

RESIN-COATED METAL SHEET AND MANUFACTURING METHOD THEREOF

BACKGROUND OF THE INVENTION

The present invention relates to a resin-coated metal sheet excellent in corrosion resistance which is preferably employable for use in household electrics, construction materials, or the like, and a manufacturing method thereof.

Conventionally, as the metal sheets employable for use in household electronics and construction materials, other than aluminum sheets and stainless steel sheets, surface treated steel sheets such as electrogalvanized steel sheets and hot-dip galvanized steel sheets have found a wide range of uses. Out of these, the galvanized type surface-treated steel sheets have been conventionally subjected to a chromate treatment or a phosphate treatment, and widely used for various structural components of acoustic instruments, computer components, and the bottom plates of microwave ovens, including predominantly household electronics. However, in recent years, the level of the users' needs for these surface-treated steel sheets has become increasingly higher, leading up to a demand for various film performances.

For example, when the surface-treated steel sheets are used in the bare form, they are required to have the corrosion resistance, the grounding property, the anti-fingerprint property such that fingerprints are less conspicuous even when attached thereon, the chemical resistance, the contamination resistance, and the like against an alkali, a solvent, or the

like. Whereas, when the steel sheets are press formed or blanked, they are required to have the lubricity, the flaw resistance, the drawability, the die abrasion resistance, the punchability, the blackening resistance of the forming sliding surface, and the oil resistance against a press forming oil / a quick drying oil, or the like.

In order to satisfy such requirements for characteristics, for example, Japanese Laid-Open Patent Publication No. 6-246229 discloses an organic composite-coated steel sheet including, on a chromated layer, a resin film in which 60 to 80 % of the carboxyl groups in an ethylenic ionomer have been neutralized with sodium ions. Whereas, Japanese Patent No. 2759620 discloses a resin-coated metal sheet including a film resulting from a composition containing a polyolefin copolymer resin emulsion intermolecularly associated through ion clusters and an organic compound having an aziridinyl group formed on a metal sheet surface. The Japanese Patent No. 2759620 describes to the effect that the metal sheet has been preferably chromated.

However, in recent years, due to a move toward chrome-free (non-chromated) products for the global environmental conservation, and the like, the resin films have become required to have higher corrosion resistance than ever before.

As described above, the resin films each to be stacked on a chrome-free metal sheet also have become required to have the corrosion resistance of the same level as with the resin films each coated on a chromated metal sheet. Under such circumstances, the present inventors have consistently

conducted a continuous study even after the application of Japanese Patent No. 2759620. The resin film described in Japanese Patent No. 2759620 shows a somewhat excellent corrosion resistance also for a chrome-free sheet. However, for example, after removing a lubricating oil applied during press forming in a degreasing step, the resin film is unfavorably degraded due to an alkali treatment, resulting in a reduction of the corrosion resistance. Whereas, a resin film is coated on a chrome-free metal sheet, and then, an adhesive tape is attached on the resin film surface, and allowed to stand for a long time. Then, the adhesive tape is peeled off therefrom, so that even the resin film is also peeled off. Thus, there is such a problem of shortage of tape peeling resistance (adhesion between the metal sheet and the resin film).

SUMMARY OF THE INVENTION

Under such circumstances, it is therefore an object of the present invention to provide a resin-coated metal sheet having a resin film excellent in various characteristics such as coatability (film adhesion ability on the resin-coated metal sheet), lubricity, formability, and grounding property as given characteristics, and further excellent in corrosion resistance after a degreasing step and tape peeling resistance.

One aspect of the present invention resides in a resin-coated metal sheet which includes: a metal sheet; and a resin film coated on the surface of the metal sheet, the resin film being obtained from an emulsion composition, wherein the

emulsion composition includes: an ethylene / unsaturated carboxylic acid copolymer as a main component; an amine in an amount equal to 0.2 to 0.8 mol per mole of the carboxyl groups contained in the ethylene / unsaturated carboxylic acid copolymer, the amine having a boiling point of 100 °C or less; a monovalent metal compound in an amount equal to 0.02 to 0.4 mol per mole of the carboxyl groups contained in the ethylene / unsaturated carboxylic acid copolymer; and a crosslinking agent in an amount of 1 to 20 mass% per 100 mass% of the solid content of the emulsion composition, the crosslinking agent having two or more functional groups capable of reacting with the carboxylic groups contained in the ethylene / unsaturated carboxylic acid copolymer, and wherein the emulsion composition does not substantially contain an amine having a boiling point of more than 100 °C, and does not substantially contain ammonia.

According to the aspect, in the ethylene / unsaturated carboxylic acid copolymer, it is preferable that 10 to 40 mass% of the unsaturated carboxylic acid has been copolymerized, and it is most preferable that 15 to 25 mass% of the unsaturated carboxylic acid has been copolymerized. It is also a preferred embodiment of the present invention that the amine having a boiling point of 100 °C or less is triethylamine.

