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RESIN-COATED METAL SHEET WITH GOOD WORKABILITY

AND HEAT RESISTANCE

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BACKGROUND OF THE INVENTION

1. Field of the Invention:

The present invention relates to a resin-coated metal sheet with good workability and heat resistance.

2. Description of the Related Art:

Metal sheets, particularly galvanized steel sheets, used for domestic electric appliances, OA apparatus, and buildings need not only such characteristic properties as corrosion resistance, paintability, fingerprint resistance, and silk printability but also good workability and scratch resistance for their working. This need is met by resin-coated steel sheets which are galvanized steel sheets with chromate treatment and ensuing resin coating.

The resin coating layer is conventionally formed from a matrix organic resin having functional groups which is incorporated with a crosslinking agent. Crosslinking makes the resin coating layer hard and compact. The matrix organic resin is further incorporated with silica or the like which imparts corrosion resistance and scratch resistance. The coating layer is also improved in workability and lubricity by incorporation with an organic lubricant (wax) which has a softening point of

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80-140°C depending on the die temperature at the time of working.

Resin-coated steel sheets vary in paintability (film adhesion after painting or silk screen printing) which improves according to the number of functional groups remaining without reaction with the crosslinking agent in the resin coating layer. This is because unreacted functional groups in the resin coating layer react with the crosslinking agent contained in the paint applied later. In the case of resin coating layer containing an organic lubricant (wax), the smaller the wax content, the better the paintability, because wax hardly contains functional groups. A conventional way of meeting the contradictory requirements for workability (lubricity) and paintability was to control the amount of crosslinking agent in the resin coating layer so that the number of unreacted functional groups remaining in the matrix resin balances with the amount of the organic lubricant.

Meanwhile, painting or silk screen printing is conventionally followed by baking at 130-160°C for 20-30 minutes to give a hard painting film. However, the recent trend to improve efficiency is toward a higher baking temperature (about 200°C) and a shorter baking time (1-5 minutes). It turned out that conventional resin-coated steel sheets heated to 200°C or above encounter the problem of the resin coating layer getting soft if it has a low degree of crosslinking. Softening takes

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place more easily as wax softens and melts. A resin coating layer which has got soft makes the painting film thereon look poor after its curing and decreases in adhesion to steel sheets and also decreases in cohesion therein. Such a resin coating layer would cause the painting film to peel off together with it in stringent performance tests. Thus, the resin coating layer should have improved heat resistance if painting film thereon is to exhibit good appearance and adhesion after its curing.

A possible way to improve heat resistance is to increase the amount of the crosslinking agent added to the matrix resin so that the coating layer becomes harder and compacter and to reduce to the utmost the amount of the organic lubricant which decreases the strength of the painting film at high temperatures. It is apprehended that workability gets poor. Heat resistance is improved to some extent by increasing the amount of the crosslinking agent so as to highly crosslink the coating layer while keeping the amount of the organic lubricant (wax) at a fixed level in order to keep good workability. This way of improving heat resistance suffers the disadvantage of presenting difficulties in balancing the amount of the crosslinking agent with the amount of the lubricant. Moreover, there is the possibility of the resin coating layer not containing sufficient unreacted functional groups to react with the crosslinking agent in the painting film at the time of final baking. This leads

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to poor paintability. Under these circumstances, a means to make workability (lubricity) paintability, and heat resistance compatible with each other has been sought.

OBJECT AND SUMMARY OF THE INVENTION

The present invention, which was completed in view of the foregoing, is directed to a resin-coated metal sheet, a process for producing it, and a method for using it. The resin-coated metal sheet has as good workability, corrosion resistance, paintability, and scratch resistance as conventional resin-coated steel sheets. It also has good heat resistance that permits high-temperature baking to finally cure the painting film and silk screen print film. This good heat resistance, therefore, leads to good paintability.

According to the present invention, the resin-coated metal sheet with good workability and heat resistance is characterized in that the resin coating layer comprises a matrix resin having in the molecule at least either active hydrogen or functional groups, an organic lubricant, a first crosslinking agent capable of reacting with said matrix resin, and a second crosslinking agent capable of reacting with said matrix resin, wherein said second crosslinking agent starts crosslinking reaction with said matrix resin at a higher temperature than said first crosslinking agent does.

The foregoing constitution permits the matrix resin to

undergo crosslinking reaction in two stages. In the first stage, the first crosslinking agent brings about crosslinking reaction to such an extent that the resin coating layer has sufficient scratch resistance in subsequent steps. In the second stage (for baking at a high temperature for a short time), the second crosslinking agent, which has remained unreacted in the first stage, crosslinks the matrix resin to give a compact resin coating layer which resists softening by heat. In this way it is possible to make workability and heat resistance compatible with each other.

The temperature at which crosslinking reaction starts should preferably be 130°C or below for the first crosslinking agent and 135°C or above for the second crosslinking agent. A combination of a low-temperature crosslinking epoxy resin (as the first one) and a melamine resin (as the second one) is adequate. These two crosslinking agents significantly differ in the temperature at which they start crosslinking reaction.

