Laid-Open Nos. H6-57441 and H5-57442). These steel sheets having an inorganic polymer-based film are indeed improved in scratching resistance and generation of the blackened film during deep drawing. However, the steel sheets still had problems, for example, that the steel sheets occasionally lead to coating defects such as cissing during application of the solution and thus to generation of spotty black and white rusts because of higher water permeability of the film and that the adhesiveness of the film after coating is unsatisfactory. That is, these steel sheets are improved in scratching resistance and deep-drawing resistance, but still carried problems in corrosion resistance and film adhesiveness.

On the other hand, some of electronic home appliances demand conductive materials for prevention of static electrification. When a film is formed on a galvanized steel sheet, the lower the electric resistance is, the more conductive the film is. If the film is a resin film, it is necessary to reduce the amount of the adhered film to secure the plate's conductivity, because the resin film is more electrically resistant. However, decrease in the amount of adhered resin film results in deterioration on corrosion resistance and processability, eliminating the advantages of resin film described above. Accordingly, inorganic surface-treated steel sheets, i.e., galvanized steel sheets chemically treated for example with chromate, phosphoric acid, or the like, have been used for applications that demand conductivity.

Urethane resins superior in hardness and elongation are now used partially as the resins for such organic resin films, but the urethane resins, which contain a greater number of polar groups, carry the problem that are inferior in corrosion resistance to other resins.

In the recent heightened concern about the environment, use of steel sheets that are not treated with chromate or hexavalent chromium, which have been used for improvement of corrosion resistance of galvanized steel sheets, is gradually expanding. Thus, there exists an increasing need

for films further superior in corrosion resistance.

Problems to be solved by the Invention

As described above, even for the resin films formed on
5 chromium free metal sheets, there is a demand for corrosion
resistance at the same level as that for the resin films
formed on chromate-treated metal sheets.

However, the surface-treated metal sheet with a
conventional urethane resin film formed thereon is still
10 not satisfactory in corrosion resistance, and further
improvement in coating property (adhesiveness with coated
film), conductivity, abrasion resistance, and alkaline
degreasing resistance is demanded.

An object of the present invention, which was made
15 under the above circumstances, is to further improve
corrosion resistance, coating property, alkaline degreasing
resistance, abrasion resistance, and conductivity of
surface-treated metal sheets, more specifically of metal
sheets with a polyurethane resin film formed on the surface.

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Means for solving the Problems

The surface-treated metal sheet according to the
present invention, which solved the problems above, is the
surface-treated metal sheet with a resin film coated
25 thereon obtained from an aqueous resin solution;

the aqueous resin solution, comprising:

an aqueous carboxyl group-containing polyurethane resin solution and an aqueous ethylene-unsaturated carboxylic acid copolymer dispersion in an amount of 5 to 45 parts by mass as nonvolatile resin components, silica particles having an average particle size of 4 to 20 nm in an amount of 55 to 95 parts by mass,

a total amount of the resin solutions and the silica particles being 100 parts by mass; and

10 a silane coupling agent in an amount of 5 to 25 parts by mass with respect to the total amount of the resin solutions and the silica particles of 100 parts by mass;

the compounding ratio of the nonvolatile resin component in the aqueous polyurethane resin solution (PU) to the nonvolatile resin component in the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion (EC) being 9:1 to 2:1.

The carboxyl group-containing polyurethane resin is preferably a resin prepared in the chain-extending reaction of a urethane prepolymer with a chain extender.

20 A polyisocyanate component constituting the urethane prepolymer includes at least one compound selected from the group consisting of tolylene diisocyanate, diphenylmethane diisocyanate, and dicyclohexylmethane diisocyanate, and polyol components constituting the urethane prepolymer

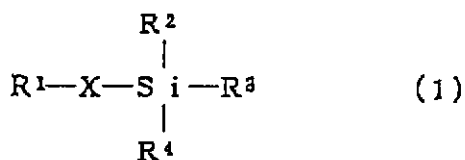
includes at least 1,4-cyclohexanedimethanol, a polyether polyol, and a polyol containing a carboxyl group.

The chain extender is favorably, for example, ethylenediamine or hydrazine. A mass ratio of 1,4-cyclohexanedimethanol to the polyether polyols (1,4-cyclohexanedimethanol: polyether polyols) is preferably 1:1 to 1:19. The polyether polyol is preferably, for example, polyoxypropylene glycol or polytetramethylene ether glycol. A acid value of the carboxyl group-containing polyurethane resin is preferably 10 to 60 mg-KOH/g.

The aqueous ethylene-unsaturated carboxylic acid copolymer dispersion for use in the present invention preferably contains an ethylene-unsaturated carboxylic acid copolymer, an amine having a boiling point of 100°C or lower in an amount equivalent to 0.2 to 0.8 mole with respect to 1 mole of the carboxyl group in the ethylene-unsaturated carboxylic acid copolymer, and a monovalent metal compound in an amount equivalent to 0.02 to 0.4 mole with respect to 1 mole of the carboxyl group in the ethylene-unsaturated carboxylic acid copolymer. The ethylene-unsaturated carboxylic acid copolymer is preferably a copolymer containing an unsaturated carboxylic acid component in an amount of 10 to 40 % by mass. The amine described above having the boiling point of 100°C or lower is favorably, for example, triethylamine.

In another preferable embodiment of the present invention, the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion contains additionally a crosslinking agent having two or more functional groups reactive with a carboxyl group in an amount of 1 to 20 parts by mass with respect to 100 parts by mass of the nonvolatile resin components (EC) in the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion. In addition, the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion preferably does not contain an amine having a boiling point of over 100°C or ammonia substantially.

The silane-coupling agent for use in the present invention is favorably, for example, a silane-coupling agent represented by the following Chemical Formula (1).



in which R¹ represents a glycidoxy group, R² and R³ represent respectively a lower alkoxy group, R⁴ represents a lower alkoxy or alkyl group, and X represents a lower alkylene group.

An amount of the resin film adhered onto the surface-treated metal sheet according to the present invention is preferably 0.05 to 1 g/m² after drying.

The present invention provides the surface-treated metal sheet superior in corrosion resistance, film adhesiveness (coating property), abrasion resistance, conductivity, and alkaline degreasing resistance. In particular, the present invention is favorably applicable for improvement in corrosion resistance of non-chromate-finished metal sheets.

Preferred Embodiments of the Invention

The surface-treated metal sheet according to the present invention is a surface-treated metal sheet with a resin film coated thereon obtained from an aqueous resin solution;

the aqueous resin solution, comprising:

an aqueous carboxyl group-containing polyurethane resin solution and an aqueous ethylene-unsaturated carboxylic acid copolymer dispersion in an amount of 5 to 45 parts by mass as nonvolatile resin components, silica particles having an average particle size of 4 to 20 nm in an amount of 55 to 95 parts by mass,

a total amount of the resin solutions and the silica particles being 100 parts by mass; and

a silane coupling agent in an amount of 5 to 25 parts by mass with respect to the total amount of the resin solutions and the silica particles of 100 parts by mass;

the compounding ratio of the nonvolatile resin component in the aqueous polyurethane resin solution (PU) to the nonvolatile resin component in the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion (EC) being
5 9:1 to 2:1. The present invention will be described in detail.

(1) Resin components contained in aqueous resin solution

(1-1) The aqueous carboxyl group-containing
10 polyurethane resin solution for use in the present invention will be described. The aqueous carboxyl group-containing polyurethane resin solution for use in the present invention may be an aqueous dispersion of the carboxyl group-containing polyurethane resin dispersed in
15 an aqueous medium or an aqueous solution of the carboxyl group-containing polyurethane resin dissolved in an aqueous medium. In addition to water, other hydrophilic solvent such as alcohol, N-methylpyrrolidone, or acetone may be contained in a trace amount in the aqueous medium.