According to the aspect, it is preferable that silica particles with an average particle diameter of 1 to 200 nm are contained in an amount of 5 to 40 mass% in every 100 mass% of the solid content of the emulsion composition. It is also preferable that a spherical polyethylene wax is contained in

an amount of 0.5 to 20 mass%. This results in a resin film which can have various characteristics such as coatability, lubricity, formability, and grounding property, and further, which is also excellent in corrosion resistance after a degreasing step and tape peeling resistance. Incidentally, the resin-coated metal sheet of the present invention shows an excellent corrosion resistance even when a chromate film is not formed.

According to the aspect of the present invention, in the resin-coated metal sheet, by using a specific amount of an amine with a boiling point of 100 °C or less and a metal compound in combination, the ethylene / unsaturated carboxylic acid copolymer is neutralized, resulting in an emulsion. Accordingly, it is possible to obtain an emulsion composition having a very small particle diameter. Therefore, it is possible to obtain a resin-coated metal sheet coated with a film excellent in various characteristics such as coatability, lubricity, formability, and grounding property, and further, excellent in corrosion resistance after a degreasing step and tape peeling resistance.

Another aspect of the present invention resides in a method for manufacturing the resin-coated metal sheet which includes the steps of: preparing the emulsion composition; coating the emulsion composition on the metal sheet; and heating and drying the metal sheet coated with the emulsion composition.

DESCRIPTION OF PREFERRED EMBODIMENTS

A resin-coated metal sheet of the present invention

includes a resin film formed from a specific emulsion composition on at least one side of a metal sheet. The metal sheet has no particular restriction. For example, mention may be made of a zinc or zinc system plated steel sheet, an aluminum sheet, an aluminum system alloy sheet, or a titanium sheet. Further, it is also acceptable that the metal sheet is subjected to a known rust-proofing surface treatment such as a phosphate treatment, or other surface treatments, and that a resin film is formed thereon. From the viewpoint of the environmental problem, it is preferable that the sheet is not subjected to a chromate treatment.

The emulsion composition for use in the present invention for the formation of the resin film contains an ethylene / unsaturated carboxylic acid copolymer (including the neutralized state) as a main component, an amine with a boiling point of 100 °C or less in an amount equal to 0.2 to 0.8 mol (20 to 80 mol%) per mole of the carboxyl groups contained in the ethylene / unsaturated carboxylic acid copolymer, and a monovalent metal compound in an amount equal to 0.02 to 0.4 mol (2 to 40 mol%) per mole of the carboxyl groups contained in the ethylene / unsaturated carboxylic acid copolymer, and in addition, a crosslinking agent having two or more functional groups capable of reacting with carboxylic groups in an amount of 0.5 to 20 mass% per 100 mass% of the solid content of the emulsion composition, and does not substantially contain an amine with a boiling point of more than 100 °C and ammonia.

The ethylene / unsaturated carboxylic acid copolymer is

the copolymer of ethylene and an ethylenic unsaturated carboxylic acid. As the unsaturated carboxylic acid, mention may be made of (meth)acrylic acid, crotonic acid, isocrotonic acid, maleic acid, fumaric acid, itaconic acid, or the like. By polymerizing one or more of these and ethylene by a known high-temperature high-pressure polymerization method or the like, it is possible to obtain the copolymer. The copolymer is most preferably a random copolymer. However, it may also be a block copolymer or such a copolymer as that grafted at the unsaturated carboxylic acid moiety. Incidentally, the unsaturated carboxylic acid is preferably (meth)acrylic acid. Further, an olefinic monomer such as propylene or 1-butene may also be used in place of a part of the ethylene. Still further, other known vinyl type monomers may also be copolymerized partially (in an amount of about 10 mass% or less) so long as the object of the present invention is not impaired.

As for the copolymerization ratio of the unsaturated carboxylic acid to ethylene, the unsaturated carboxylic acid is preferably in an amount of 10 to 40 mass% when the total amount of monomers is taken as 100 mass%. When the amount of the unsaturated carboxylic acid is less than 10 mass%, the amount of the carboxyl groups serving as the base point for the intermolecular association through ion clusters, or a crosslinking point with a crosslinking agent is small. Accordingly, unfavorably, the film strength effects are not exerted, so that the tape peeling resistance and the corrosion resistance after the degreasing step may be insufficient. In

addition, the emulsification stability of the emulsion composition is inferior. The more preferred lower limit of the amount of the unsaturated carboxylic acid is 15 mass%. On the other hand, when the amount of the unsaturated carboxylic acid exceeds 40 mass%, the corrosion resistance and the water resistance of the resin film are inferior. Accordingly, unfavorably, the corrosion resistance after the degreasing step is reduced likewise. The more preferred upper limit is 25 mass%.

The ethylene / unsaturated carboxylic acid copolymer has carboxyl groups. Therefore, it can be neutralized with an organic base or metal ions, thereby to be made into an emulsion (made into a water dispersion). In the present invention, an amine with a boiling point of 100 °C or less is used as the organic base. The amines with a boiling point of more than 100 °C tend to remain on the steel sheet when the resin-coated film is dried, resulting in an increase in water absorption property of the resin-coated film. This causes a reduction of the corrosion resistance. For this reason, the amines with a boiling point of more than 100 °C are not included in the emulsion compositions to be used for the film formation in the present invention. Further, ammonia is not also included because the addition effect of ammonia has not been observed. As the boiling point, the boiling point under an atmospheric pressure is adopted.

