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(54) **METHODE DE REVETEMENT POUR CARROSSERIE
D'AUTOMOBILE**
(54) **COATING METHOD FOR CAR BODY**

(57) According to the present invention, provided is a coating method for a car body, comprising: applying an organic solvent base thermosetting first colored paint (B) containing a neutralized product of a polyvalent carboxylic acid resin having an acid value of 5 to 100 mg KOH/g and an amino resin on both interior and exterior parts of a car body on which a cation electrodeposition paint (A) is applied to cure paint films thereof by heating, applying in order a thermosetting water based second colored paint (C) and a thermosetting water based clear paint (D) on the exterior part, then curing the three layer paint films of the paints (B), (C) and (D) described above at the same time by heating, and further applying a thermosetting clear paint (E) on the exterior part to cure a paint film thereof by heating.

Abstract of the Disclosure

According to the present invention, provided is a coating method for a car body, comprising:

applying an organic solvent base thermosetting first colored paint (B) containing a neutralized product of a polyvalent carboxylic acid resin having an acid value of 5 to 100 mg KOH/g and an amino resin on both interior and exterior parts of a car body on which a cation electrodeposition paint (A) is applied to cure paint films thereof by heating,

applying in order a thermosetting water based second colored paint (C) and a thermosetting water based clear paint (D) on the exterior part,

then curing the three layer paint films of the paints (B), (C) and (D) described above at the same time by heating, and

further applying a thermosetting clear paint (E) on the exterior part to cure a paint film thereof by heating.

COATING METHOD FOR CAR BODY

The present invention relates to a coating method for an
5 interior part and an exterior part of a car body.

A body of a car is composed mainly of an interior part such
as a trunk room, an engine room and a door inside and an exterior
part such as a roof, a front hood, a trunk lid, a door panel and a
fender, and both interior and exterior parts are coated by, for exam-
10 ple, methods described below.

That is, (1) a method in which an organic solvent base
intermediate coat paint is applied on the exterior part of a body on
which an electrodeposition paint is applied and cured by heating, and
it is cured by heating; then, an organic solvent base top coat paint is
15 applied on both interior and exterior parts, and an organic solvent
base clear top coat paint is applied on the exterior part; and then,
both paint films are cured by heating at the same time; (2) a method
in which an organic solvent base color paint for an interior parts is
applied on the interior plate part of a body on which an electrodepo-
20 sition paint is applied and cured by heating, and then an organic
solvent base intermediate coat paint is applied on the exterior part
and cured by heating; a water base colored paint and an organic
solvent base clear paint are applied on the exterior part, and then
these paint films are cured by heating at the same time; and (3) a
25 method in which an intermediate coat paint is applied on the exterior
part of a body on which an electrodeposition paint is applied and
cured by heating, followed by heating and curing, and then a water
base color top coat paint is applied on both interior and exterior
parts; an organic solvent base clear top coat paint is applied on the
30 exterior part, and then both paint films are cured.

However, these coating methods have various problems,

and it is strongly desired to solve them. There are the problems that, for example, in the coating method (1), both of the colored paint and the clear paint are organic solvent types and therefore are not preferred from a viewpoint of pollution prevention and resource saving, and in the coating method (2), an organic solvent type paint for an interior part has to be prepared separately, and the paint film of the exterior part formed by applying the water base colored paint has an unsatisfactory finished appearance and that in the coating method (3), the paint films of both interior and exterior parts formed by applying the water base color paint have an unsatisfactory finished appearance.

An object of the present invention is to provide a novel coating method for an interior part and an exterior part of a car body, in which the preceding problems in the coating methods (1) to (3) described above are solved.

According to the present invention, provided is a coating method for a car body, comprising:

applying an organic solvent base thermosetting first colored paint (B) containing a neutralized product of a polyvalent carboxylic acid resin having an acid value of 5 to 100 mg KOH/g and an amino resin on both interior and exterior parts of a car body on which a cation electrodeposition paint (A) is applied to cure a paint film thereof by heating,

applying in order a thermosetting water based second colored paint (C) and a thermosetting water based clear paint (D) on the exterior part,

then curing the three layer paint films of the paints (B), (C) and (D) described above at the same time by heating, and

further applying a thermosetting clear paint (E) on the exterior part to cure a paint film thereof by heating.