20 The carboxyl group-containing polyurethane resin is preferably a resin prepared in the chain-extending reaction of an urethane prepolymer with a chain extender, and the urethane prepolymer can be prepared, for example, in the reaction of a polyisocyanate and a polyol component
25 described below. At least one polyisocyanate selected from

the group consisting of tolylene diisocyanate (TDI),
diphenylmethane diisocyanate (MDI) and dicyclohexylmethane
diisocyanate (hydrogenated MDI) is preferably used as the
polyisocyanate component for the urethane prepolymer,

5 because use of such a polyisocyanate provides a resin film
superior in corrosion resistance and reliability in
controlling reaction. Other polyisocyanates may be used in
combination with the polyisocyanate above in the range that
does not impair corrosion resistance and reliability in
10 controlling reaction, but a content of the polyisocyanate
component above is preferably 70 % by mass or more in all
polyisocyanate components. The polyisocyanate component
content of less than 70 % by mass may result in
deterioration in corrosion resistance and reliability in
15 controlling reaction. Examples of the polyisocyanates
other than the polyisocyanate components above include
tetramethylene diisocyanate, hexamethylene diisocyanate,
dodecamethylene diisocyanate, isophorone diisocyanate,
xylene diisocyanate, phenylene diisocyanate, and the like.
20 The polyisocyanates may be used alone or in combination of
two or more.

All three kinds of polyols, 1,4-cyclohexanedimethanol,
the polyether polyol, and a polyol containing a carboxyl
group, are preferably used as the polyol components for the
25 urethane prepolymer, and preferably, all the three polyols

are diols, because use of such polyol components provides a resin film superior in corrosion resistance and lubrication. Use of 1,4-cyclohexanedimethanol as one of the polyol components increases the rustproof efficiency of a
5 resultant polyurethane resin.

The polyether polyol is not particularly limited when it contains two or more hydroxyl groups on its molecular chain and the main chain is constituted by an alkylene oxide; and examples thereof include polyoxyethylene glycol
10 (may referred to simply as "polyethylene glycol"), polyoxypropylene glycol (may referred to simply as "polypropylene glycol"), polyoxytetramethylene glycol (may be referred to simply as "polytetramethylene glycol" or "polytetramethylene ether glycol"), and the like; and any
15 one of commercially available products may be used. Among the polyether polyols above, polyoxypropylene glycol or polytetramethylene ether glycol is preferably used. The number of the functional groups in the polyether polyol is not particularly limited when it is 2 or more, for example,
20 trifunctional, tetrafunctional, or higher.

The polyether polyols are prepared, for example, in the addition reaction of an alkylene oxide such as ethylene oxide or propylene oxide by using a compound containing an active hydrogen as an initiator. Examples of the compounds
25 containing an active hydrogen include diols such as

propylene glycol and ethylene glycol; triols such as glycerol, trimethylolpropane, hexanetriol, and triethanolamine; tetraols such as diglycerin and pentaerythritol; sorbitol, sucrose, phosphoric acid, and
5 the like. When a diol is used as the initiator, a bifunctional polyether polyol is obtained. When a triol is used, a trifunctional polyether polyol is obtained.

Polyoxytetramethylene polyol is prepared, for example, by ring-opening polymerization of tetrahydrofuran.

10 The polyether polyol used is preferably a commercially available product having an average molecular weight, for example, of about 400 to 4,000. The polyether polyol having an average molecular weight of less than about 400 may provide a hard resin film, while that of more than
15 4,000 may provide an excessively soft film. The average molecular weight can be determined by measuring an OH value (hydroxyl value) of the resin.

In a preferable embodiment of the present invention, a mass ratio of 1,4-cyclohexanedimethanol to the polyether
20 polyol (1,4-cyclohexanedimethanol: polyether polyol) is 1:1 to 1:19, because use of 1,4-cyclohexanedimethanol at a particular ratio allows production of a polyurethane resin film having rustproof efficiency further improved.

The polyol containing a carboxyl group for use in the
25 present invention is not particularly limited so long as it

contains one or more carboxyl groups and two or more hydroxyl groups, and examples thereof include dimethylolpropionic acid, dimethylolbutanoic acid, dihydroxypropionic acid, dihydroxysuccinic acid, and the like.

In addition to the three kinds of polyol components above, other polyols may be used in the range that does not impair corrosion resistance of film, and a content of the three kinds of polyol components is preferably 70 % by mass or more in all polyol components. The content of the three kinds of polyol components of less than 70 % by mass may lead to deterioration in corrosion resistance. The polyol other than the three kinds of polyol components described above is not particularly limited so long as it contains multiple hydroxy groups, and examples thereof include low-molecular weight polyols, high-molecular weight polyols, and the like. The low-molecular weight polyol has an average molecular weight of approximately 500 or less, and examples thereof include diols such as ethylene glycol, diethylene glycol, triethylene glycol, 1,3-butanediol, 1,4-butanediol, neopentyl glycol, and 1,6-hexanediol; and triols such as glycerol, trimethylolpropane, and hexanetriol.

The high-molecular weight polyol has an average molecular weight of over approximately 500, and examples

thereof include condensation polyester polyols such as polyethylene adipate (PEA), polybutylene adipate (PBA), and polyhexamethylene adipate (PHMA); lactone-based polyester polyols such as poly- ϵ -caprolactone (PCL); polycarbonate polyols such as polyhexamethylene carbonate; and acrylic polyols, and the like.

The chain extender for use in the chain-extending reaction of the urethane prepolymer described above is not particularly limited, and examples thereof include polyamines, low-molecular weight polyols, alkanol amines, and the like. The low-molecular weight polyol same as those described above may be used as the low-molecular weight polyol, and examples of the polyamines include aliphatic polyamine such as ethylenediamine, propylenediamine, and hexamethylenediamine; aromatic polyamine such as tolylenediamine, xylylenediamine, and diaminodiphenylmethane; alicyclic polyamines such as diaminocyclohexylmethane, piperazine, and isophoronediamine; hydrazines such as hydrazine, succinic dihydrazide, adipic dihydrazide, and phthalic dihydrazide; and the like. Among them, use of ethylenediamine and/or hydrazine as the chain extender components is preferable. Examples of the alkanol amines include diethanolamine, monoethanolamine, and the like.

An aqueous solution of the carboxyl group-containing

polyurethane resin for use in the present invention can be prepared by a conventional method, and for example, by emulsifying the carboxyl group-containing urethane prepolymer in an aqueous medium by neutralizing the
5 carboxyl groups thereof with a base and then allowing the prepolymer to react in a chain-extending reaction, by emulsifying the carboxyl group-containing polyurethane resin under high-shearing force in the presence of an emulsifier and then allowing the prepolymer to react in a
10 chain-extending reaction, or the like. Hereinafter, the method of producing an aqueous polyurethane resin solution will be described, taking the method of emulsifying the carboxyl group-containing urethane prepolymer in water by neutralizing the carboxyl groups thereof as an example, but
15 the present invention is not limited to the method.

A relatively low-molecular weight carboxyl group-containing urethane prepolymer containing isocyanate groups at the terminal is first prepared by using the polyisocyanate described above and the polyol described
20 above at a NCO/OH ratio in excess of isocyanate group. The temperature of the reaction for preparing the urethane prepolymer is not particularly limited, but normally 50 to 200°C. Any one of known catalysts may be used for preparation of the urethane prepolymer. Examples of the
25 catalysts include monoamines such as triethylamine, and

N,N-dimethylcyclohexylamine; polyamines such as N,N,N,N'-tetramethylethylenediamine, and N,N,N',N'',N''-pentamethyldiethylenetriamine; cyclic diamines such as 1,8-diazabicyclo[5,4,0]-7-undecene (DBU), and
5 triethylenediamine; tin catalysts such as dibutyltin dilaurate and dibutyltin diacetate; and the like.

Either a one-shot method or a prepolymer method may be used in preparing the urethane prepolymer. The one-shot method is a method of reacting a polyisocyanate and a
10 polyol at the same time, while the prepolymer method is a method of reacting a polyisocyanate and a polyol stepwise in multiple steps, for example, by first preparing a low-to medium-molecular weight urethane prepolymer and then elongating the intermediate prepolymer.