Specific examples of the amines with a boiling point of 100 °C or less may include: tertiary amines such as triethylamine, N,N-dimethylbutylamine, N,N-dimethylallylamine, N-

methyldipyrrolidine, tetramethyldiaminomethane, and trimethylamine; secondary amines such as N-methylethylamine, diisopropylamine, and diethylamine; and primary amines such as propylamine, t-butylamine, sec-butylamine, isobutylamine, 1,2-dibutylpropylamine, and 3-pentylamine. These may be used alone, or in mixture of two or more thereof. Out of these, the tertiary amines are preferred, and triethylamine is most preferred.

The amount of an amine with a boiling point of 100 °C or less is set to fall within a range of 0.2 to 0.8 mol (20 to 80 mol%) per mole of the carboxylic groups in the ethylene / unsaturated carboxylic acid copolymer. This is because the amount within this range results in good corrosion resistance and tape peeling resistance. When the amount of the amine with a boiling point of 100 °C or less is smaller than 0.2 mol, the particle diameter of the resin particles in the emulsion is large. For this reason, conceivably, the foregoing effects are not exerted. Whereas, when the amine with a boiling point of 100 °C or less is used in an amount of more than 0.8 mol, the emulsion composition may unfavorably be increased in viscosity, and gel. The more preferred upper limit of the amount of the amine is 0.6 mol, and more preferably 0.5 mol. The more preferred lower limit of the amount of the amine is 0.3 mol.

In the present invention, monovalent metal ions are also used for neutralization. This is effective for the improvements of the solvent resistance and the film hardness. Therefore, a monovalent metal compound has been added to the

emulsion composition. The monovalent metal compound preferably contains one or two or more metals selected from sodium, potassium, and lithium. The hydroxides, the carboxides, or the oxides of these metals are preferred. Out of these, NaOH, KOH, LiOH, and the like are preferred, and NaOH is most preferred because it has the best performances. Further, for the di- or more-valent metal compounds, the effects produced by the addition thereof are not observed. Therefore, the emulsion composition to be used for the film formation in the present invention does not contain a di- or more-valent metal compound for acting as a reaction partner of the ethylene / unsaturated carboxylic acid copolymer.

The amount of the monovalent metal compound is set to fall within a range of 0.02 to 0.4 mol (2 to 40 mol%) per mole of the carboxyl groups in the ethylene / unsaturated carboxylic acid copolymer. When the amount of the metal compound is less than 0.02 mol, the emulsification stability becomes insufficient. However, when the amount exceeds 0.4 mol, the hygroscopic property of the resulting resin film (particularly, to an alkali solution) is increased, unfavorably resulting in deterioration of the corrosion resistance after the degreasing step. The more preferred lower limit of the metal compound amount is 0.03 mol. The further preferred lower limit is 0.1 mol. The more preferred upper limit of the metal compound amount is 0.5 mol, and the further preferred upper limit is 0.2 mol.

The amine with a boiling point of 100 °C or less and the

monovalent metal compound are used in respective amounts preferably within the foregoing ranges. Both of these are used for neutralizing the carboxyl groups in the ethylene / unsaturated carboxylic acid copolymer, and emulsifying the copolymer. Therefore, when the total amount (neutralization amount) thereof is too large, unfavorably, the viscosity of the emulsion composition may rapidly increase and solidify, and in addition, excessive alkali component causes the deterioration of the corrosion resistance. Further, a large energy for volatilizing the excessive alkali component is required. However, when the neutralization amount is too small, unfavorably, the emulsifiability is also unfavorably inferior. Therefore, the total amount of the amine with a boiling point of 100 °C or less and the monovalent metal compound is preferably set to fall within a range of 0.3 to 1.0 mol per mol of the carboxyl groups in the ethylene / unsaturated carboxylic acid copolymer.

The emulsion composition for use in the present invention is formed by using an amine with a boiling point of 100 °C or less and the monovalent metal compound in combination for emulsification. As a result, the resin particles in the composition are present in an aqueous medium in very small fine particles (oil droplets) with a size of 5 to 50 nm with stability. This presumably implements the film forming property of the resulting resin film, the adhesion to the metal sheet, and the densification of the film, resulting in improvements of the corrosion resistance and the tape peeling resistance. The

aqueous medium may contain, other than water, a hydrophilic solvent such as alcohol or ether. Incidentally, the particle diameter of the resin particles in the emulsion can be measured by, for example, a laser diffraction method using a light scattering photometer (manufactured by OTSUKA ELECTRONICS Co., Ltd.).

In the neutralization step of the ethylene / unsaturated carboxylic acid copolymer with an amine with a boiling point of 100 °C or less and a monovalent metal compound (emulsification step), desirably, the amine with a boiling point of 100 °C or less and the monovalent metal compound are added to the copolymer roughly at the same time, or the amine with a boiling point of 100 °C or less is added first. This is because the post-addition of the amine with a boiling point of 100 °C or less may results in insufficient improvement effects of the corrosion resistance / tape peeling resistance, although the reason for this is uncertain.