The coating method of the present invention for a car body

(hereinafter called the present method) shall be explained below in further details.

Automobiles are intended to be coated by the method of the present invention include, for example, passenger cars, recreational vehicles, small cars, wagon, buses and trucks, and the bodies of these automobiles are composed principally of "an interior part" which is hard to be seen from the outside, such as a trunk room, an engine room and a door inside and "an exterior part" which is exposed to the outside, such as a roof, a front hood, a trunk lid, a door panel, a fender and a bumper. The materials of both parts thereof are mainly metals, but plastic parts exist together in a certain case. In the present specification, a general term of "a body" shall be given to these interior parts and exterior parts of a car.

According to the present method, the cation electrodeposition paint (A) is first applied on both interior and exterior parts of a body. This cation electrodeposition paint (A) is a water based under coat paint, and conventionally known paints can be used. To be specific, included are, for example, electrodeposition paints which are paints containing water base resins obtained by neutralizing with neutralizing agents, cationic resins such as epoxy resins, acryl resins and polybutadiene resins modified with amino group-containing compounds and in which further compounded, if necessary, are a cross-linking agent (for example, block polyisocyanate, alicyclic epoxy resins and the like), a colored pigment, a rust preventive pigment, an extender pigment and a hydrophilic organic solvent. The neutralizing agents described above include, for example, organic acids such as acetic acid, hydroxyacetic acid, propionic acid, butyric acid, lactic acid and glycine, and inorganic acids such as sulfuric acid, hydrochloric acid and phosphoric acid.

The cation electrodeposition paint (A) can be applied on a body, for example, by dipping the body in a bath of the cation electro-

deposition paint (A) which is adjusted to a solid matter concentration of about 5 to about 40 % by weight, preferably about 10 to about 30 % by weight and a pH of 5.5 to 8 to electrodeposit it according to a conventional method. The paint film has suitably a thickness of
5 about 10 to about 60 μm , particularly about 15 to about 30 μm in terms of a cured paint film, and the paint film can be cured by heating at about 140 to about 210°C for about 5 to about 40 minutes.

According to the present method, the organic solvent base first colored paint (B) is applied on the body on which the cation
10 electrodeposition paint (A) has been applied in the manner described above. The organic solvent base first colored paint (B) is an organic solvent base paint containing a neutralized product (B-1) of a polyvalent carboxylic acid resin having an acid value of 5 to 100 mg KOH/g, an amino resin (B-2) and a color pigment (B-3), and a paint
15 which forms a paint film of a solid colored or a metallic tone having a base covering property is advantageously used. This organic solvent base first colored paint (B) is applied on the cured paint film of the cation electrodeposition paint (A) prior to applying the thermosetting water based second colored paint (C).

20 Use of this first colored paint (B) makes it possible to finish evenly and smoothly the paint film of the second colored paint (C) described later applied on the coated surface thereof without having an effect exerted by an ambient humidity in coating.

The polyvalent carboxylic acid resin in the preceding
25 component (B-1) of the organic solvent base first colored paint (B) is a resin containing at least two carboxyl groups on an average in a molecule and having an acid value of 5 to 100 mg KOH/g, and conventionally known various resins which are described below can be used.

30 i) Acryl resins or vinyl resins obtained by copolymerizing carboxyl group-containing polymerizable monomers, hydroxyl

group-containing polymerizable monomers and other polymerizable monomers.