According to the present invention, the resin-coated metal sheet with good workability and heat resistance is characterized in that the resin coating layer comprises a matrix resin having in the molecule at least either active hydrogen or functional groups, an organic lubricant, a first crosslinking agent capable of reacting with said matrix resin, and a second crosslinking agent capable of reacting with said matrix resin,



wherein said first crosslinking agent is present in a form resulting from reaction with said matrix resin and said second crosslinking agent is present in a substantially intact form without reaction with said matrix resin. The foregoing constitution may be realized by utilizing the fact that the two crosslinking agents start reaction with the matrix resin at different temperatures or by carrying out the process such that only the first crosslinking agent reacts with the matrix resin.

The foregoing constitution of the resin-coated metal sheet is characterized in that the resin coating layer contains a reaction product of the matrix resin and the first crosslinking agent before it undergoes baking at a high temperature for a short time. The resin-coated metal sheet in this state is also within the scope of the present invention. A desirable state is such that the first crosslinking agent does not remain substantially intact without reaction with the matrix resin before the high-temperature short-time baking step. The resin coating layer in this state has good scratch resistance during fabrication. Another desirable state is such that the second crosslinking agent in an amount of 1-20 mass% remains substantially intact without reaction with the matrix resin before the high-temperature short-time baking step. The resin coating layer in this state effectively resists softening due to crosslinking reaction by the first crosslinking agent in the



baking step.

The above-mentioned resin coating layer may optionally contain silica. The above-mentioned organic lubricant should preferably be contained in the resin coating layer in an amount of 0.5-20 mass%.

The present invention is also directed to a process for producing a resin-coated metal sheet with good workability and heat resistance, said process comprising the steps of coating a metal sheet with a composition to form a resin coating layer, said composition containing a matrix resin having in the molecule at least either active hydrogen or functional groups, an organic lubricant, and more than two kinds of crosslinking agents capable of crosslinking reaction with said matrix resin, and treating the coated metal sheet under the condition that one of said crosslinking agents reacts with said matrix resin but the other of said crosslinking agents does not react with said matrix resin.

The present invention is also directed to a process for producing a resin-coated metal sheet with good workability and heat resistance, said process comprising the steps of coating a metal sheet with a composition to form a resin coating layer, said composition containing a matrix resin having in the molecule at least either active hydrogen or functional groups, an organic lubricant, and more than one kind of crosslinking agent capable of crosslinking reaction with said matrix resin, and heating and



drying the coated metal sheet at a temperature which is higher than the crosslinking reaction starting temperature of one of the crosslinking agents having the lowest crosslinking reaction starting temperature but is lower than the crosslinking reaction starting temperature of the other of the crosslinking agents having the highest crosslinking reaction starting temperature. The heating and drying step should be carried out in such a way that substantially no crosslinking reaction takes place between the matrix resin and one of the crosslinking agents having the highest crosslinking reaction starting temperature. A preferred temperature for the heating and drying step is 80-120°C.

The resin-coated metal sheet of the present invention may undergo an additional step of heating a painting film formed on the surface of the resin coating layer at a temperature high enough for the matrix resin to react with the crosslinking agent remaining intact in the resin coating layer. This coating method is also within the scope of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic representation of DTA chart illustrating the temperature at which the crosslinking reaction starts.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The resin-coated metal sheet of the present invention



consists of a metal sheet and a resin coating layer formed on at least one side thereof. It does not suffer sticking or blocking during storage in piled or coiled form because the resin coating layer is made of a matrix resin which has already been crosslinked by one crosslinking agent. Moreover, the resin coating layer is not liable to scratching during fabrication (such as slitting, punching, and forming) because it has an adequate hardness owing to the first crosslinking system and it contains an organic lubricant which imparts good corrosion resistance and scratch resistance. In addition, the resin coating layer offers good paintability when painted with baking finish under ordinary conditions (at 130-160°C for 20-30 minutes) because the matrix resin therein still contains an adequate amount of unreacted functional groups before baking.

Besides, the resin coating layer exhibits good heat resistance without getting soft and good adhesion to the metal sheet and painting film when it is painted (or silk screen printed) and baked at a higher temperature for a shorter time than ordinary baking. This is because the resin coating layer contains a second crosslinking agent remaining unreacted before baking and it comes into play during baking. The second crosslinking system also helps the baked painting film to have a good appearance. A detailed description of the invention will be given below.



The matrix resin is not specifically restricted so long as it possesses active hydrogen and/or functional groups capable of reaction with the crosslinking agent. Its preferred examples include modified polyolefin resin, polyurethane resin, acrylic resin, epoxy resin, and polyester resin. They may be used alone or in combination with one another if they have good compatibility. Those in the form of aqueous dispersion or solution are desirable for environment conservation. Modified polyolefin resin and polyurethane resin are desirable from the standpoint of workability, scratch resistance, and paintability. The former is most desirable if corrosion resistance is taken into account.

Modified polyolefin resin has functional groups. Preferred functional groups are carboxyl groups. (A polyolefin resin modified with carboxyl groups can be made into an ionomer.) The modified polyolefin resin is obtained by polymerization from an olefin (such as ethylene, propylene, and butene) and an ethylenic unsaturated carboxylic acid (such as (meth)acrylic acid, maleic acid, fumaric acid, and itaconic acid) together with one or more optional comonomers. The amount of ethylenic unsaturated carboxylic acid should preferably be 1-40 mass% of the total amount of monomer, so that the resulting modified polyolefin resin contains an adequate amount of functional groups (or carboxyl groups). If the amount of carboxylic acid is less than 1 mass%, the resulting modified polyolefin resin



does not have sufficient functional groups and hence the object of the present invention is not achieved. Moreover, it cannot be readily made into an aqueous dispersion desirable for environmental conservation. Conversely, with carboxylic acid in excess of 40 mass%, the modified polyolefin resin yields a resin coating layer poor in corrosion resistance and water resistance. A preferred olefin is ethylene and a preferred unsaturated carboxylic acid is (meth)acrylic acid.