The ethylene / unsaturated carboxylic acid copolymer having the carboxyl groups neutralized with the amine with a boiling point of 100 °C or less and the monovalent metal compound forms the intermolecular association through ion clusters (transformation into an ionomer), to form a resin film excellent in corrosion resistance / tape peeling resistance. However, in order to form a stronger film, it is desirable that polymer chains are crosslinked to each other through a chemical bond utilizing the reaction between functional groups. Under such circumstances, the emulsion composition of the present

invention contains a crosslinking agent having two or more functional groups capable of reacting with a carboxyl group as an essential component. The amount thereof is set to be 1 to 20 mass% of 100 mass% of the solid content in the emulsion composition. When the amount is less than 1 mass%, the effects of the crosslinking by the chemical bond become insufficient. Accordingly, the effects of improving the corrosion resistance / tape peeling resistance are less likely to be exerted. On the other hand, when the crosslinking agent is mixed in an amount of more than 20 mass%, the crosslinking density of the resin film excessively increases, resulting in an increase in hardness. Accordingly, the resin film becomes incapable of following the deformation upon press forming, which causes the formation of cracks. As a result, the corrosion resistance and the coatability are unfavorably reduced. The more preferred crosslinking agent amount is 5 to 10 mass% of 100 mass% of the solid content of the emulsion composition. Incidentally, for the ratio of the crosslinking agent amount to the ethylene / unsaturated carboxylic acid copolymer amount, the amount of crosslinking agent is desirably changed appropriately according to the amount of the carboxyl groups in the copolymer. In general, the amount of the crosslinking agent is preferably 0.5 to 50 parts by mass (more preferably 5 to 20 parts by mass) per 100 parts by mass of the copolymer.

The crosslinking agent having two or more functional groups capable of reacting with a carboxyl group per molecule has no particular restriction. However, preferred examples

thereof may include: glycidyl group-containing crosslinking agents including polyglycidyl ethers such as sorbitol polyglycidyl ether, (poly)glycerol polyglycidyl ether, pentaerythritol polyglycidyl ether, trimethylolpropane polyglycidyl ether, neopentyl glycol diglycidyl ether, and (poly)ethylene glycol diglycidyl ether, and polyglycidyl amines; bifunctional aziridine compounds such as 4,4'-bis(ethylenimine carbonylamino)diphenylmethane, N,N'-hexamethylene-1,6-bis(1-aziridine carboxyamide), N,N'-diphenylmethane-4,4'-bis(1-aziridine carboxyamide), and toluene bisaziridine carboxyamide; and aziridinyl group-containing crosslinking agents including tri- or more-functional aziridine compounds such as tri-1-aziridinyl phosphine oxide, tris[1-(2-methyl)aziridinyl]phosphine oxide, trimethylolpropane tris(β -aziridinyl propionate), tris-2,4,6-(1-aziridinyl)-1,3,5-triazine, and tetramethylpropane tetraaziridinyl propionate, or derivatives thereof. These may be used alone, or in combination of two or more thereof. Out of these, the aziridinyl group-containing crosslinking agent are preferred. Incidentally, a multifunctional aziridine and monofunctional aziridine (such as ethylenimine) may be used in combination.

The emulsion composition for use in the present invention may contain silica particles in an amount of 5 to 40 mass% on a solid content basis. This is effective for the improvement of the corrosion resistance, the coatability, the flaw resistance, or the like, and in addition, also effective for

the improvements of the corrosion resistance after degreasing and the tape peeling resistance. When the amount is less than 5 mass%, these effects are less likely to be exerted. However, when the amount exceeds 40 mass%, the proportion of the silica particles excessively increases, resulting in the reduction of the film forming property. Accordingly, cracks may occur in the resin film during a drying step, unfavorably resulting in the reduction of the corrosion resistance. Further, the silica particles serve as a polishing agent, which increases the lubricity of the film, resulting in the reduction of the coefficient of friction. This causes the abrasion of a die during forming, which shortens the life of the die. The more preferred lower limit of the amount of the silica particles is 20 mass%, and the upper limit thereof is 30 mass%.

In order to maximize the effects of the silica particles as described above, the average particle diameter of the silica particles preferably falls within a range of 1 to 200 nm. The corrosion resistance of the film is improved with a decrease in particle diameter of the silica particles. This is conceivably due to the following fact. The resin film is densified, and the adhesion is improved, which further enhances the corrosion resistance. From such a viewpoint, the silica particles desirably have a smaller particle diameter. However, when they are extremely minute particles, the foregoing effects are saturated. For this reason, the lower limit of the particle diameter is preferably 1 nm. On the other hand, when the particle diameter of the silica particles exceeds 200 nm, the

surface of the resin film is roughened. Accordingly, it is not possible to form a dense resin film. Further, the silica particles also serve as a polishing agent, unfavorably leading to a deterioration of the formability. In particular, when importance is attached to the corrosion resistance after degreasing, the average particle size of the silica particles is preferably set to fall within a range of 4 to 20 nm.