The carboxyl group-containing polymerizable monomer is a compound having a carboxyl group and a polymerizable unsaturated bond in a molecule and includes, for example, acrylic acid, methacrylic acid, maleic acid, itaconic acid and crotonic acid. The hydroxyl group-containing polymerizable monomer is a compound having a hydroxyl group and a polymerizable unsaturated bond in a molecule and includes, for example, hydroxyalkyl esters of (meth)acrylic acid having 1 to 8 carbon atoms, such as 2-hydroxyethyl (meth)acrylate and hydroxypropyl (meth)acrylate. The other polymerizable monomers are compounds which can be copolymerized with the carboxyl group-containing polymerizable monomers and the hydroxyl group-containing polymerizable monomers and which have a polymerizable unsaturated bond in a molecule and include, for example, alkyl or cycloalkyl esters of (meth)acrylic acid having 1 to 24 carbon atoms, such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate and decyl acrylate; functional (meth)acrylamides such as (meth)acrylamide, N-methyl(meth)acrylamide, N-ethyl(meth)acrylamide, diacetoneacrylamide, N-methylol(meth)acrylamide and N-butoxymethylacrylamide; glycidyl group-containing vinyl monomers such as glycidyl (meth)acrylate, glycidyl (meth)acrylamide and allyl glycidyl ether; and vinyl monomers such as styrene, vinyltoluene, vinyl propionate, α -methylstyrene, vinyl acetate, (meth)acrylonitrile, vinyl pivalate and Veova Monomer (product of Shell Chemical Co., Ltd.).

The acryl resins or vinyl resins described above can usually have a number average molecular weight falling in a range of 5000 to 40000, preferably 8000 to 30000.

ii) Polyester resins prepared by subjecting polyhydric

alcohols and polybasic acids to esterification reaction in an excess state of the acid components

The polyhydric alcohols are compounds having two or more alcoholic hydroxyl groups in a molecule and include, for example, ethylene glycol, diethylene glycol, propylene glycol, butanediol, pentanediol, 2,2-dimethylpropanediol, glycerin, trimethylolpropane and pentaerythritol. The polybasic acids are compounds having two or more carboxyl groups in a molecule and include, for example, phthalic acid, isophthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, maleic acid, succinic acid, adipic acid, sebacic acid, trimellitic acid, pyromellitic acid, and acid anhydrides thereof. Further, in the esterification reaction of these polyhydric alcohols with the polybasic acids, capable of being used are, if necessary, monohydric alcohols and epoxy compounds having glycidyl groups as a part of the alcohol components and/or monobasic acids such as benzoic acid and t-butylbenzoic acid as a part of the acid components. Further, included in the polyester resins are polyester resins modified with oil components such as castor oil, china wood oil, safflower oil, soybean oil, linseed oil, tall oil and coconut oil, or fatty acids thereof. These polyester resins can usually have a number average molecular weight falling in a range of 500 to 10000, preferably 1000 to 5000.

These polyvalent carboxylic acids resin can have an acid value falling in a range of 5 to 100 mg KOH/g, preferably 10 to 50 mg KOH/g and more preferably 30 to 50 mg KOH/g. If the acid value is smaller than 5, a compatibility thereof with the second colored paint (C) coated on the painted surface thereof is deteriorated, and moisture in the second colored paint (C) is not absorbed, so that produced are the defects of uneven run and sagging on the paint film of the above second colored paint (C), and a good appearance of the paint film is degraded. On the other hand, the acid value of larger than

100 reduces a water resistance of the coated film itself of the first colored paint (B) and therefore is not preferred.

The polyvalent carboxylic acid resin in the component (B-1) described above has preferably a hydroxyl group in order to
5 accelerate a cross-linking reaction thereof with the amino acid (B-2), and this elevates the performances such as a hardness, a water resistance and a weatherability of the paint film formed. The content of the hydroxyl group falls preferably in a range of 10 to 200 mg KOH/g, particularly 25 to 70 mg KOH/g in terms of a hydroxyl group
10 value.

These polyvalent carboxylic acid resins can be made water-soluble or water-dispersible by neutralizing with a basic material. Capable of being used as the above basic material are various basic materials such as, for xample, ammonia, methylamine,
15 ethylamine, dimethylamine, diethylamine, trimethylamine, triethylamine, dimethylethanolamine, diethanolamine and triethanolamine. The use amount thereof falls preferably in a range of about 0.1 to about 2 equivalents, particularly about 0.3 to about 1.2 equivalent based on the carboxylic group in the resin.