15 In the present invention, for example, the urethane prepolymer may be prepared in suitable selected method from the following methods: simultaneous reaction of a polyisocyanate with the three kinds of polyols; stepwise reactions first between a polyisocyanate and a polyether
20 polyol among the three kinds of polyol components, followed by the reaction with 1,4-cyclohexanedimethanol, and then with a polyol containing a carboxyl group; stepwise reactions first between polyisocyanate with the polyether polyol and 1,4-cyclohexanedimethanol among the essential
25 polyol components, followed by the reaction with a polyol

containing a carboxyl group; and the like.

In a preferable embodiment, a solvent is used in preparation of the carboxyl group-containing isocyanate group-terminal urethane prepolymer, for adjustment of the viscosity and improvement of the emulsification efficiency of the prepolymer. The solvent is preferably inert to the isocyanate group and relatively high in hydrophilicity, and examples thereof include N-methylpyrrolidone, acetone, ethyl acetate, methylethylketone, N,N- dimethylformamide, and the like. N-methylpyrrolidone is preferable, because N-methylpyrrolidone is effective in dissolving the polyol containing a carboxyl group, making the reaction for preparing the isocyanate group-terminal urethane prepolymer more uniform. The degree of the urethane prepolymer-preparing reaction can be determined, for example, by determining a concentration of isocyanate groups according to dibutylamine titration method.

The carboxyl group-containing isocyanate group-terminal urethane prepolymer obtained after the urethane prepolymer reaction is emulsified in water by neutralization with a base. The neutralizer is not particularly limited, and ammonia, a tertiary amine such as triethylamine or triethanolamine, an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide, or the like may be used. Triethylamine is preferably used.

After emulsification, the carboxyl group-containing isocyanate group-terminal urethane prepolymer may be subject to a chain-extending reaction in water by using a chain extender such as polyamine. The chain-extending reaction may be carried out before, during or after emulsification, according to the reactivity of the chain extender used.

An acid value of the carboxyl group-containing polyurethane resin for use in the present invention is 10 mg-KOH/g or more, preferably 60 mg-KOH/g or less. The acid value of less than 10 mg-KOH/g may result in deterioration in stability of the aqueous polyurethane resin dispersion. The acid value of over 60 mg-KOH/g may result in deterioration of corrosion resistance of the resin film obtained. The acid value is determined in accordance with JIS K0070.

(1-2) The aqueous ethylene-unsaturated carboxylic acid copolymer dispersion for use in the present invention will be described below. The aqueous ethylene-unsaturated carboxylic acid copolymer dispersion for use in the present invention is not particularly limited so long as it is a solution of an ethylene-unsaturated carboxylic acid copolymer dispersed in an aqueous medium and the ethylene-unsaturated carboxylic acid copolymer is a copolymer of ethylene and an ethylenic unsaturated carboxylic acid.

Examples of the unsaturated carboxylic acids include (meth)acrylic acid, crotonic acid, isocrotonic acid, maleic acid, fumaric acid, itaconic acid, and the like, and the copolymer is prepared by copolymerizing ethylene and one or more of them by any one of known high-temperature high-pressure polymerization methods. Random copolymers are preferable, but block copolymers or copolymers grafted with unsaturated carboxylic acid portions may also be used. The unsaturated carboxylic acid is favorably (meth)acrylic acid.

A part of ethylene may be replaced with an olefin monomer such as propylene or 1-butene, and other known vinyl monomers (approximately 10 % by mass or less) may be partially copolymerized so long as the object of the present invention is not impaired.

The ethylene-unsaturated carboxylic acid copolymer is preferably a copolymer containing unsaturated carboxylic acid components in an amount of 10 to 40 % by mass with respect to 100 % by mass of the total monomer amount. A unsaturated carboxylic acid copolymerization ratio of less than 10 % by mass, i.e., a smaller number of carboxyl groups which play a role as the base points for intermolecular association by ion clustering or the crosslinking points with a crosslinking agent, is undesirable, because it may result in decrease in coating-strengthening effect, corrosion resistance of the resulting

film after the degreasing step and emulsion stability of the aqueous dispersion. More preferably, the lower limit of unsaturated carboxylic acid content is 15 % by mass. An unsaturated carboxylic acid content of 40 % by mass is also undesirable, because the resulting resin film is inferior in corrosion and water resistance, consequently leading to deterioration in corrosion resistance after the alkaline degreasing step. More preferably, the upper limit is 25 % by mass.

10 The ethylene-unsaturated carboxylic acid copolymer for use in the present invention contains carboxyl groups, and thus, it is possible to prepare an aqueous dispersion thereof by neutralizing the carboxyl groups with an organic base or a metal ion.

15 The organic base used is preferably an amine having a boiling point of 100°C or lower. Amines having a boiling point of higher than 100°C, which remains in the resin film on the metal sheet after the aqueous resin solution is dried, increase water absorbency of the resin film and
20 cause deterioration in corrosion resistance. For that reason, the ethylene-unsaturated carboxylic acid copolymer dispersion for use in the present invention aqueous preferably contains no amines having a boiling point of higher than 100°C. Ammonia, which was found to be less
25 effective when added, is also preferably not contained

therein. The boiling point above is that determined under atmospheric pressure.

The aqueous ethylene-unsaturated carboxylic acid copolymer dispersion preferably contains an amine having a boiling point of 100°C or lower in an amount equivalent to 0.2 to 0.8 mole (20 to 80 mole %) with respect to 1 mole of the carboxyl group in the ethylene-unsaturated carboxylic acid copolymer and a monovalent metal compound in an amount equivalent to 0.02 to 0.4 mole (2 to 40 mole %) with respect to 1 mole of the carboxyl group in the ethylene-unsaturated carboxylic acid copolymer.

Typical examples of the amines having a boiling point of 100°C or lower include tertiary amines such as triethylamine, N,N-dimethylbutylamine, N,N-dimethylarylamine, N-methylpyrrolidine, tetramethyldiaminomethane, and trimethylamine; secondary amines such as N-methylethylamine, diisopropylamine, and diethylamine; primary amines such as propylamine, t-butylamine, sec-butylamine, isobutylamine, 1,2-dibutylpropylamine, and 3-pentylamine; and the like, and these amines may be used alone or in combination of two or more. Among them, tertiary amines are preferable; and most preferable is triethylamine.

An amount of the amine having a boiling point of 100°C or lower is preferably in the range of 0.2 to 0.8 mole (20

to 80 mole %) with respect to 1 mole of the carboxyl group in the ethylene-unsaturated carboxylic acid copolymer, because corrosion resistance is kept favorable in the range.

A content of an amine having a boiling point of 100°C or lower at less than 0.2 mole seems to increase the diameter of resin particles in the aqueous dispersion, prohibiting the advantageous effects described above. Use of an amine having a boiling point of 100°C or lower in an amount of more than 0.8 mole is also undesirable, as it results in increase in viscosity of the aqueous dispersion and leads to gelation thereof. More preferably, the upper limit of amine content is 0.6 mole, still more preferably 0.5 mole, and the lower limit is 0.3 mole.

In the present invention, in addition to an amine having a boiling point of 100°C or lower, a monovalent metal ion is preferably used for neutralization. The addition of metal ion is effective in improving solvent resistance and hardness of film. The monovalent metal compound preferably contains one or more metals selected from sodium, potassium, and lithium, and is preferably a hydroxide, carbonate or oxide of these metals. Among them, NaOH, KOH, and LiOH are preferable, and NaOH is most effective and preferable.

An amount of the monovalent metal compound added is preferably in the range of 0.02 to 0.4 mole (2 to 40

mole %) with respect to 1 mole of the carboxylic group in the ethylene-unsaturated carboxylic acid copolymer. The metal compound content of less than 0.02 mole leads to insufficient emulsion stability, while the content of more than 0.4 mole unfavorably leads to increase in the hygroscopic property of the resin film obtained (in particular, to the alkaline solution) and deterioration of corrosion resistance after the degreasing step. More preferably, the lower limit of metal compound content is 0.03 mole, still more preferably 0.1 mole, and the preferable upper limit is 0.5 mole, more preferably 0.2 mole.