Such silica particles are generally known as colloidal silica. In the present invention, for example, "XS", "SS", "40", "N", "UP", and the like of "Snow Tex series" (colloidal silica manufactured by Nissan Chemical Industries, Ltd.) may be preferably used.

In the emulsion composition of the present invention, a wax may be contained in an amount in the range of 0.5 to 20 mass% on a solid content basis. The wax has effects of improving the lubricity and the flaw resistance of the resulting resin film. Further, it is preferably used for improving the drawability and the punchability required for press forming and blanking, the die abrasion resistance, and the blackening resistance of the sliding surface in forming, and providing excellent formability.

When the amount of the wax is less than 0.5 mass% on a solid content basis, the lubricity of the resulting resin film becomes insufficient. Accordingly, it is not possible to improve the flaw resistance and obtain satisfactory formability. On the other hand, when the amount exceeds 20 mass%, the resulting resin film has a sufficient lubricity, but it is

inferior in film adhesion (coatability) when it has been subjected to post-coating by electrodeposition, powder coating, or silk printing. Further, the corrosion resistance after degreasing and the tape peeling resistance are also deteriorated. This is conceivably due to the following fact. The wax is softened / liquefied, or bloomed by heating in the post-coating step or changes with time, to be concentrated at the interface between the resin film and the post-coated film or at the interface between the metal sheet and the resin film. Accordingly, the adhesion with the post-coated film or the adhesion with the metal sheet is deteriorated. The more preferred upper limit value is 10 mass%, and the still more preferred upper limit value is 5.0 mass%.

The wax has no particular restriction, and the usable waxes are natural waxes and synthetic waxes, and mixtures thereof, and the like. Examples of the usable natural waxes may include carnauba wax, rice wax, candelilla wax, and montan type wax, and derivatives thereof, mineral oil type wax, microcrystalline wax, paraffin wax, and the like, and in addition, derivatives obtained by adding carboxyl groups thereto.

As the synthetic waxes, mention may be made of polyethylene, polyethylene oxide, polypropylene, ethylene / propylene copolymer type wax, and oxidized waxes of copolymer wax of ethylene and other monomers. As this system, a wide variety of types also including a terpolymer type can be used according to the change in copolymerization partners. Further,

mention may be made of a maleic acid adduct wax, a fatty acid ester type, and the like. Further, waxes of fluorine type resins such as polytetrafluoroethylene, polyvinyl fluoride, polyvinylidene fluoride, and tetrafluoroethylene are also usable.

As the waxes, the ones with a softening point of 80 to 140 °C are preferably selected out of the ones exemplified above. When the softening point is less than 80 °C, the wax particles are softened / liquefied with an increase in die temperature upon press forming or blanking. Accordingly, at the sliding surface between the resin-coated steel sheet and the die, the liquid depletion phenomenon of the liquefied wax occurs, resulting in a reduction of the formability. This unfavorably causes scratches and the seizure with a die. Further, a blacked substance may be attached on the sliding portion to considerably deteriorate the product appearance. Further, also from the viewpoints of the corrosion resistance after a degreasing step and the tape peeling resistance, it has been shown that an excessively low softening point is not preferred. On the other hand, when the softening point exceeds 140 °C, the lubricity by the wax becomes insufficient. Accordingly, the punchability, the die abrasion resistance, the drawability, or the like shows no improvement. The corrosion resistance after degreasing also shows a tendency of being slightly reduced.

The wax is most preferably a spherical polyethylene wax. In that case, in order to maximize the effects of the spherical polyethylene wax, the particle diameter of the wax particles

is preferably 0.1 to 3 μm . When the particle diameter of the wax particles is less than 0.1 μm , it is difficult to remarkably improve the lubricity, the punchability, the die abrasion resistance, and the drawability. On the other hand, when the particle diameter of the wax particles exceeds 3 μm , it is difficult to uniformly disperse the wax particles in the emulsion composition in the form of fine particles. This may reduce the adhesion of the resin film to the metal sheet. The more preferred particle diameter of the spherical polyethylene wax is 0.3 to 1.0 μm .

As the foregoing spherical polyethylene waxes, there may be used, for example, commercially available products such as "DAIJETE-17" (manufactured by GOO Chemical Co., Ltd.), "KUE-1", "KUE-5", and "KUE-8" (manufactured by Sanyo Chemical Industries, Ltd.), "W-100", "W-200", "W-300", "W-400", "W-500", "W-640", "W-700", and the like of the "Chemipearl" series (manufactured by Mitsui Chemicals), and "Elepon E-20" (manufactured by NICCA Chemical Co., Ltd.).

The emulsion composition of the present invention preferably contains an ethylene / unsaturated carboxylic acid copolymer as an essential component, an amine with a boiling point of 100 °C or less, a monovalent metal compound, a crosslinking agent such as an aziridine compound, and further silica particles to be used, if required, a wax, and the like. The ethylene / unsaturated carboxylic acid copolymer is desirably contained in such an amount as to adjust the amount of the aziridine compound, the silica particles, the wax, and

the like so that the content of these resin components is 50 mass% or more of the solid content of the emulsion composition.