20 The amino resin (B-2) is a cross-linking agent for curing the polyvalent carboxylic acid resin and includes, for example, resins obtained by condensation or copolycondensation of melamine, benzo-guanamine, triazine base compounds, urea and dicyandiamide with formaldehyde, and resins obtained by modifying them with modifiers.
25 Among them, a melamine-formaldehyde resin is preferred.

The blending proportion of the neutralized product (B-1) of the polyvalent carboxylic acid resin to the amino resin (B-2) falls preferably in a range of 50 to 90 %, particularly 60 to 85 % for the (B-1) component and 10 to 50 %, particularly 15 to 40 % for the (B-2)
30 component based on the total solid matter weight of the both.

The first colored paint (B) is an organic solvent base paint

which contains the (B-1) component and the (B-2) component described above and which is prepared by dissolving or dispersing them in an organic solvent together with the color pigment (B-3). In particular, the so-called high solid type in which a solid content in coating is controlled to about 35 % by weight or more, particularly about 40 to about 60 % by weight is preferred from a viewpoint of pollution prevention.

The color pigment (B-3) is to provide the paint film of the first colored paint (B) with a base hiding property of a solid color or a metallic tone and, to be specific, includes, for example, solid color pigments such as titanium dioxide, zinc white, carbon black, red iron oxide, cadmium red, molybdenum red, cadmium yellow, chrome yellow, titan yellow, phthalocyanine blue, phthalocyanine green, carbazole violet, anthrapyridine, azo orange, flavanthrone yellow, isoindoline yellow, azo yellow, indathrone blue, dibromoanzathrone red, perylene red, azo red, anthraquinone red, quinacridone red and violet; and metallic pigments such as flaky aluminum, mica and micas covered with metal oxides. They can be used alone or in combination of two more kinds thereof.

The blending amount of the color pigment (B-3) is suitably such an amount that a light transmission ratio of the single paint film (thickness of the cured paint film: 30 μm) of the first colored paint (B) becomes 5 % or less, preferably 3 % or less in a wavelength of 400 to 700 nm. To be specific, it is varied depending on the coloring power of the pigment and can fall usually in a range of 1 to 250 parts by weight, preferably 5 to 150 parts by weight per 100 parts by weight of the resin solid matter (the total amount of the base resin and the curing agent). The light transmission ratio of the paint film of the first colored paint (B) is an average spectral light transmission ratio determined by means of a self-recording spectrophotometer (EPS-3T type manufactured by Hitachi, Ltd.) in a wavelength of 400

to 700 nm, wherein the paint (B) is applied on a glass plate so that a prescribed cured film thickness is obtained, and after curing, it is dipped in warm water of 60 to 70°C, peeled and dried to obtain a single paint film, which is used as a sample.

5 Conventional solvents for paints can be used for the organic solvent in the first colored paint (B) and include, for example, ester base solvents, ether base solvents, alcohol base solvents, amide base solvents, ketone base solvents, aliphatic hydrocarbon base solvents, alicyclic hydrocarbon base solvents and aromatic hydrocar-
10 bon base solvents. In particular, among them, preferably used as at least a part of the organic solvent are hydrophilic organic solvents such as ethylene glycol monomethyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, dioxane, ethylene glycol monomethyl ether, ethylene glycol mono-
15 ethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol monobutyl ether, methyl alcohol, ethyl alcohol, allyl alcohol, n-propyl alcohol, isopropyl alcohol, ter-
20 tiary butyl alcohol, ethylene glycol, 1,2-propylene glycol and monoethers thereof, 1,3-butylene glycol, 2,3-butylene glycol, hexylene glycol, hexaenediol, dipropylene glycol and monoethers thereof, acetone and diacetone alcohol. Organic solvents which are dissolved in water at 20°C in an amount of 50 parts by weight or more per 100 parts by weight of water are suited as the hydrophilic organic sol-
25 vent. The ratio of the hydrophilic organic solvent to the whole organic solvents falls suitably in a range of 20 % by weight or more, particularly 40 to 100 % by weight based on the total weight of the organic solvents contained in the first colored paint (B) in coating.