Other copolymerizable monomers include alkyl esters of (meth)acrylic acid such as methyl (meth)acrylate, ethyl (meth)acrylate, and propyl (meth)acrylate; aromatic monomers such as α -methylstyrene, chlorostyrene, and vinyltoluene; hydroxyl group-containing (meth)acrylate esters such as hydroxyethyl (meth)acrylate and hydroxypropyl (meth)acrylate; amide monomers such as N-methylol (meth)acrylamide; epoxy group-containing (meth)acrylate esters such as glycidyl (meth)acrylate; and (meth)acrylonitrile. They may be used alone or in combination with one another. Any modified polyolefin resin having hydroxyl groups, amide groups, or epoxy groups can be crosslinked with a crosslinking agent having functional groups capable of reaction with them.

The carboxyl group-containing polyolefin resin thus obtained should preferably be used in the form of aqueous dispersion (emulsion) or ionomer after reaction with alkali



(such as ammonia water) or cations. Preferred cations are metal ions formed from lithium, sodium, potassium, magnesium, calcium, iron, aluminum, etc. Of these, sodium ions are most desirable. They give rise to ionic crosslinking for improvement in corrosion resistance and scratch resistance.

Polyurethane resin contains active hydrogen derived from hydroxyl groups and amino groups. A commercial aqueous dispersion of polyurethane resin ("Superflex" from Dai-ichi Kogyo Seiyaku Co., Ltd.) may be used. It is possible to produce aqueous dispersions of polyurethane resin by any of the following known processes.

(1) A process which consists of reacting a so-called urethane prepolymer having terminal isocyanate groups with a compound having an amino group or hydroxyl group and a sulfonic group or carboxyl group (such as alkali or ammonium salt of diaminocarboxylic acid in the form of aqueous solution), in such a way that chain extension and emulsification take place simultaneously.

(2) A process which consists of reacting a polyisocyanate compound with a polyol compound, a compound having a quaternary ammonium group and hydroxyl group, a compound having an epoxy group and hydroxyl group, and dispersing the reaction product into water.

(3) A process which consists of reacting polyesterpolyol or



a polyol, an aromatic polyisocyanate or aliphatic diisocyanate, and a chain extender with one another in an inert organic solvent, mechanically stirring the reaction product with water containing an adequate amount of emulsifier, and distilling away the solvent.

The polyesterpolyol results from dehydration condensation reaction between a polyol (such as polyether, polyethylene glycol, polypropylene glycol, butanediol, and hexanediol which are (co)polymer of tetrahydrofuran, ethylene oxide, propylene oxide) and a dicarboxylic acid (such as maleic acid, succinic acid, and adipic acid). The polyol is exemplified polyester, polyacetal, polyester amide, and polythioether obtained from a cyclic ester by ring-opening polymerization.

The aromatic polyisocyanate is exemplified by 1,5-naphthalene diisocyanate, 4,4-diphenylmethane diisocyanate (MDI), phenylene diisocyanate, xylylene diisocyanate, and toluene diisocyanate (TDI).

The aliphatic diisocyanate is exemplified by hexamethylene diisocyanate and dicyclohexylmethane diisocyanate.

The chain extender is exemplified by any of the above-mentioned polyols and low-molecular-weight diamine (such as ethylene diamine, propylene diamine, diethylene triamine, hexamethylene diamine, and xylylene diamine).

The inert organic solvent is exemplified by tetrahydrofuran,



acetone, methyl ethyl ketone, ethyl acetate, and toluene.

(4) A process which consists of reacting a urethane prepolymer having terminal isocyanate groups with polyalkylene polyamine (such as diethylene triamine) to give polyurethane urea polyamine, and adding to it an aqueous solution of an acid. An alternative process which consists of subjecting the polyurethane urea polyamine to addition reaction with epichlorohydrin and adding to the reaction product an aqueous solution of an acid.

(5) A process which consists of reacting the above-mentioned polyurethane urea polyamine or its adduct with an alkylisocyanate or epihalohydrin with a cyclic dicarboxylic acid anhydride, and mixing the reaction product with a basic aqueous solution.

(6) A process which consists of reacting the above-mentioned polyurethane urea polyamine or its adduct with an epihalohydrin with any of sulfonic acid, lactonic acid, and sodium salt of monohalogenated carboxylic acid, or with (meth)acrylic ester, acrylonitrile, etc., hydrolyzing the reaction product, and mixing the hydrolyzate with water. (7) A process which consists of reacting a urethane prepolymer having terminal hydroxyl or isocyanate groups (which is obtained from a polyol and a polyisocyanate) with a diamine to give a compound having terminal amino groups, dispersing the reaction product into



water with the aid of an emulsifier, and adding to the aqueous dispersion a polyisocyanate for increase in molecular weight.

The acrylic resin is obtained by polymerization from one or more of the following monomers.