The emulsion composition is prepared in the following manner. First, the ethylene / unsaturated carboxylic acid copolymer as the essential component is charged together with an aqueous medium in, for example, a homogenizer device or the like, if required, under heating at 70 to 250 °C. The amine with a boiling point of 100 °C or less, and the monovalent metal compound are appropriately added in the form of an aqueous solution or the like (the amine with a boiling point of 100 °C or less is first added, or the amine with a boiling point of 100 °C or less and the monovalent metal compound are added roughly at the same time), with stirring at high shearing force. The silica particles, the wax, the crosslinking agent, and the like may be added at any stage. However, after the addition of the crosslinking agent, desirably, heat is not applied so as to prevent proceeding of the crosslinking reaction and gelation.

To the emulsion composition, a dilution solvent, an anti-skinning agent, a levelling agent, a defoaming agent, a penetrating agent, an emulsifier, a film forming aid, a coloring pigment, a thickener, a silane coupling agent, and other resins and the like may be appropriately added so long as the object of the present invention is not impaired.

A resin film may be formed on a metal sheet in the following manner. The emulsion composition is coated on one side surface or the opposite side surfaces of the metal sheet by a known

coating method, namely, a roll coater method, a spray method, a curtain flow coater method, or the like, and heated and dried. The heating and drying are preferably carried out at a temperature such that the crosslinking reaction between the crosslinking agent used and the carboxyl groups proceeds. Further, when a spherical polyethylene wax is used as a lubricant, keeping of the spherical shape results in more excellent formability in the subsequent forming step. Accordingly, drying is desirably carried out at a temperature in the range of 70 to 130 °C.

The amount (thickness) of the resin film coated is preferably 0.2 to 2.5 g/m² after drying. When the resin film is too thin, uniform coating onto the metal sheet is difficult, and the objective balanced film characteristics such as formability, corrosion resistance, and coatability are difficult to obtain. However, when the coating amount exceeds 2.5 g/m², the grounding property when the resin-coated metal sheet is used in a computer housing or the like, namely, the conductivity is unfavorably reduced. Further, the amount of the resin film to be peeled during press forming increases, so that deposition of the peeled film onto the die occurs. This inhibits the press forming, and is useless in terms of the manufacturing cost. The more preferred lower limit of the amount of the resin film to be deposited is 0.5 g/m², and the upper limit is 2.0 g/m².

By forming a resin film, it is possible to obtain the resin-coated metal sheet of the present invention. The

resin-coated metal sheet may be subjected to a forming steps, and used as it is according to the intended purpose. Alternatively, it may also be subjected to an electrodeposition / powder coating / silk printing under conventional conditions (at 130 to 160 °C for about 20 to 30 minutes) to be used.

Examples

Below, the present invention will be described by way of examples in more details. However, the following examples should not be construed as limiting the scope of the present invention, and it is understood that the present invention can be practiced with appropriate modification within a scope of the present invention, all of which is included in the present invention.

[Testing method]

The testing methods used in the following examples are as follows.

(1) Corrosion resistance after degreasing step

In 20 g/l of an alkali degreasing agent ("CL-N364S" manufactured by Nihon Parkerizing Co., Ltd.) adjusted to 60 °C, a resin-coated metal sheet was dipped for 2 minutes, and then pulled up, followed by water washing and drying. Then, a neutral salt spray test was carried out according to JIS Z2371, and the length of time until white rust is formed in an amount of 1 % was measured. The evaluation criteria are as follows: double circle: 240 hours or more, circle: less than 120 to 240 hours, triangle: less than 72 to 120 hours, and cross: less than 72 hours

(2) Tape peeling resistance

To the resin-coated metal sheet, an adhesive tape (filament tape No. 9510, manufactured by Sliontec Corp.; rubber type adhesive) was attached. The metal sheet was stored under a 40 °C, 98 %RH atmosphere in a constant-temperature constant-humidity device for 24 hours. Then, the tape was peeled off therefrom according to JIS K 5400 to determine the residual areal ratio of the film. The evaluation criteria are as follows: double circle: film remaining ratio 100 %, circle: film remaining ratio 90 to 99 %, triangle: film remaining ratio 89 to 70 %, and cross: film remaining ratio 70 % or less.

(3) Coefficient of dynamic friction

In order to evaluate the lubricity of the resin-coated metal sheet, the load due to sliding at a pressuring force of 5.4 MPa and a drawing speed of 300 mm/min was determined by means of a sliding test device, thereby to calculate the coefficient of dynamic friction

Experimental Example 1 (Effects of type and amounts of the organic base and the metal salt)

As the metal sheet material, an electrogalvanized steel sheet (Zn coating amount 20 g/m², sheet thickness 0.8 mm) was used.

In order to prepare an emulsion composition, into an autoclave, 626 parts by mass (which is hereinafter simply referred to as "parts") of water, and 160 parts of an ethylene / acrylic acid copolymer (acrylic acid 20 mass%, melt index (MI) 300) were added. Further, an organic base and a metal compound

were added in amounts each shown in Table 1, with high speed stirring under a 150 °C, 5 Pa atmosphere, resulting in an emulsion of an ethylene / acrylic acid copolymer. Subsequently, to the resulting emulsion, 4,4'-bis(ethylenimino carbonylamino)diphenylmethane ("CHEMITITE DZ-22E"; "CHMITITE" is a trade name; manufactured by NIPPON SHOKUBAI Co., Ltd.) was added as a crosslinking agent in an amount of 5 mass% on a solid content basis (the value when the solid content of the emulsion composition is taken as 100 mass%; the same applies to the following).