 The first colored paint (B) has preferably a color tone
30 which is approximate to that of a multi-layer coated film comprising the first colored paint (B), the water based second colored paint (C),

the water based clear paint (D) and the clear paint (E) which are coated on the exterior part.

The first colored paint (B) is coated on the electrodeposited paint film surfaces of both interior part and exterior part of the body which are formed by applying the cation electrodeposition paint (A) and curing the paint film thereof by heating. Coating is preferably carried out by a method such as air spray, airless spray and electrostatic coating so that the film thickness becomes about 2 to about 60 μm , particularly about 5 to about 25 μm in terms of a cured paint film, wherein the viscosity in coating is controlled to about 15 to about 60 seconds, particularly about 15 to about 35 seconds (20°C) in terms of Ford cup #4.

In the present method, the first colored paint (B) is coated on the electrodeposited paint film surfaces of both interior part and exterior part of the body in the manner described above and left standing at a room temperature to 100°C or lower for 1 to 10 minutes, and then the thermosetting water based second colored paint (C) is coated on an uncured paint surface of the first colored paint (B) on the exterior part.

Used as the thermosetting water based second colored paint (C) is a water based liquid paint which uses water as a principal solvent or dispersant and contains a water-soluble or water-dispersible thermosetting resin composition and which forms a paint film of a solid color or a metallic tone.

The thermosetting resin composition described above includes, for example, a composition comprising a base resin such as an acryl resin, a vinyl resin and a polyester resin which have cross-linking functional groups such as a hydroxyl group and are water-soluble or water-dispersible and an amino resin as a cross-linking agent.

The water-soluble acryl resin and vinyl resin include

resins which are obtained by copolymerizing carboxyl group-containing polymerizable monomers, hydroxyl group-containing polymerizable monomers and other polymerizable monomers and which have an acid value falling in a range of 20 to 100 mg KOH/g, particularly 30 to 80 mg KOH/g and a hydroxyl group value falling in a range of 20 to 200 mg KOH/g, particularly 30 to 120 mg KOH/g.

The polymerizable monomers given as the examples in i) of the component (B-1) can be used for these polymerizable monomers, and the polymerizable monomers described above can be polymerized in an organic solvent which is compatible with water such as butyl cellosolve using a radical polymerization initiator such as azobisisobutyronitrile, benzoyl peroxide and dibutyl peroxide.

The water-soluble acryl resin and vinyl resin are neutralized with basic substances including ammonia or amines such as triethylamine, monoethanolamine, diethanolamine, triethanolamine and dimethylaminoethanol, or hydroxides of alkaline metals such as sodium hydroxide, and then water and, if necessary, an organic solvent which is compatible with water are added, whereby they are diluted with water in order to obtain the suitable solid content.

The water-dispersible acryl resin can be produced, for example, by emulsion-polymerizing the polymerizable monomers described above in a water base medium by a conventionally known method using an ionic or non-ionic, low molecular or high molecular surface active substance or a water-soluble resin as a dispersion stabilizer.

The water-soluble polyester resin can be obtained, for example, by using a resin having an acid value falling in a range of 15 to 100 mg KOH/g, particularly 20 to 80 mg KOH/g and a hydroxyl group value falling in a range of 20 to 200 mg KOH/g, particularly 40 to 150 mg KOH/g among the polyester resins explained in the first colored paint (B) and neutralizing it with a basic substance in the

same manner as in the water-soluble acryl resin described above.

An amino resin is preferably used as the cross-linking agent, and this is reacted with the base resin by heating to form a three-dimensional cured paint film. Such amino resin includes
5 compounds obtained by condensation or copolycondensation of melamine, benzoguanamine, urea and dicyandiamide with formaldehyde, and compounds obtained by modifying them with alcohols having 1 to 8 carbon atoms and carboxyl group-containing amino resins can be used as well. These amino resins can be produced by reacting them
10 in an alkalinity or acidity by a conventionally known method usually using about 0.5 to about 2 equivalents of formaldehyde based on one equivalent of the amino group as a pH controlling agent (for example, ammonia, sodium hydroxide and amines). The cross-linking agent suited in the second colored paint (C) is a water-soluble melamine-
15 formaldehyde resin.