The amine having a boiling point of 100°C or lower and the monovalent metal compound, of which the preferable use ranges are respectively described above, are used for neutralizing the carboxyl groups in the ethylene-unsaturated carboxylic acid copolymer and make it aqueous. Therefore, when the total amount of these compounds (neutralization amount) is excessive, it may result in drastic increase in viscosity of the aqueous dispersion, occasionally leading to solidification. Excessive alkaline compounds, which cause deterioration in corrosion resistance, demand a great amount of energy for evaporation or removal. However, an excessively smaller neutralization degree is also undesirable, as it may cause deterioration

in emulsion stability. Thus, a total amount of the amine having a boiling point of 100°C or lower and the monovalent metal compound is preferably in the range of 0.3 to 1.0 mole with respect to 1 mole of the carboxyl group in the ethylene-unsaturated carboxylic acid copolymer.

It is possible to obtain an aqueous dispersion of extremely fine particles (oil droplets) having an average particle size of 5 to 50 nm as the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion for use in the present invention, by emulsifying the copolymer with the amine having a boiling point of 100°C or lower and the monovalent metal ion in combination. Therefore, it is estimated that improvement in coating property, adhesiveness to metal sheet, densification, as well as corrosion resistance of the resin film may be obtained. The aqueous medium above may contain a hydrophilic solvent such as alcohol, ether, or the like in addition to water. The diameter of resin particles in the aqueous dispersion is determined, for example, by laser diffraction by using a light scattering photometer (e.g., manufactured by Otsuka Electronics Co., Ltd.).

In the neutralization step (hydration step) of neutralizing the ethylene-unsaturated carboxylic acid copolymer with the amine having a boiling point of 100°C or lower and the monovalent metal ion, it is preferably to add

the amine having a boiling point of 100°C or lower and the monovalent metal compound almost simultaneously to the copolymer or to add the amine having a boiling point of 100°C or lower first. Later addition of the amine having a boiling point of 100°C or lower results in insufficient increase in corrosion resistance, although the reason is not clearly understood.

The ethylene-unsaturated carboxylic acid copolymer dispersion for use in the present invention aqueous is prepared by adding an ethylene-unsaturated carboxylic acid copolymer and an aqueous medium, for example, in a homogenizer, heating the mixture to 70 to 250°C as needed, adding an amine having a boiling point of 100°C or lower and a monovalent metal compound suitably, for example, as an aqueous solution (firstly the amine having a boiling point of 100°C or lower, or almost simultaneously the amine having a boiling point of 100°C or lower and the monovalent metal compound), and stirring the mixture under high-shearing force.

(1-3) Compounding amounts of resin components

The aqueous resin solution for use in the present invention contains a mixture of the aqueous carboxyl group-containing polyurethane resin solution and the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion described above in an amount of 5 to 45 parts by mass as

nonvolatile resin components, and silica particles in an amount of 55 to 95 parts by mass in the total amount of 100 parts by mass, and further contains the silane-coupling agent in an amount of 5 to 25 parts by mass with respect to the above total amount of 100 parts by mass. In the present invention, the combined use of the carboxyl group-containing polyurethane resin and the ethylene-unsaturated carboxylic acid copolymer allows production of the surface-treated metal sheet superior in film adhesiveness, corrosion resistance, abrasion resistance, and alkaline degreasing resistance. An excessively smaller amount of the nonvolatile resin components may lead to deterioration in corrosion resistance, alkaline degreasing resistance, and film adhesiveness. An excessively larger amount of the nonvolatile resin components may lead to deterioration in abrasion resistance and conductivity. From the viewpoints above, the aqueous resin solution preferably contains the aqueous carboxyl group-containing polyurethane resin solution and the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion in an amount of 20 parts or more by mass, more preferably 25 parts or more, and 40 parts or less by mass, more preferably 35 parts or less by mass, as nonvolatile resin components. The nonvolatile resin component in the polyurethane aqueous solution is the carboxyl group-containing polyurethane resin described

above, and the nonvolatile resin component in the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion is the ethylene-unsaturated carboxylic acid copolymer described above. The amount of the nonvolatile resin components can be determined by any one of the methods known in the technical field of aqueous solution or dispersion, for example, by heating and drying the aqueous solution or dispersion at 100 to 130°C for 1 to 3 hours and measuring the amount of the evaporation residue.

10 A compounding ratio of the carboxyl group-containing polyurethane resin (PU) to the ethylene-unsaturated carboxylic acid copolymer (EC), that is, PU:EC is 9:1 to 2:1, preferably 6.5:1 to 3.3:1, and more preferably 5:1 by mass. The PU content higher than 9:1 as a compounding
15 ratio of the nonvolatile components (PU) in aqueous polyurethane resin solution to the nonvolatile components (EC) in the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion, results in deterioration in corrosion resistance and alkali resistance. The PU content lower
20 than a ratio of 2:1 leads to deterioration in abrasion resistance.

 It is generally regarded that it is difficult to use different resins in combination for a metal sheet resin film, because the resin film does not show desirable
25 properties due to predominant influence in properties by

one of the resins used. However, the resin film prepared in combination of two kinds of resins according to the present invention shows well-balanced properties of both resins. In addition, the combined use of the two kinds of resins together with the silica particles and the silane coupling agent provides the surface-treated metal sheet superior in film adhesiveness, corrosion resistance, abrasion resistance, and alkaline degreasing resistance by synergistic interaction of these materials.

10 (2) Silica particles

With respect to 5 to 45 parts by mass of the nonvolatile resin components in the aqueous carboxyl group-containing polyurethane solution and the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion described above, the aqueous resin solution for use in the present invention contains the silica particles in an amount of 55 parts or more, preferably 60 parts or more, and 95 parts or less, preferably 80 parts or less, more preferably 75 parts or less by mass (the total nonvolatile resin components is 100 parts by mass in total).

The silica particles provide the resultant resin film with conductivity, corrosion resistance, and film adhesiveness, and raise hardness to improve abrasion resistance of the film. The silica particle content of less than 55 parts by mass may lead to deterioration in

conductivity and abrasion resistance. The silica content of more than 95 parts by mass may lead to deterioration in coating property and corrosion resistance of the resin film. The silica particles preferably have an average particle size in the range of 4 to 20 nm so that the silica particles can exert the maximum advantageous effect. As the average particle size of the silica particles decreases, corrosion resistance of the resulting resin film increases, but the improvement in corrosion resistance seems to be saturated at an average particle size of approximately less than 4 nm, and the stability of the aqueous resin solution decreases, resulting in tendency of gelation. The silica particles having an average particle size of larger than 20 nm may lead to deterioration in film-forming property of the dispersion and in corrosion resistance, film adhesiveness, and alkaline degreasing resistance of the resulting resin film.

Use of the Sears method (4 to 6 nm) or the BET method (4 to 20 nm) is preferable for determination of the average particle size of the silica particles. A dynamic light scattering method is preferably used for determination of the average particle size of chain silica. Such silica particles are known normally as colloidal silica, and for example, XS, SS, 40, N, and UP in Snowtex series products (manufactured by Nissan Chemical Industries Ltd.) and the

like are favorably used in the present invention.

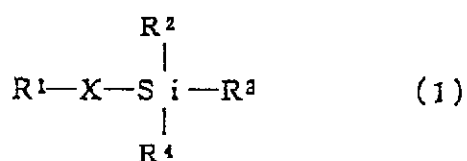
(3) Silane-coupling agent

The aqueous resin solution for use in the present invention contains a silane-coupling agent. The silane-coupling agent is used for improvement in abrasion resistance, film adhesiveness, corrosion resistance, and the like as well as in the adhesiveness between a metal sheet and a resin film formed thereon.