Carboxyl group-containing (meth)acrylic acid and hydroxyl group-containing (meth)acrylic esters such as hydroxyethyl (meth)acrylate and hydroxypropyl (meth)acrylate; amides such as N-methylol (meth)acrylamide; epoxy group-containing (meth)acrylic esters such as diglycidyl (meth)acrylate; alkyl esters of (meth)acrylic acid such as methyl (meth)acrylate, ethyl (meth)acrylate, and propyl (meth)acrylate; aromatic polymers such as styrene, α -methylstyrene, chlorostyrene, and vinyltoluene; and (meth)acrylonitrile.

The resulting acrylic resin contains carboxyl groups, hydroxyl groups, amide groups, or epoxy groups as functional groups.

Usable epoxy resins include any known ones having epoxy groups as functional groups. Usable polyester resins include those which have such functional groups as carboxyl groups and hydroxyl groups. They include glyptal resin, phthalic acid resin, isophthalic acid resin, maleic acid resin, aliphatic polyester resin, and oxyacid resin.

The present invention requires more than or equal to two kinds of crosslinking agents in order to form a resin coating layer. The present invention requires that the resin coating



layer on the resin-coated metal sheet should be formed from the above-mentioned matrix resin, two kinds of crosslinking agents differing in the temperature at which the crosslinking reaction with said matrix resin starts, and an organic lubricant. The resin coating layer after heating and drying but before high-temperature baking should contain the matrix resin which has been crosslinked by the first crosslinking agent and the second crosslinking agent remaining unreacted which comes into play in the subsequent high-temperature baking. It is not always necessary that the matrix resin be completely crosslinked. Part of the matrix resin may remain intact because the first crosslinking agent is not usually added in large excess.

The above-mentioned constitution permits the resin coating layer, which has been adequately crosslinked by the first crosslinking agent and contains an organic lubricant, to exhibit good workability, corrosion resistance, scratch resistance, and paintability before the high-temperature short-time baking. With heating in the high-temperature short-time baking, the second stage of crosslinking proceeds in the resin coating layer, preventing the resin coating layer from getting soft. This permits painting film to be cured uniformly on the surface of the resin coating layer. Thus, there is obtained a cured painting film having a good appearance. In addition, during the high-temperature short-time baking, crosslinking proceeds



further in the resin coating layer to make the matrix resin compacter. This prevents the migration of the organic lubricant in a molten state and hence prevents any adverse effect of decreasing adhesion between the resin coating layer and the metal sheet surface and decreasing cohesion in the resin coating layer.

There are several ways of performing the crosslinking reaction separately in two stages. One possible way is by heating and ensuing irradiation with electron beams. It is most desirable to carry out the first crosslinking at a low temperature for the second crosslinking not to take place and to carry out the second crosslinking at a high temperature, which is usually about 200°C for the high-temperature short-time baking.

The present invention employs two (or more) kinds of crosslinking agents which differ in the temperature at which they start the crosslinking reaction with the matrix resin. Of these crosslinking agents, the one having the lowest reaction starting temperature is designated as the first crosslinking agent and the one having the highest reacting starting temperature is designated as the second crosslinking agent. The resin coating film, which has been heated and dried but does not yet undergo high-temperature baking, contains a compound resulting from reaction between the first crosslinking agent and the matrix resin and the second crosslinking agent remaining unreacted but does not substantially contain any compound resulting from



reaction between the second crosslinking agent and the matrix resin and the first crosslinking agent remaining unreacted.

In other words, the first stage of crosslinking is carried out for the first crosslinking agent which has the lowest reaction starting temperature, and the second stage of crosslinking is carried out for the second crosslinking agent which has the highest reaction starting temperature. It follows, therefore, that the resin coating layer (before the high-temperature short-time baking) contains a product left after reaction between the first crosslinking agent and the matrix resin and the second crosslinking agent remaining unreacted. Ideally, it does not contain the first crosslinking agent remaining unreacted and any product resulting from reaction between the second crosslinking agent and the matrix resin. However, by the nature of chemical reactions, there is an inevitable case where the second crosslinking agent immaturely reacts with the matrix resin in the first stage of crosslinking or the first crosslinking agent partly remains unreacted. This situation is not precluded from the scope of the present invention but is construed as "substantially" absent. Moreover, there will be a case where the resin coating layer contains the matrix resin partly remaining intact, reaction products of the matrix resin and the first and second crosslinking agents, or reaction products of the first and second crosslinking agents. This situation is also



within the scope of the present invention.

The reaction starting temperature is determined by heating a mixture (prepared in film form at room temperature) of the matrix resin and the crosslinking agent in a thermal differential analyzer. It is defined as the temperature at which an exothermic reaction begins to occur between the matrix resin and the crosslinking agent, indicating a temperature rise. Fig. 1 schematically shows the DTA chart and the reaction starting temperature.

The second crosslinking agent, which starts crosslinking at a higher temperature, should preferably be one which starts crosslinking at 135°C or above. The exact temperature varies depending on the temperature at which the first crosslinking agent starts crosslinking and the temperature at which the painting film is formed in the final step. It includes, for example, melamine resin and blocked isocyanate. Melamine resin reacts with hydroxyl groups and carboxyl groups and also with urethane through active hydrogen, hydroxyl groups, epoxy groups, etc. contained therein. Their commercial products include "Suminal M40W" and "Sumimar M50W" from Sumitomo Chemical Co., Ltd. and "Cymel 303" from Mitsui Saitech Co., Ltd.