With respect to the blending proportion of the base resin to the cross-linking agent in the second colored paint (C), that of the former falls preferably in a range of about 50 to about 90 % by weight, particularly about 60 to about 85 % by weight, and that of the
20 latter falls preferably in a range of about 10 to about 50 % by weight, particularly about 15 to about 40 % by weight based on the total solid matter weight of both components.

The second colored paint (C) is a water based paint prepared by blending these thermosetting resin compositions with a
25 solid color pigment and/or a metallic pigment, and those explained in the first colored paint (B) are suitably used for the pigment which can be blended. These pigments can be used alone or in combination of two or more kinds thereof.

The blending amount of these pigments is preferably such
30 an amount as to colored the paint film of the second colored paint (C) and provide the composite layer paint film formed on the exterior

part with a good appearance in terms of a color and to provide a base covering property of such a degree or more that a color tone of the paint film of the first colored paint (B) present on a lower layer thereof can not be visible through the above paint film. Accordingly, 5 the single paint film (cured paint film thickness: 15 μm) of the second colored paint (C) has preferably a light transmission ratio of 5 % or less, particularly preferably 3 % or less in a wavelength falling in a range of 400 to 700 nm.

The second colored paint (C) is controlled to a solid matter 10 concentration of 15 to 65 % by weight, preferably 18 to 40 % by weight and a viscosity of 15 to 60 seconds, preferably 20 to 50 seconds in terms of Ford cup #4/20°C, and it is preferably coated on the uncured coated surface of the paint (B) coated on the exterior part by a method such as air spray, airless spray and electrostatic coating so 15 that the film thickness becomes about 5 to about 25 μm , particularly about 10 to about 20 μm in terms of a cured paint film thickness.

In the present method, after coating the second colored paint (C) on the exterior part, the thermosetting water based clear paint (D) is coated on the uncured coated surface thereof. In prior to 20 coating of this thermosetting water based clear paint (D), it is possible to pre-dry both paint films of the first colored paint (B) and the second colored paint (C) at a temperature of about 50 to about 100°C. This pre-drying is preferably carried out in such a manner that a cross-linking reaction of both paint films described above does not 25 nearly or completely proceed (gel content: 0 to 5 %) and that the organic solvent and water are nearly or completely evaporated.

Then, the thermosetting water based clear paint (D) is coated on the uncured coated surface of the second colored paint (C) coated on the exterior part. Used as this water based clear paint (D) 30 is a water based liquid paint which contains a water-soluble or water-dispersible thermosetting resin composition and is prepared by

blending, if necessary, a solid color pigment or a metallic pigment and which forms a colorless, transparent or colored, transparent paint film.

The clear paint (D) can be prepared by blending the
5 components removing a part or all of the solid color pigment or metallic pigment from the composition of the second colored paint (C) described above, and the content of these pigments resides preferably in such a degree that the single paint film has a transparency and that a color tone of the paint film of the second colored paint (C) can
10 be visible through the above paint film, and it is preferably smaller than the content of the pigment contained in the second colored paint (C).

To be specific, the pigment is preferably blended in such an amount that the single paint film (film thickness of the cured
15 paint film: 15 μm) of the clear paint (D) has a light transmission ratio falling in a range of 6 to 95 %, particularly 10 to 90 % and more particularly 20 to 80 % in a wavelength falling in a range of 400 to 700 nm.

The clear paint (D) is controlled to a viscosity of about 10
20 to about 50 seconds, preferably about 20 to about 40 seconds (20°C) in coating in terms of Ford cup #4 and preferably applied on the uncured paint film of the second colored paint (C) by a method such as air spray coating, airless spray coating and rotary type electrostatic coating so that the film thickness becomes about 5 to about 30 μm ,
25 particularly about 10 to about 25 μm in terms of a cured paint film.