A content of the silane-coupling agent in the aqueous resin solution is preferably 5 parts or more, preferably 7 parts or more by mass and 25 parts or less, preferably 15 parts or less, by mass with respect to 100 parts by mass of the total amount of the nonvolatile resin components and the silica particles in the mixture of the aqueous carboxyl group-containing polyurethane solution and the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion described above. When the content of the silane-coupling agent is too small, the reactivities between the silane-coupling agent and the carboxyl group-containing polyurethane resin and the ethylene-unsaturated carboxylic acid copolymer described above and between the silane-coupling agent and the metal sheet surface decrease, resulting in deterioration in abrasion resistance, coating property, corrosion resistance, and the like. When the content of the silane-coupling agent is too large, the

stability of the aqueous resin solution deteriorates, which may result in gelation, and the amount of the silane-coupling agent not involved in the reaction above increases, resulting in lowering of the adhesiveness between the metal
 5 sheet and the resin film formed thereon.

In a preferable embodiment, the silane-coupling agent is the silane-coupling agent represented by the following Chemical Formula (1).



10

in which R^1 represents a glycidoxy group, R^2 and R^3 represent respectively a lower alkoxy group, R^4 represents a lower alkoxy group or a lower alkyl group, and X represents a lower alkylene group.

15

Presence of the silane-coupling agent increases coating property of the aqueous resin solution and corrosion resistance of the resin film formed. Examples of the silane-coupling agents containing a glycidoxy group at the terminal represented by the chemical formula (1)

20

include γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropylmethyldiethoxysilane, vinyltris(β -methoxyethoxy)silane, and the like. The silane-coupling agent containing the glycidoxy group is used, because it is

highly crosslinkable with the carboxyl group-containing polyurethane resin and the ethylene-unsaturated carboxylic acid copolymer and increases hardness and lubricity of the resin film obtained.

5 (4) Other additives

 The carboxyl group-containing ethylene-unsaturated carboxylic acid copolymer neutralized with the amine having a boiling point of 100°C or lower and the monovalent metal ion described above associates with each other
10 intermolecularly (ionomerization) by ion clustering, giving a resin film superior in corrosion resistance. However, it is more preferable to crosslink the polymer chains via chemical bonds by using the reaction between functional groups.

15 In a preferable embodiment, the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion for use in the present invention contains a crosslinking agent having two or more functional groups reactive with a carboxyl group, and a content of the crosslinking agent is
20 preferably 1 part or more, more preferably 5 parts or more by mass and 20 parts or less, more preferably 10 parts or less by mass with respect to 100 parts by mass of the nonvolatile resin component (EC) in the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion.

25 The content of less than 1 part by mass may result in

insufficient effect of the crosslinking by chemical bonds and insufficient improvement in corrosion resistance.

Addition in an amount of more than 20 parts by mass is also unfavorable, because it may lead to increase in hardness of the resin film due to excessive increase in crosslinking density, consequently to generation of cracks in the resin film because of inability to follow deformation during pressing and thus deterioration in corrosion resistance and film adhesiveness.

10 The crosslinking agent having two or more functional groups reactive with a carboxyl group in the molecule is not particularly limited, and favorable examples thereof include glycidyl group-containing crosslinking agent such as polyglycidylethers [e.g., sorbitol polyglycidylether, 15 (poly)glycerol polyglycidylether, pentaerythritol polyglycidylether, trimethylolpropane polyglycidylether, neopentylglycol diglycidylether and (poly)ethylene glycol diglycidylether], and polyglycidylamines; aziridiny group-containing crosslinking agents such as bifunctional 20 aziridine compounds [e.g., 4,4'-bis(ethyleneiminecarbonylamino)diphenylmethane, N,N'-hexamethylene-1,6-bis (1-azilidinecarboxyamide), N,N'-diphenylmethane-4.4'-bis(1-azilidinecarboxyamide), toluene-bisazilidinecarboxyamide], trifunctional or higher 25 aziridine compounds [e.g., tri-1-aziridinyolphosphine oxide,

tris[1-(2-methyl)aziridinyl]phosphine oxide,
trimethylolpropane tris(β -aziridinylpropionate), tris-
2,4,6-(1-aziridinyl)-1,3,5-triazine, and tetramethylpropane
tetraaziridinylpropionate], and the derivatives thereof;

5 and the like, and these crosslinking agents may be used
alone or in combination of two or more. Among them,
aziridinyl group-containing crosslinking agents are
preferable. A multifunctional aziridine and a
monofunctional aziridine (ethyleneimine, etc.) may be used
10 in combination.

(5) Methods for preparing an aqueous resin solution
and forming a resin film

The aqueous resin solution for use in the present
invention may contain various additives such as diluent
15 solvent, skinning inhibitor, leveling agent, anti-form agent,
penetrant, emulsifier, filming aid, coloring pigment,
thickener, and lubricant in the range that does not impair
the advantageous effects of the present invention. The
method for preparing the aqueous resin solution is not
20 particularly limited, and the aqueous resin solution may be
prepared by mixing the aqueous carboxyl group-containing
polyurethane solution, the aqueous ethylene-unsaturated
carboxylic acid copolymer dispersion, the silica particles,
the silane-coupling agent, and as needed a wax, the
25 crosslinking agent, and the like in predetermined amounts.

The silica particles, the silane-coupling agent, wax, crosslinking agent, and the like may be added in any step, but it is preferable not to apply any heat after addition of the crosslinking agent and the silane-coupling agent,
5 for prevention of the progress of crosslinking and gelation.

In forming a resin film on a metal sheet, the aqueous resin solution may be coated and dried under heat on one side or both faces of the metal sheet surface, by using a known application method such as a roll coater method, a
10 spraying method, or a curtain-flow coater method. The heat drying is preferably performed at a temperature allowing the cross-linking reaction between the crosslinking agent used and carboxyl groups to progress. When a spherical polyethylene wax is used as a lubricant, it is preferable
15 to dry the film at a temperature in the range of 70 to 130°C, because the wax in spherical shape is advantageous in the processability in the later steps.

The two kinds of resins for use in the present invention are emulsion particles, which melt and fuse to
20 each other, forming a film during the rise in temperature after vaporization of water. Silica particles are dispersed inside the film. The silane-coupling agent, which improves adhesiveness between the metal sheet surface (in particular, plated surface) and the resin film, seems
25 to be present in the region close to the interface.

The metal sheet for use in the present invention is not particularly limited, but a galvanized steel sheet is preferable. Favorable examples thereof include hot dip pure zinc-coated steel sheet (G1), or hot dip Zn-Fe alloy-coated steel sheet (GA), hot dip Zn-5% Al alloy-coated steel sheet (GF), pure zinc electroplated steel sheet (EG), Zn-Ni electroplated steel sheet, aluminum sheet, Ti sheet, and the like. Before forming a resin film, the metal sheet surface may be treated with Co or Ni, or treated with an inhibitor, or alternatively, subjected to various non-chromate surface treatments.

An amount of the resin film adhered onto the metal sheet (thickness) after drying is 0.05 g/m^2 or more, preferably 0.2 g/m^2 or more and 1 g/m^2 or less, more preferably 0.5 g/m^2 or less. An excessively small adhesion amount may result in deterioration in abrasion resistance, corrosion resistance, and alkaline degreasing resistance. An excessively large adhesion amount may lead to tendency of deterioration in conductivity and welding efficiency.

The surface-treated metal sheet may be used as it is after a suitable processing step, or may be used after additional electrodeposition coating, powder coating, or silk-screen printing (approximately at 130 to 160°C for 20 to 30 minutes) under the conventional conditions, according to applications.

[Example]

[Evaluation methods]

(1) Corrosion resistance

5 The surface-treated metal sheets obtained (resin-coated steel sheet) were subjected to Salt Spray Test of edge-sealed plate according to JIS Z2371, and the period until white rust appears in an amount of 1% was determined.

(Evaluation criteria)

10 ◎: White rust appeared after 240 hours or more

○: White rust appeared in the period of 120 to less than 240 hours

△: White rust appeared in the period of 72 to less than 120 hours

15 ×: White rust appeared within less than 72 hours

(2) Abrasion resistance

 The surface-treated metal sheets obtained (resin-coated steel sheet) were subjected to the vibration test according to Packaged-Goods Vibration -Test (JIS Z0232),
20 and the appearance of the samples after a particular time was evaluated according to the following criteria. The vibration test apparatus used is that manufactured by IDEX CO., LTD. (trade name: "BF-500UC").