To the resulting mixture, as another crosslinking agent (external crosslinking agent), a glycidyl group-containing compound ("EPICLON CR5L" (which is hereinafter referred as CR5L: "EPICLON" is a trade name; manufactured by DAINIPPON INK AND CHEMICALS Inc.) in an amount of 5 mass% on a solid content basis, silica particles with a particle diameter of 10 to 20 nm ("SNOWTECHS 40"; manufactured by NISSAN CHEMICAL INDUSTRIES Ltd.) in an amount of 30 mass% on a solid content basis, and a spherical polyethylene wax with a softening point of 120 °C and an average particle diameter of 1 μm in an amount of 5 mass% on a solid content basis were added with stirring to prepare each emulsion composition.

Onto one side of the galvanized steel sheet, each composition was coated by means of a bar coater, and heated and dried at a sheet temperature of 90 °C for 1 minute. This resulted in a resin-coated steel sheet in which a resin film was formed in a coating amount of 1.0 g/mm². The respective evaluation

results are shown in Table 1.

Table 1

No.	Type of amine, and amount thereof ¹⁾ (mol%)		Type of metal salt, and amount thereof ¹⁾ (mol%)		Corrosion resistance after degreasing	Tape peeling resistance
1	Triethylamine	20	NaOH	15	◎	◎
2	Triethylamine	40	NaOH	15	◎	◎
3	Triethylamine	60	NaOH	15	◎	◎
4	Triethylamine	70	NaOH	15	◎	◎
5	Triethylamine	80	NaOH	15	○	◎
6	Triethylamine	40	NaOH	2	○	○
7	Triethylamine	40	NaOH	5	◎	○
8	Triethylamine	40	NaOH	10	◎	◎
9	Triethylamine	40	NaOH	20	◎	◎
10	Triethylamine	40	NaOH	30	◎	◎
11	Triethylamine	40	NaOH	40	○	◎
12	Triethylamine	20	NaOH	2	○	○
13	Triethylamine	80	NaOH	40	○	◎
14	Triethylamine	20	NaOH	40	○	◎
15	Triethylamine	80	NaOH	2	○	○
16	Triethylamine	40	KOH	15	○	○
17	Triethylamine	40	LiOH	15	○	○
18	Triethylamine	40	NaOH	1	△	×
19	Triethylamine	40	NaOH	45	△	○
20	Triethylamine	18	NaOH	15	△	△
21	Triethylamine	85	NaOH	15	△	△
22	Tetramethyldiaminomethane	20	NaOH	15	◎	○
23	Tetramethyldiaminomethane	40	NaOH	15	◎	◎
24	Tetramethyldiaminomethane	60	NaOH	15	◎	◎
25	Tetramethyldiaminomethane	80	NaOH	15	◎	○
26	Ammonia	40	NaOH	15	△	×
27	Ethylenediamine	40	NaOH	15	△	×
28	Monoethanolamine	40	NaOH	15	×	×
29	Diethanolamine	40	NaOH	15	×	×
30	Ammonia	60	NaOH	15	×	×

1), 2): Mol% per mole of the carboxylic groups in an ethylene-acrylic acid copolymer

Experimental Example 2 (Effects of crosslinking agent amount)

Each resin-coated steel sheet was obtained in the same manner as with Experimental Example 1, except that the amount of triethylamine used was made constant at 40 %, that the amount of NaOH used was made constant at 15 %, and that the amount of the "CHEMITITE DZ-22E" was changed as shown in Table 2. Then, each resin-coated steel sheet was evaluated for the characteristics. The results are shown in Table 2.

Table 2

No.	DZ-22E Mixing concentration ¹⁾ (mass%)	Corrosion resistance after degreasing	Tape peeling resistance
31	1	○	○
32	3	◎	○
33	5	◎	◎
34	10	◎	◎
35	15	○	○
36	20	○	○
37	0.3	×	△
38	25	×	×

1): Concentration in the solid content of an emulsion composition

Experimental Example 3 (Effects of silica particles)

Each resin-coated steel sheet was obtained in the same manner as with Experimental Example 2, except that the amount of the crosslinking agent was the same as with Experimental Example 1, and that the particle diameter and the mixing concentration of the silica particles were changed as shown in Table 3. Then, each resin-coated steel sheet was evaluated for the characteristics. The results are shown in Table 3.