The blocked isocyanate is a compound whose active isocyanate groups are blocked with a compound containing active hydrogen. Upon heating, it releases the blocking compound to



become active. It can be used as the first crosslinking agent which starts crosslinking at a lower temperature. The temperature for the blocking compound to be released can be controlled by selecting an adequate compound to block active isocyanate groups in polyisocyanate compounds such as TDI and MDI. Because of its high thermal dissociation temperature (180°C or above in some cases), an aliphatic alcohol (such as methanol, ethanol, and butyl cellosolve) is suitable for use as a blocking compound for the second crosslinking agent which comes into play at the time of high-temperature baking. Other blocking compounds include lactams such as ϵ -caprolactam; phenols such as phenol and cresol; oximes such as methyl ethyl ketooxime and cyclohexane oxime; and methylene-containing active compounds such as dimethyl malonate and ethyl acetoacetic acid. They decrease in the thermal dissociation temperature (down to about 110°C) in order listed. A proper selection should be made from the first and second crosslinking agents in consideration of their crosslinking temperature.

The first crosslinking agent, which starts crosslinking at a lower temperature, should preferably be one which starts crosslinking at 130°C or below. A preferred example is an epoxy resin capable of crosslinking at a low temperature. An epoxy resin contains epoxy groups which react with hydroxyl groups, carboxyl groups, and active hydrogen of amines. Examples of



commercial epoxy resins include "EX-313", "EX-314", "EX-321", "EX-421", "EX-512", "EX-521", "EX-147", "EX-810", and "EX-614 (included in "Denacol" series from Nagase Chemicals, Ltd.); and "Rikabond EX-8S" and "Rikabond AP-355B" from Chuo Rika Kogyo Co., Ltd.

The first and second crosslinking agents may be used in combination with an additional crosslinking agent which has an intermediate reaction starting temperature so long as it has no adverse effect on the present invention. The additional crosslinking agent may be used when the first crosslinking agent is used or when the second crosslinking agent is used. Examples of such an additional crosslinking agent include methylool compounds, amine compounds, epoxy compounds for crosslinking at high temperatures, and aziridinyl group-containing compounds.

The amount of the first and second crosslinking agents in the resin coating layer should be 1-20 mass% each and no more than 30 mass% in total (as solids). Ideally, the second crosslinking agent in the resin coating layer should remain intact without reaction with the matrix resin, and the first crosslinking agent in the resin coating layer should be present in the form of a compound left after reaction with the matrix resin.

If the amount of the second crosslinking agent is less than 1 mass%, the resin coating layer is poor in heat resistance



and gets soft at the time of high-temperature baking. A preferred amount is 2 mass% of above. If the amount of the second crosslinking agent exceeds 20 mass%, the resin coating layer is poor in corrosion resistance before high-temperature baking. If the amount of the first crosslinking agent is less than 1 mass%, the resin coating layer is poor in corrosion resistance and scratch resistance. If the amount of the first crosslinking agent exceeds 20 mass%, the resin coating layer is excessively hard and liable to break during fabrication and hence is poor in corrosion resistance. A preferred upper limit is 10 mass%.

If the total amount of the two crosslinking agents (and an additional one) exceeds 30 mass%, the resin coating layer is poor in corrosion resistance on account of the excess crosslinking agent remaining unreacted.

According to the present invention, the resin coating layer should contain an organic lubricant as an essential component, so that it has good lubricity and protects itself from scratch during fabrication. A preferred amount of the organic lubricant is 0.5-20 mass%. With an amount less than 0.5 mass%, the organic lubricant does not produce the effect of improving workability and scratch resistance. With an amount exceeding 20 mass%, the organic lubricant does not produce any additional effect but adversely affects the heat resistance of the resin coating layer in the baking step that follows painting or silk



screen printing.

Examples of the organic lubricant include polyolefin wax (such as polyethylene, polyethylene oxide, and polypropylene), fluorocarbon resin (such as polytetrafluoroethylene, polyvinyl fluoride, and polyvinylidene fluoride), and paraffin wax. Of these examples, polyethylene wax is desirable because of its lubricity. The one composed of spherical particles having an average particle diameter of 0.1-3 μm is preferable. With a particle diameter smaller than 0.1 μm , the wax does not fully produce its effect of improving scratch resistance. With a particle diameter larger than 3 μm , the wax does not disperse uniformly in the resin coating layer. The polyethylene wax should preferably have a softening point in the range of 80-140°C. With a softening point lower than 80°C, the wax flows during fabrication and hence aggravates workability. With a softening point higher than 140°C, the wax is poor in lubricity.

The polyethylene wax composed of spherical particles is commercially available under the trade name of "Daijet E-17" (from Goou Kagaku Co., Ltd.), "KUE-1", "KUE-5", and "KUE-8" (from Sanyo Chemical Industries, Ltd.), "W-100", "W-200", "W-300", "W-400", "W-500", "W-640", and "W-700" (included in "Chemipearl" series from Mitsui Kagaku Co., Ltd.), and "Elepon E-200" (from Nicca Chemical Co., Ltd.).