(Evaluation criteria)

25 ◎: No damage on film

O: Some damage on film but none on galvanized surface

△: Visually observable damage on galvanized surface

×: Significant damage on galvanized surface

(3) Coating property

5 A melamine alkyd paint (Amilac #1000, manufactured by
Kansai Paint Co., Ltd.) was spray-applied onto the surface-
treated metal sheet obtained (resin-coated steel sheet) to
give a film thickness of about 20 μm after dried, and baked
at 130°C for 20 minutes. Thus, the post-coating was
10 carried out to give a film. Then, the sample was immersed
in boiling water for 1 hour, taken out and left for 1 hour
at room temperature, and then engraved with a cutter knife
to form 100, 1-mm squares on the surface. After the sample
was subjected to a tape-peeling test, the number of the
15 film-squares remaining unpeeled was counted, and the coated
film adhesiveness was evaluated as the following four ranks.
(Evaluation criteria)

◎: Residual ratio: 100%

O: Residual ratio: 90% or more and less than 100%

20 △: Residual ratio: 80% or more and less than 90%

×: Residual ratio: 70% or more and less than 80%

(4) Conductivity

The surface resistance was measured at ten points on
the surface-treated metal sheet obtained (resin-coated
25 steel sheet) by using a surface resistance meter (Loresta

EP, 4-probe type, manufactured by Dia Instrument, Co., Ltd.).

(Evaluation criteria)

◎: 1 mΩ or less, and overload 0 time/ten sites

5 ○: 1 mΩ or less, and overload 1 time/ten sites

△: 1 mΩ or less, and overload 2 times/ten sites

×: 1 mΩ or more, and overload 5 times/ten sites

(5) Alkaline degreasing resistance

A sample was immersed in a solution of an alkaline
 10 degreasing agent (CL-N364S, manufactured by Nihon
 Parkerizing Co., Ltd.) at concentration of 20 g/l
 previously adjusted to liquid temperature of 60°C for 2
 minutes; the sample was then taken out, washed with water,
 dried and subjected to Salt Water-Spraying test according
 15 to JIS Z2371; and a period until white rust appears in the
 amount of 1% was determined to be ranked as follows.

(Evaluation criteria)

◎: 168 hours or more

○: 96 hours or more and less than 168 hours

20 △: 48 hours or more and less than 96 hours

×: Less than 48 hours

[Preparation of the aqueous carboxyl group-containing
 polyurethane resin solution]

25 In a reaction vessel having a capacity of 0.8 L

equipped with a stirrer, a thermometer, and a temperature controller, placed were 60 g of polytetramethylene ether glycol (average molecular weight: 1,000) manufactured by Hodogaya Chemical Co., Ltd. as a polyol component, 14 g of 1,4-cyclohexanedimethanol, and 20 g of dimethylol propionic acid, and additionally 30.0 g of N-methylpyrrolidone as a reaction solvent. Tolyene diisocyanate (hereinafter, referred to simply as "TDI") (104g) as an isocyanate component was added thereto, and the mixture was heated to 80 to 85°C and left for 5 hours to allow the reaction to proceed. The prepolymer obtained had a NCO content of 8.9%. Then, after neutralization by addition of 15 g of triethylamine and addition of a mixed aqueous solution of 16 g of ethylenediamine and 480 g of water, the mixture was emulsified at 50°C for 4 hours to allow a chain-extending reaction to proceed, to give an aqueous polyurethane resin dispersion (nonvolatile resin component: 29.1%, and acid value: 41.4).

[Preparation of the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion]

In an emulsifying autoclave equipped with a stirrer, a thermometer, and a temperature controller having a capacity of 0.8 L, placed were 626 parts by mass of water, 160 parts by mass of ethylene-acrylic acid copolymer (acrylic acid

20: % by mass, melt index (MI): 300); then, triethylamine and sodium hydroxide were added respectively in amounts of 40 mole % and 15 mole % respectively with respect to 1 mole of the carboxyl group in the ethylene-acrylic acid

5 copolymer; and the mixture was stirred at high speed in an environment at 150°C and 5Pa and then cooled to 40°C, to give an aqueous ethylene-acrylic acid copolymer dispersion. Then, to the aqueous dispersion added was 4,4'-

10 bis(ethyleneiminocarbonyamino)diphenylmethane (Chemitite® DZ-22E, manufactured by Nippon Shokubai Co., Ltd.) as a crosslinking agent in an amount of 5 parts by mass with respect to 100 parts by mass of the nonvolatile resin component of the ethylene-acrylic acid copolymer.

15 [Preparation of aqueous resin solution and surface-treated metal sheet]

(Example 1)

The aqueous carboxyl group-containing urethane resin solution and the aqueous ethylene-acrylic acid copolymer
20 dispersion obtained above, and the silica particles (Snowtex XS, manufactured by Nissan Chemical Industries Ltd., average particle size: 4 to 6 nm) were compounded at the compounding ratio shown in Table 1 in a total amount of 100 parts by mass as nonvolatile components, and γ -
25 glycidoxypropyltrimethoxysilane (KBM403, manufactured by

Shin-Etsu Chemical Co., Ltd.) was added as a silane-coupling agent in an amount of 15 parts by mass with respect to the total of 100 parts by mass, to give an aqueous resin solution.

5 The aqueous resin solution was applied onto the surface of a pure zinc electroplated steel sheet with a squeezing roll and dried at a sheet temperature of 90°C, to give a surface-treated metal sheet (resin-coated steel sheet) with a resin film formed in an adhesion amount of
10 0.4 g/m². Corrosion resistance, conductivity, abrasion resistance, alkaline degreasing resistance, coating property (film adhesiveness), and others of the resin-coated steel sheet were evaluated, and the results are summarized in Table 1.

15 The pure zinc electroplated steel sheet used was a non-chromate-treated electroplated steel sheet (Zn adhesion amount: 20 g/m², and thickness: 0.8 mm).

Table 1

Steel sheet No.	Compounding ratio (parts by mass) of nonvolatile resin silica particles		Compounding ratio of resin (parts by mass)		Corrosion resistance	Conductivity	Abrasion resistance	Alkaline degreasing resistance	Coating property (film adhesiveness)
	Resin component	Silica	PU	EC					
steel sheet 1	5	95	5	1	○	◎	◎	○	○
steel sheet 2	10	90	5	1	○	◎	◎	○	○
steel sheet 3	15	85	5	1	○	◎	◎	○	○
steel sheet 4	20	80	5	1	○	◎	◎	○	○
steel sheet 5	25	75	5	1	◎	◎	◎	○	◎
steel sheet 6	30	70	5	1	◎	◎	◎	◎	◎
steel sheet 7	35	65	5	1	◎	◎	◎	◎	◎
steel sheet 8	40	50	5	1	◎	○	○	◎	◎
steel sheet 9	45	55	5	1	◎	○	○	◎	◎
steel sheet 10	30	70	9	1	○	◎	◎	○	○
steel sheet 11	30	70	6.5	1	◎	◎	◎	◎	◎
steel sheet 12	30	70	4	1	◎	◎	◎	◎	◎
steel sheet 13	30	70	3.3	1	◎	◎	◎	◎	◎
steel sheet 14	30	70	2	1	○	◎	◎	○	◎
steel sheet 15	4	96	5	1	△	◎	◎	△	△
steel sheet 16	3	97	5	1	x	◎	◎	x	△
steel sheet 17	47	53	5	1	◎	△	△	◎	◎
steel sheet 18	50	50	5	1	◎	x	x	◎	◎
steel sheet 19	30	70	14	1	x	◎	△	x	△
steel sheet 20	30	70	29	1	x	◎	△	x	x
steel sheet 21	30	70	1	1	x	◎	x	x	x