Table 3

No.	Silica particles		Corrosion resistance after degreasing	Tape peeling resistance
	Particle diameter (nm)	Mixing concentration ¹⁾ (mass%)		
39	4 to 6	30	◎	◎
40	10 to 20	30	◎	◎
41	30 to 50	30	○	◎
42	40 to 200	30	○	◎
43	10 to 20	5	○	○
44	10 to 20	10	○	○
45	10 to 20	15	○	○
46	10 to 20	20	◎	◎
47	10 to 20	26	◎	◎
48	10 to 20	30	◎	◎
49	10 to 20	35	◎	◎
50	10 to 20	40	○	○
51	10 to 20	3	△	△
52	10 to 20	45	△	△
53	1 or less	30	○	○
54	200 or more	30	△	△

1): Concentration in the solid content of an emulsion composition

Experimental Example 4 (Effects of wax)

Each resin-coated steel sheet was obtained in the same manner as with Experimental Example 2, except that the particle diameter and the mixing concentration of the silica particles were as the same as with Experimental Example 1, and that the particles diameter, the mixing concentration, and the softening temperature of the spherical polyethylene wax were changed as shown in Table 4. Then, each resin-coated steel sheet was evaluated for the characteristics. The results are shown in

Table 4.

Table 4

No.	Spherical polyethylene wax			Coefficient of dynamic friction	Corrosion resistance after degreasing	Tape peeling resistance
	Particle diameter (μm)	Mixing concentration ¹⁾ (mass%)	Softening temperature ($^{\circ}\text{C}$)			
55	1.0	0.5	120	0.085	◎	◎
56	1.0	1	120	0.070	◎	◎
57	1.0	5	120	0.065	◎	◎
58	1.0	10	120	0.065	◎	◎
59	1.0	15	120	0.065	◎	◎
60	1.0	20	120	0.065	○	○
61	1.0	0.3	120	0.125	◎	◎
62	1.0	25	120	0.065	△	△
63	0.1	5	120	0.085	◎	◎
64	0.3	5	120	0.065	◎	◎
65	0.5	5	120	0.065	◎	◎
66	1.0	5	120	0.065	◎	◎
67	1.5	5	120	0.077	◎	◎
68	3.0	5	120	0.085	○	○
69	<0.1	5	120	0.248	◎	◎
70	3.5	5	120	0.125	△	△
71	1.0	5	80	0.068	○	◎
72	1.0	5	100	0.064	◎	◎
73	1.0	5	120	0.065	◎	◎
74	1.0	5	140	0.072	◎	◎
75	1.0	5	70	0.070	△	△
76	1.0	5	150	0.262	△	◎

1): Concentration in the solid content of an emulsion composition

The foregoing invention has been described in terms of preferred embodiments. However, those skilled, in the art will recognize that many variations of such embodiments exist. Such variations are intended to be within the scope of the present invention and the appended claims.

What is claimed is:

1. A resin-coated metal sheet, comprising:
a metal sheet; and
a resin film coated on the surface of the metal sheet, the resin film being obtained from an emulsion composition,

wherein the emulsion composition comprises:
an ethylene / unsaturated carboxylic acid copolymer as a main component;

an amine in an amount equal to 0.2 to 0.8 mol per mole of the carboxyl groups contained in the ethylene / unsaturated carboxylic acid copolymer, the amine having a boiling point of 100 °C or less;

a monovalent metal compound in an amount equal to 0.02 to 0.4 mol per mole of the carboxyl groups contained in the ethylene / unsaturated carboxylic acid copolymer; and

a crosslinking agent in an amount of 1 to 20 mass% per 100 mass% of the solid content of the emulsion composition, the crosslinking agent having two or more functional groups capable of reacting with the carboxylic groups contained in the ethylene / unsaturated carboxylic acid copolymer, and

wherein the emulsion composition does not substantially contain an amine having a boiling point of more than 100 °C, and does not substantially contain ammonia.

2. The resin-coated metal sheet according to claim 1, wherein in the ethylene / unsaturated carboxylic acid copolymer, 10 to 40 mass% of the unsaturated carboxylic acid has been

copolymerized.

3. The resin-coated metal sheet according to claim 1, wherein the amine having a boiling point of 100 °C or less is triethylamine.

4. The resin-coated metal sheet according to claim 1, wherein silica particles with an average particle diameter of 1 to 200 nm are contained in an amount of 5 to 40 mass% in every 100 mass% of the solid content of the emulsion composition.

5. The resin-coated metal sheet according to claim 1, wherein a spherical polyethylene wax is contained in an amount of 0.5 to 20 mass% in every 100 mass% of the solid content of the emulsion composition.

6. The resin-coated metal sheet according to claim 1, wherein a chromate film is not formed on the metal sheet.

7. A method for manufacturing the resin-coated metal sheet according to claim 1, comprising the steps of:

preparing the emulsion composition;

coating the emulsion composition on the metal sheet; and

heating and drying the metal sheet coated with the emulsion composition.

8. The method for manufacturing the resin-coated metal

sheet according to claim 7, wherein in the heating and drying step, heating and drying are carried out at such a temperature as to enable the reaction between the crosslinking agent and the carboxyl groups contained in the ethylene / unsaturated carboxylic acid copolymer to proceed.

9. The method for manufacturing the resin-coated metal sheet according to claim 7, wherein in the coating step, the emulsion composition is coated such that the amount of the resin film coated after having been subjected to the heating and drying step becomes 0.2 to 2.5 g/m².