The resin coating layer may optionally contain silica in



an amount of 5-30 mass% (as solids). Silica contributes to corrosion resistance and scratch resistance. Silica in an amount less than 5 mass% does not produce the desired effect. Silica in an amount more than 30 mass% causes the resin coating layer to crack during drying, which leads to decreased corrosion resistance.

The silica may be of spherical particles or chain-like particles. The spherical particles should preferably have an average particle diameter of 1-200 nm. Excessively fine silica prevents cracking and hence contributes to corrosion resistance but makes unstable the composition of the resin coating layer. Excessively coarse silica makes it difficult to form the resin coating layer. A preferred particle diameter is 4-20 nm. This requirement is met by colloidal silica and fumed silica. Preferred commercial silica is "XS", "SS", "40", "N", and "UP" included in "Snowtex" series of colloidal silica from Nissan Chemical Industries, Ltd.

The resin-coated metal sheet of the present invention is obtained by mixing the above-mentioned components, applying the resulting composition to a metal sheet, and drying the coating layer. The composition for the resin coating layer is prepared by incorporating an aqueous dispersion of the matrix resin with crosslinking agents, organic lubricant, and optional silica mentioned above. (The matrix resin in aqueous dispersion (or



emulsion) form is desirable from the view point of environmental conservation as mentioned above.) The resulting mixture may be incorporated with optional components (which have no adverse effect on the present invention) such as diluent solvent, anti-skinning agent, leveling agent, anti-foaming agent, penetrating agent, emulsifier, film-forming auxiliary, dye and pigment, thickener, silane coupling agent, and resin free of functional groups and active hydrogen.

The metal sheet is not specifically restricted. It includes zinc-coated steel sheets, galvanized steel sheets, zinc-alloy coated steel sheets, aluminum sheets, aluminum alloy sheets, and titanium sheets. For better corrosion resistance and adhesion, it is desirable to perform chromate treatment or phosphate treatment on the plating film or the surface of the metal sheet before the resin coating layer is formed thereon. The chromate treatment may be of reaction type, coating type, or electrolysis type.

To form the resin coating layer on the metal sheet, it is necessary to apply the above-mentioned composition for the resin coating layer to one or both surfaces of the metal sheet by any known coating method such as roll coating, spraying, or curtain flow coating. The coating layer is subsequently heated and dried. The step for heating and drying should be carried out above the temperature at which the first stage of crosslinking



takes place or the first crosslinking agent starts its crosslinking reaction. In other words, the step for heating and drying should be carried out below the temperature at which the second stage of crosslinking does not take place or the second crosslinking agent does not start its crosslinking reaction. This is because the second stage of crosslinking should be carried out at the time of high-temperature short-time baking as the final step, so that the resin coating layer exhibits good heat resistance while keeping good paintability and workability, as mentioned above. However, by the nature of chemical reactions, there is the possibility that the second crosslinking agent partly reacts with the matrix resin. The resin coated metal sheet obtained in this manner is also acceptable in the present invention.

An actual drying temperature should be established in consideration of the reaction starting temperature of the first and second crosslinking agents used. A drying temperature of 70-130°C is preferable in the case where the organic lubricant is polyethylene wax of spherical particles. The first crosslinking agent used in such a case should preferably be one which does crosslink within the above-mentioned temperature range. In view of the fact that a water-based composition is used for the resin coating layer, a temperature in the range of 80-120°C is more desirable for heating and drying.



The resin coating layer should be formed such that its thickness or weight (after drying) is 0.2-2.5 g/m². It will not fully exhibit its corrosion resistance and scratch resistance if it is excessively thin, and it will peel off during fabrication if it is excessively thick. A thickness in the range of 0.4-1.5 g/m² is desirable from the standpoint of electrical conductivity and weldability.

The resin-coated metal sheet produced as mentioned above may be used as such or after painting or silk screen printing according to the intended use. The painting or silk screen printing is usually followed by baking at 130-160°C for 20-30 minutes. During this conventional baking step, the second stage of crosslinking proceeds to some extent. Therefore, the thus obtained painting film has good corrosion resistance. Undoubtedly, the best result is obtained when baking for the painting film is carried out at about 200°C for 1-5 minutes, so that the second stage of crosslinking is completed. Thus it is possible to form an externally good painting film in a short time on the resin-coated metal sheet having good heat resistance. Since the final baking step is carried out at about 200°C, the second crosslinking agent should be one whose crosslinking reaction proceeds rapidly at this temperature. This requirement is met by those which start crosslinking at 135°C or above. Their preferred examples include melamine resin and



blocked isocyanate having a high dissociation temperature.

The resin-coated metal sheet of the present invention is composed of a metal sheet and a resin coating layer formed on at least one side thereof. This resin coating layer before the final high-temperature baking has the matrix resin in a crosslinked state created by one of the two crosslinking agents in the first stage of crosslinking. It has an adequate degree of hardness owing to crosslinking and it also has good corrosion resistance and scratch resistance owing to the organic lubricant contained therein. Thus the resin coated metal sheet can undergo slitting and punching without the resin coating layer being scratched. Moreover, the matrix resin in the resin coating layer before the final high-temperature baking contains an adequate number of residual functional groups which contribute to paintability when the resin-coated metal sheet undergoes conventional painting (with baking at 130-160°C for 20-30 minutes).