Steel sheets Nos. 1 to 14 are surface-treated metal sheets with a resin film prepared with an aqueous resin solution; the aqueous resin solution contains the aqueous carboxyl group-containing polyurethane resin solution and the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion in an amount of 5 to 45 parts by mass as nonvolatile resin components, and silica particle in an amount of 55 to 95 parts by mass, in the total amount of 100 parts by mass, and additionally the silane-coupling agent in an amount of 5 to 25 parts by mass with respect to the total amount of 100 parts by mass; and the compounding ratios of the nonvolatile resin component in the aqueous polyurethane resin solution (PU) to the nonvolatile resin component in the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion (EC) (PU:EC) were 9:1 to 2:1 by mass. All of these steel sheets are superior in corrosion resistance, conductivity, abrasion resistance, alkaline degreasing resistance, and coating property (film adhesiveness). Steel sheets Nos. 15 and 16, which contain the nonvolatile resin components in an amount of less than 5 parts by mass, showed deterioration in corrosion resistance, alkaline degreasing resistance and film adhesiveness. Steel sheets Nos. 17 and 18, which contain the nonvolatile resin components in an amount of more than 45 parts by mass, showed deterioration in conductivity and

abrasion resistance. Steel sheets Nos.19 and 20, which contain an excessive ratio of the carboxyl group-containing polyurethane resin to the ethylene-unsaturated carboxylic acid copolymers in the nonvolatile resin components, showed deterioration in corrosion resistance, abrasion resistance, alkaline degreasing resistance, and film adhesiveness.

Steel sheet No.21, which has an excessively low ratio of the carboxyl group-containing polyurethane resin to the ethylene-unsaturated carboxylic acid copolymers in the nonvolatile resin components, showed also deterioration in corrosion resistance, abrasion resistance, alkaline degreasing resistance, and film adhesiveness.

(Example 2)

The aqueous carboxyl group-containing polyurethane resin solution and the aqueous ethylene-acrylic acid copolymer dispersion obtained above, and the silica particles were compounded respectively in amounts of 30 parts by mass as nonvolatile resin components and 70 parts by mass as silica particles in a total amount of 100 parts by mass, and the silane-coupling agent γ -glycidoxypyrpyltrimethoxysilane (KBM403, manufactured by Shin-Etsu Chemical Co., Ltd.) was added additionally in an amount of 0 to 30 parts by mass with respect to the total 100 parts by mass, to give an aqueous resin solution. The

silica particles used were Snowtex XS manufactured by Nissan Chemical Industries Ltd. (average particle size: 4 to 6 nm), and the compounding ratio of the carboxyl group-containing polyurethane resin (PC) to the ethylene-unsaturated carboxylic acid copolymer (EC) in nonvolatile resin component (PC:EC) was 5:1.

The aqueous resin solution was applied onto the surface of a pure zinc electroplated steel sheet surface with a squeezing roll and dried at a sheet temperature of 90°C, to give a surface-treated metal sheet (resin-coated steel sheet) with a resin film formed in an adhesion amount of 0.4 g/m². The composition of the resin film, corrosion resistance, conductivity, abrasion resistance, alkaline degreasing resistance, film adhesiveness, and others of the resin-coated steel sheet obtained were evaluated and the results are summarized in Table 2.

The pure zinc electroplated steel sheet used was a non-chromate-treated electroplated steel sheet (Zn adhesion amount: 20 g/m², and thickness: 0.8 mm).

Table 2

Steel sheet No.	Content of silane-coupling agent (parts by mass)	stability of aqueous solution for forming film	Corrosion resistance	Conductivity	Abrasion resistance	Alkaline degreasing resistance	Coating property (film adhesiveness)
steel sheet 22	5	○	○	◎	○	○	○
steel sheet 23	7	○	◎	◎	○	○	◎
steel sheet 24	10	○	◎	◎	◎	◎	◎
steel sheet 25	15	○	◎	◎	◎	◎	◎
steel sheet 26	20	○	◎	◎	○	○	○
steel sheet 27	25	○	○	◎	○	○	○
steel sheet 28	0	○	x	◎	x	x	x
steel sheet 29	30	○	○	◎	x	△	x

As clearly shown in Table 2, it was possible to produce a surface-treated metal sheet superior in corrosion resistance, conductivity, abrasion resistance, alkaline degreasing resistance, and film adhesiveness, by preparing an aqueous resin solution for use in the present invention by adding the aqueous carboxyl group-containing polyurethane resin solution and the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion in a total amount of 5 to 45 parts by mass as nonvolatile resin components, and the silica particles in an amount of 55 to 95 parts by mass, in a total amount of 100 parts by mass, and additionally the silane-coupling agent in an amount of 5 to 25 parts by mass with respect to the total amount of 100 parts by mass.

(Example 3)

An aqueous resin solution was prepared by mixing the polyurethane resin aqueous solution and the aqueous ethylene-acrylic acid copolymer dispersion obtained above, the silica particles having an average particle size of 4 to 100 nm (Snowtex series, manufactured by Nissan Chemical Industries Ltd.), respectively in a total amount of 30 parts by mass as nonvolatile resin components and in an amount of 70 parts by mass as silica particles, in a total amount of 100 parts by mass, and additionally the silane-

coupling agent γ -glycidoxypyrtrimethoxysilane
(manufactured by Shin-Etsu Chemical Co., Ltd. KBM403) in
an amount of 15 parts by mass with respect to the total 100
parts by mass. The ratio of the carboxyl group-containing
5 polyurethane resin (PC) to the ethylene-unsaturated
carboxylic acid copolymer (EC) in nonvolatile resin
component (PC:EC) was 5:1 by mass.

The aqueous resin solution was applied onto the
surface of a pure zinc electroplated steel sheet surface
10 with a squeezing roll and dried at a sheet temperature of
90°C, to give a surface-treated metal sheet (resin-coated
steel sheet) with a resin film formed in an adhesion amount
of 0.4 g/m². The composition of the resin film, corrosion
resistance, conductivity, abrasion resistance, alkaline
15 degreasing resistance, film adhesiveness, and others of the
resin-coated steel sheet obtained were evaluated and the
results are summarized in Table 3.

The pure zinc electroplated steel sheet used was a
non-chromate-treated electroplated steel sheet (Zn adhesion
20 amount: 20 g/m², and thickness: 0.8 mm).

Table 3

Steel sheet No.	Average particle size of silica particles (nm)	Corrosion resistance	Conductivity	Abrasion resistance	Alkaline degreasing resistance	Coating property (film adhesiveness)
steel sheet 30	4~6	◎	◎	◎	◎	◎
steel sheet 31	10~20	◎	◎	○	○	◎
steel sheet 32	40~60	○	x	x	x	x
steel sheet 33	70~100	△	x	x	x	x

As clearly shown by the results in Table 3, it was possible to produce a surface-treated metal sheet superior in corrosion resistance, conductivity, abrasion resistance, alkaline degreasing resistance, and film adhesiveness, by using the silica particle having an average particle size of 4 to 20 nm.

10 (Example 4)

An aqueous resin solution was prepared by mixing the polyurethane resin aqueous solution and the aqueous ethylene-acrylic acid copolymer dispersion obtained above, and the silica particles (manufactured by Nissan Chemical Industries Ltd. Snowtex X5, average particle size 4 to 6 nm) respectively in amounts of 30 parts by mass as nonvolatile resin components and 70 parts by mass as silica particles in a total amount of 100 parts by mass, and additionally the silane-coupling agent shown in Table 4 in an amount of 15 parts by mass with respect to the total 100 parts by mass. The ratio of the carboxyl group-containing

polyurethane resin (PC) to the ethylene-unsaturated carboxylic acid copolymer (EC) in nonvolatile resin component (PC:EC) was 5:1 by mass.

5 The aqueous resin solution was applied onto the surface of the pure zinc electroplated steel sheet surface with a squeezing roll and dried at a sheet temperature of 90°C, to give a surface-treated metal sheet (resin-coated steel sheet) with a resin film formed in an adhesion amount of 0.4 g/m². The composition of the resin film, corrosion
10 resistance, conductivity, abrasion resistance, alkaline degreasing resistance, film adhesiveness, and others of the resin-coated steel sheet obtained were evaluated and the results are summarized in Table 4.