In the present method, the second colored paint (C) has an affinity with the clear paint (D). To be specific, a part or all of the thermosetting resin compositions contained in the above both paints are preferably common or analogous, or if varied, an affinity is
30 preferably present between them.

In the present method, the electrodeposition paint (A) is

coated on the interior part and the exterior part of a car body, and the paint films thereof are cured by heating; then, the first colored paint (B) is coated on the interior part and the exterior part; the second colored paint (C) and the clear paint (D) are applied in order
5 on the exterior part without curing the paint films by heating and then heated usually at about 100 to about 170°C, preferably about 130 to about 150°C for about 10 to about 40 minutes to cure these three layer paint films at the same time; and then, the thermosetting clear paint (E) is coated on the cured paint surface of the clear paint
10 (D).

The thermosetting clear paint (E) is a paint which forms a colorless, transparent or colored, transparent paint film, and conventionally known liquid paints of an organic solvent solution type, a nonaqueous dispersion type (NAD) and a powder slurry type and
15 powder paints which scarcely or do not completely contain solvents can be used. Further, high solid content type paints having a solid content of 35 % by weight or more, preferably 40 to 80 % by weight in coating can suitably be used as well.

The clear paint (E) is applied on the cured paint surface of
20 the clear paint (D) as an uppermost layer paint film for the purpose of further elevating a good appearance, a finished appearance, a weatherability, a chemical resistance, a water resistance, a moisture resistance and a sharpness of the composite layer paint film formed on the exterior part. To be specific, included are paints containing a
25 thermosetting resin composition comprising a base resin such as an acryl resin or vinyl resin having a cross-linking functional group such as a hydroxyl group and a carboxyl group, an amino resin, a block polyisocyanate compound and a cross-linking agent such as an epoxy group-containing compound.

30 The liquid clear paint (E) is controlled to a viscosity of about 10 to about 60 seconds, preferably about 20 to about 50 seconds

(20°C) in coating in terms of Ford cup #4 and preferably applied on the cured paint film of the color paint (D) by a method such as air spray, airless spray and electrostatic coating so that the film thickness becomes about 5 to about 60 μm , particularly about 10 to about 50 μm in terms of a cured paint film. The paint film of the clear paint (E) can be cured by heating usually at a temperature of about 100 to 170°C, preferably about 130 to about 150°C for about 10 to about 40 minutes.

Effects which shall be described below are obtained according to the method of the present invention described above.

(1) The neutralized polyvalent carboxylic acid resin contained in the uncured paint film of the first colored paint (B) shows a strong water absorbing property, so that moisture contained in the colored paint (C) coated on the paint surface thereof is absorbed, and the viscosity goes up suddenly. As a result thereof, sagging, poor hiding and popping of the paint film of the colored paint (C) are prevented from being produced and in addition thereto, when the paint film thereof has a metallic tone, the metallic pigments are aligned parallel to the paint surface, uniformly and regularly, whereby the paint film which is free of metallic mottling and has a uniform metallic feeling can be formed.

(2) The paint film of the first colored paint (B) has an excellent base covering property, and therefore the composite layer paint film formed on the exterior part of the body prevents solar beams coming from the outside from reaching the electrodeposited paint film, so that the interlayer adhesive property can be elevated.

(3) The second colored paint (C) has a good compatibility with the first colored paint (B), and therefore even if coated under a low humidity atmosphere, defects such as face roughening are not caused.

(4) The clear paint (E) is coated on the cured paint sur-

face of the clear paint (D), so that defects such as mixed layer are not caused, and a selection range thereof is not restricted.

(5) The clear paint (D) has clearness, and therefore the finished coated surface which is excellent in a finished appearance
5 such as glamourness, flatness, distinctness of image, deepness, high glossiness and a high metallic feeling can be obtained.

(6) Both interior part and exterior part are painted with the hydrophilic first colored paint (B) which forms a hydrophilic paint film, so that even if coated on the interior part having a complicated
10 shape, poor hiding and sagging are prevented.