The resin-coated metal sheet of the present invention is constituted such that the resin coating layer before the high-temperature short-time baking contains the other of the two crosslinking agents in an unreacted state and this crosslinking agent comes into play in the second stage of crosslinking when the resin-coated metal sheet is painted and the painting film is finally baked. Therefore, the resin coating layer exhibits



good heat resistance without getting soft and provides good adhesion between the metal sheet and the resin coating layer and between the resin coating layer and the painting film. And the painting film after baking has a good external appearance.

EXAMPLES

To further illustrate the invention, but not by way of limitation, the following examples are given. They may be modified without departing from the spirit and scope of the invention.

[Test methods]

The following test methods were used in the examples.

(1) Temperature at which crosslinking reaction starts

The matrix resin is mixed with the crosslinking agent, and the resulting mixture is spread into film over a polytetrafluoroethylene plate at room temperature. After drying, the film sample is heated in a differential thermal analyzer. The DTA chart as shown in Fig. 1 gives the temperature (°C) at which the crosslinking agent starts reaction.

(2) Pencil scratch test (for pencil hardness)

This test conforming to JIS K5400 is performed on a specimen of the resin-coated metal sheet which has been dried at 80°C for 1 minute or which has undergone high-temperature short-time baking (at 230°C for 50 seconds). Pencil hardness is rated by observing scratches with a magnifier.



(3) Workability

Single-press test with an 80-ton crank press is performed on a specimen of the resin-coated metal sheet, and the worked surface of the specimen is visually inspected and rated by the following criterion,

5 : almost no scratching, 4 : slight scratching, 3 : apparent scratching, 2 : scoring, 1 : cracking

(4) Corrosion resistance

Salt spray test conforming to JIS Z2371 is performed on a specimen of the resin-coated metal sheet, with its edges sealed. Corrosion resistance is expressed in terms of time required for white rust to cover 1% of the surface of the specimen.

(5) Heat resistance

A sample of the resin-coated metal sheet is coated by bar coating with a polyester paint such that the painting film is 20 μm thick. The painting film is baked at 230°C for 50 seconds. The specimen with a baked painting film is immersed in boiling water for 1 hour and then subjected to cross-cut test for 10×10 small squares formed by scoring at intervals of 1 mm. Heat resistance is expressed in terms of the number of remaining small squares (of both resin-coated layer and painting film).

Experiment Example 1

Samples of resin-coated metal sheet were produced from an electrogalvanized steel sheet (0.8 mm thick, 20 g/m² of zinc)



with chromate treatment (15 mg/m² of chromium) as the base.

The steel sheet was coated with a composition to form a resin coating layer thereon. This composition was prepared by mixing from the following components.

- Ethylene-acrylic acid copolymer (containing 20 mass% of acrylic acid) in emulsion form as the matrix resin. The copolymer had its carboxyl groups partly neutralized with sodium hydroxide so that it was converted into an ion-crosslinked ionomer beforehand.
- Polyethylene wax of spherical particles (with an average particle diameter of 0.6 μm) having a softening point of 100°C. 5 mass% of solids in the composition.
- Colloidal silica having an average particle diameter of 10-20 nm ("Snowtex 40" from Nissan Chemical Industries, Ltd.) 20 mass% of solids in the composition.
- Epoxy resin for crosslinking at a low temperature (which starts crosslinking reaction at 50°C) "Denacol EX-313" from Nagase Chemicals, Ltd. Amount (based on solids in the composition) is shown in Table 1.
- Melamine resin (which starts crosslinking reaction at 140°C) "Sumimal M40W" from Sumitomo Chemical Co., Ltd. Amount (based on solids in the composition) is shown in Table 1.

Each of the resulting compositions was applied by roll coating onto one side of the above-mentioned steel sheet. The



coating layer was heated and dried at 80°C (sheet temperature) for 1 minute. Thus there were obtained samples of resin-coated steel sheets, each having a resin coating film of 1 g/m². The results of their evaluation are shown in Table 1.



Table 1

	Crosslinking agent (mass%)		Pencil hardness		Heat resistance	Corrosion resistance (h)	Workability
	Epoxy resin	Melamine resin	As dried	After baking			
Working Example	5	1	2H	3H	100	760	5
	1	5	2H	4H	100	780	5
	5	5	2H	4H	100	740	5
	10	5	2H	4H	100	810	5
	15	5	3H	4H	100	790	5
	20	5	3H	4H	100	750	5
	5	10	2H	4H	100	720	5
	5	15	2H	4H	100	800	5
	5	20	2H	4H	100	770	5
Referential Example	5	0.5	2H	2H	63	760	5
	5	25	2H	4H	100	450	4
	0.5	5	H	4H	100	380	3
	25	5	3H	4H	55	600	5
Comparative Example	--	5	F	3H	100	340	3
	--	10	F	4H	100	330	3
	--	15	F	4H	100	280	3
	5	--	2H	2H	5	760	5
	10	--	2H	2H	8	780	5
	15	--	3H	3H	6	760	5
	--	--	F	F	3	260	3



Experiment Example 2

The same procedure as in Experiment Example 1 was repeated to produce samples of the resin-coated steel sheets, except that the ethylene-acrylic acid copolymer for the matrix resin was replaced by a polyurethane resin (in aqueous dispersion form) "Superflex" from Dai-ichi Kogyo Seiyaku Co., Ltd. The results of evaluation are shown in Table 2.