The pure zinc electroplated steel sheet used was the
15 non-chromate-treated electroplated steel sheet (Zn adhesion amount: 20 g/m², and thickness: 0.8 mm).

Table 4

Steel sheet No.	Kind of silane-coupling agent	stability of aqueous solution for forming film	Corrosion resistance	Conductivity	Abrasion resistance	Alkaline degreasing resistance	Coating property (film adhesiveness)
steel sheet 34	γ -glycidoxypolytrimethoxysilane	O	◎	◎	◎	◎	◎
steel sheet 35	γ -glycidoxypoly(methyldiethoxysilane	O	O	◎	◎	O	◎
steel sheet 36	vinyltris(β -methoxyethoxy)silane	O	O	◎	◎	O	◎
steel sheet 37	γ -aminopropyltriethoxysilane	Gelation after one day from preparation	—	—	—	—	—
steel sheet 38	γ -mercaptopropyltrimethoxysilane	Gelation after two days from preparation	—	—	—	—	—
steel sheet 39	γ -(methacryloxypropyl)trimethoxysilane	Gelation after one day from preparation	—	—	—	—	—

As clearly shown by the results in Table 4, it was possible to prepare an aqueous resin solution for forming a film superior in stability and thus to prepare a surface-treated metal sheet superior in corrosion resistance, abrasion resistance, and film adhesiveness by using the silane-coupling agent having a glycidyl group at the terminal.

(Example 5)

10 An aqueous resin solution was prepared by mixing the polyurethane resin aqueous solution and the aqueous ethylene-acrylic acid copolymer dispersion obtained above and the silica particles (Snowtex XS, manufactured by Nissan Chemical Industries Ltd.) respectively in amounts of 15 30 parts by mass as nonvolatile resin component and 70 parts by mass as silica particles in a total amount of 100 parts by mass and additionally the silane-coupling agent γ -glycidoxypropyltrimethoxysilane (KBM403, manufactured by Shin-Etsu Chemical Co., Ltd.) in an amount of 15 parts by 20 mass with respect to the total 100 parts by mass. The ratio of the carboxyl group-containing polyurethane resin (PC) to the ethylene-unsaturated carboxylic acid copolymer (EC) in nonvolatile resin component (PC:EC) was 5:1 by mass.

The aqueous resin solution was applied onto the 25 surface of the pure zinc electroplated steel sheet surface

with a squeezing roll under various squeezing pressure and dried at a sheet temperature of 90°C, to give a surface-treated metal sheet (resin-coated steel sheets) with a resin film formed in an adhesion amount of 0.05 to 2.0 g/m².

5 The composition of the resin film, corrosion resistance, conductivity, abrasion resistance, alkaline degreasing resistance, film adhesiveness, and others of the resin-coated steel sheet obtained were evaluated and the results are summarized in Table 5.

10 The pure zinc electroplated steel sheet used was the non-chromate-treated electroplated steel sheet (Zn adhesion amount: 20 g/m², and thickness: 0.8 mm).

Table 5

Steel sheet No.	Adhesion amount (g/m ²)	Corrosion resistance	Conductivity	Abrasion resistance	Alkaline degreasing resistance	Coating property (film adhesiveness)
steel sheet 40	0.05	○	◎	○	○	○
steel sheet 41	0.1	○	◎	○	○	◎
steel sheet 42	0.3	◎	◎	◎	◎	◎
steel sheet 43	0.5	◎	◎	◎	◎	◎
steel sheet 44	0.8	◎	○	◎	◎	◎
steel sheet 45	0.01	x	◎	x	x	x
steel sheet 46	1.5	◎	x	○	◎	x
steel sheet 47	2.0	◎	x	△	◎	x

15

As clearly shown in Table 5, it was possible to prepare a surface-treated metal sheet superior in corrosion resistance, conductivity, abrasion resistance, and film

adhesiveness by controlling an adhesion amount of the resin film on a metal sheet in the range of 0.05 to 1 g/m².

CLAIMS

1. A surface-treated metal sheet with a resin film
5 coated thereon obtained from an aqueous resin solution;
the aqueous resin solution, comprising:

an aqueous carboxyl group-containing polyurethane
resin solution and an aqueous ethylene-unsaturated
carboxylic acid copolymer dispersion in an amount of 5 to
10 45 parts by mass as nonvolatile resin components, silica
particles having an average particle size of 4 to 20 nm in
an amount of 55 to 95 parts by mass,

a total amount of the resin solutions and the silica
particles being 100 parts by mass; and

15 a silane coupling agent in an amount of 5 to 25 parts
by mass with respect to the total amount of the resin
solutions and the silica particles of 100 parts by mass;

the compounding ratio of the nonvolatile resin
component in the aqueous polyurethane resin solution (PU)
20 to the nonvolatile resin component in the aqueous ethylene-
unsaturated carboxylic acid copolymer dispersion (EC) being
9:1 to 2:1.

2. The surface-treated metal sheet according to claim
1, wherein the carboxyl group-containing polyurethane resin
25 is a resin prepared in the chain-extending reaction of a

urethane prepolymer with a chain extender,

a polyisocyanate component constituting the urethane prepolymer is at least one compound selected from the group consisting of tolylene diisocyanate, diphenylmethane

5 diisocyanate, and dicyclohexylmethane diisocyanate, and

polyol components constituting the urethane prepolymer include at least 1,4-cyclohexanedimethanol, a polyether polyol, and a polyol containing a carboxyl group.

3. The surface-treated metal sheet according to claim
10 2, wherein the chain extender is ethylenediamine or hydrazine.

4. The surface-treated metal sheet according to claim 1, wherein a mass ratio of 1,4-cyclohexanedimethanol to the polyether polyol is 1:1 to 1:19.

15 5. The surface-treated metal sheet according to claim 2, wherein the polyether polyol is polyoxypropylene glycol or polytetramethylene ether glycol.

6. The surface-treated metal sheet according to claim 1, wherein an acid value of the carboxyl group-containing
20 polyurethane resin is 10 to 60 mg-KOH/g.

7. The surface-treated metal sheet according to claim 1, wherein the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion contains, in addition to the ethylene-unsaturated carboxylic acid copolymer, an amine having a
25 boiling point of 100°C or lower in an amount equivalent to

0.2 to 0.8 mole with respect to 1 mole of the carboxyl group in the ethylene-unsaturated carboxylic acid copolymer, and a monovalent metal compound in an amount equivalent to 0.02 to 0.4 mole with respect to 1 mole of the carboxyl group in the ethylene-unsaturated carboxylic acid copolymer.

8. The surface-treated metal sheet according to claim 1, wherein the ethylene-unsaturated carboxylic acid copolymer is a copolymer containing an unsaturated carboxylic acid component in an amount of 10 to 40 % by mass.

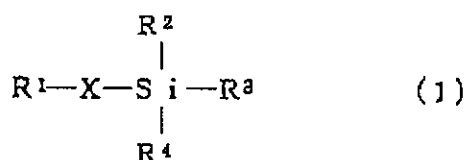
9. The surface-treated metal sheet according to claim 7, wherein the amine having the boiling point of 100°C or lower is triethylamine.

10. The surface-treated metal sheet according to claim 1, wherein the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion further comprises a crosslinking agent having two or more functional groups reactive with a carboxyl group in an amount of 1 to 20 parts by mass with respect to 100 parts by mass of the nonvolatile resin components (EC) in the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion.

11. The surface-treated metal sheet according to claim 1, wherein the aqueous ethylene-unsaturated carboxylic acid copolymer dispersion does not substantially contain an amine having a boiling point of over 100°C or

ammonia.

12. The surface-treated metal sheet according to claim 1, wherein the silane-coupling agent is a silane-coupling agent represented by the following chemical formula (1):



in which R^1 represents a glycidoxo group, R^2 and R^3 represent respectively a lower alkoxy group, R^4 represents a lower alkoxy or alkyl group, and X represents a lower alkylene group.

13. The surface-treated metal sheet according to claim 1, wherein an amount of the resin film adhered is 0.05 to 1 g/m² after drying.