Table 2

	Crosslinking agent (mass%)		Pencil hardness		Heat resistance	Corrosion resistance (h)	Workability
	Epoxy resin	Melamine resin	As dried	After baking			
Working Example	5	1	3H	3H	100	700	5
	1	5	2H	3H	100	710	5
	5	5	3H	4H	100	680	5
	10	5	3H	4H	100	670	5
	15	5	3H	4H	100	700	5
	20	5	3H	4H	100	670	5
	5	10	3H	4H	100	700	5
	5	15	3H	4H	100	790	5
	5	20	3H	4H	100	750	5
Referential Example	5	0.5	3H	3H	68	700	5
	5	25	3H	4H	100	380	4
	0.5	5	H	3H	100	330	4
	25	5	3H	4H	60	550	5
Comparative Example	--	5	H	3H	100	300	4
	--	10	H	4H	100	290	3
	--	15	H	4H	100	210	3
	5	--	3H	3H	43	660	5
	10	--	3H	3H	28	680	5
	15	--	3H	3H	51	670	5
	--	--	H	H	18	220	4

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WHAT IS CLAIMED IS:

1. A resin-coated metal sheet with good workability and heat resistance having a resin coating layer, said resin coating layer comprising:

a matrix resin having in the molecule at least either active hydrogen or functional groups;

an organic lubricant;

a first crosslinking agent capable of reacting with said matrix resin; and

a second crosslinking agent capable of reacting with said matrix resin, wherein said second crosslinking agent starts crosslinking reaction with said matrix resin at a higher temperature than said first crosslinking agent starts crosslinking reaction with said matrix resin.

2. The resin-coated metal sheet as defined in Claim 1, wherein said first crosslinking agent starts crosslinking reaction at 130°C or below and said second crosslinking agent starts crosslinking reaction at 135°C or above.

3. The resin-coated metal sheet as defined in Claim 1, wherein said first crosslinking agent is an epoxy resin and said second crosslinking agent is a melamine resin.

4. The resin-coated metal sheet as defined in Claim 1, wherein said resin coating layer contains a reaction product of said matrix resin and said first crosslinking agent.



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5. The resin-coated metal sheet as defined in Claim 4, wherein said resin coating layer does not substantially contain said first crosslinking agent intact without reaction with the matrix resin.

6. The resin-coated metal sheet as defined in Claim 1, wherein said resin coating layer contains 1-20 mass% of said second crosslinking agent substantially intact without reaction with said matrix resin.

7. The resin-coated metal sheet as defined in Claim 1, wherein said resin coating layer further contains silica.

8. The resin-coated metal sheet as defined in Claim 1, wherein said resin coating layer contains said organic lubricant in an amount of 0.5-20 mass%.

9. A resin-coated metal sheet with good workability and heat resistance having a resin coating layer, said resin coating layer comprising:

a matrix resin having in the molecule at least either active hydrogen or functional groups;

an organic lubricant;

a first crosslinking agent capable of reacting with said matrix resin; and

a second crosslinking agent capable of reacting with said matrix resin, said first crosslinking agent being present in a form resulting from reaction with said matrix resin and said



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second crosslinking agent being present in a substantially intact form without reaction with said matrix resin.

10. The resin-coated metal sheet as defined in Claim 9, wherein said resin coating layer does not substantially contain said first crosslinking agent intact without reaction with said matrix resin.

11. The resin-coated metal sheet as defined in Claim 9, wherein said resin coating layer contains 1-20 mass% of said second crosslinking agent substantially intact without reaction with said matrix resin.

12. A process for producing a resin-coated metal sheet with good workability and heat resistance, said process comprising the steps of:

coating a metal sheet with a composition to form a resin coating layer, said composition containing a matrix resin having in the molecule at least either active hydrogen or functional groups, an organic lubricant, and more than one kind of crosslinking agent capable of crosslinking reaction with said matrix resin; and

treating the coated metal sheet under the condition that one of said crosslinking agents reacts with said matrix resin but the other of said crosslinking agents does not react with said matrix resin.

13. A process for producing a resin-coated metal sheet



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with good workability and heat resistance, said process comprising the steps of:

coating a metal sheet with a composition to form a resin coating layer, said composition containing a matrix resin having in the molecule at least either active hydrogen or functional groups, an organic lubricant, and more than one kind of crosslinking agent capable of crosslinking reaction with said matrix resin; and

heating and drying the coated metal sheet at a temperature which is higher than the crosslinking reaction starting temperature of one of said crosslinking agents having the lowest crosslinking reaction starting temperature but is lower than the crosslinking reaction starting temperature of the other of said crosslinking agents having the highest crosslinking reaction starting temperature, wherein said heating and drying step is carried out in such a way that substantially no crosslinking reaction takes place between said matrix resin and one of said crosslinking agents having the highest crosslinking reaction starting temperature.

14. The process for producing a resin-coated metal sheet as defined in Claim 13, wherein said heating and drying step is carried out at a temperature of 80-120°C.

15. A process of painting the resin-coated metal sheet defined in Claims 9 to 10, said process comprising heating a



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painting film formed on the surface of the resin coating layer
at a temperature high enough for said matrix resin to react with
said crosslinking agent remaining intact in said resin coating
layer.