(7) Even if defective parts such as dusts and irregularities which are produced before this step are polished and removed by coating the clear paint (D) and curing by heating, the composite layer paint film formed by coating the paint (E) is notably excellent in
15 distinctness of image and gloss.

The present invention shall more specifically be explained below with reference to examples and comparative examples. Part and percentage are based on weight, and a film thickness of a paint film is represented by that of a cured paint film.

20

1. Preparation of samples

1) Electrodeposited steel plate

"Elecron #9400" (trade name, polyamide-modified epoxy resin·block polyisocyanate base cation electrodeposition paint manu-
25 factured by Kansai Paint Co., Ltd.) was diluted with deionized water so that the solid matter concentration became 16 %. A steel plate (size: 100 × 100 × 0.8 mm) was immersed in an electrodeposition bath in which a pH was controlled to a range of 5.5 to 8.0 and electrodeposited by a conventional method, followed by heating at about
30 175°C for 30 minutes to cure the paint film. The film thickness was 20 µm.

2) Organic solvent base thermosetting first colored paint (B)

Base resin (B1):

A reactor which was charged with 60 parts of ethyl cello-
solve and heated at 120°C was charged with a monomer mixture
5 comprising 30 parts of methyl methacrylate, 23 parts of ethyl acryl-
ate, 30 parts of butyl acrylate, 12 parts of hydroxyethyl methacrylate,
5 parts of acrylic acid and 2 parts of α,α' -azobisisobutyronitrile in 3
hours by means of a quantitative pump to polymerize them, whereby
obtained was an acryl resin solution having an acid value of 40 mg
10 KOH/g, a hydroxyl group value of 52 mg KOH/g, a number average
molecular weight of about 10000 and a resin solid content of 60 %.
Added to 100 parts of this acryl resin solution was 3.5 parts of
2-amino-2-methylpropanol to neutralize it, and then the solution was
diluted with isopropyl alcohol to obtain an acryl resin neutralized
15 solution (B1) having a resin solid content of 50 %.

Base resin (B2):

A reactor was charged with 0.7 mole of neopentyl glycol,
0.3 mole of trimethylolpropane, 0.4 mole of phthalic anhydride and
0.5 mole of adipic acid to react them at 200 to 230°C for 5 hours and
20 then charged with 0.03 mole of trimellitic anhydride to further carry
out the reaction at 180°C for one hour. Then, butyl cellosolve was
added thereto to obtain a polyester resin solution having an acid
value of 40 mg KOH/g, a number average molecular weight of about
6000 and a resin solid content of 70 %. Added to 100 parts of this
25 polyester resin solution was 4 parts of 2-amino-2-methylpropanol to
neutralize it, and then the solution was diluted with isopropyl alcohol
to obtain a polyester resin neutralized solution (B2) having a resin
solid content of 60 %.

Preparation of first colored paint (B):

30 The components described above were mixed in a blending
composition shown in the following Table 1 to obtain first colored

paints a, b and c.

Table 1

5			First colored paint (B)		
			a	b	c
	Base resin	(B1)	140	140	—
		(B2)	—	—	117
	Cymel 370 (remark 1)		34	34	34
	Titan white pigment		75	75	75
10	Blue G316 (remark 2)		5	5	5
	Carbon black		3	3	3
	Isopropyl alcohol		140	150	125
	Paint solid content (%)		36	35	38
	Viscosity (second) (remark 3)		25	25	25
15	Light transmission ratio (remark 4)		0.1 >	0.1 >	0.1 >

Remark 1: trade name, water-soluble melamine manufactured by Mitsui Cytec Industries Co., Ltd.

20 Remark 2: trade name, blue pigment manufactured by Sanyo Color Works, Ltd.

Remark 3: Ford cup #4/20°C

Remark 4: measured value in the paint film having a film thickness of 20 μm

25 3) Thermosetting water based second colored paint (C)

Preparation of 20 % acryl resin emulsion (C1):

A reactor was charged with 140 parts of deionized water, 2.5 parts of 30 % "Newcol 707SF" (surfactant manufactured by Nihon Nyukazai Co., Ltd.) and one part of the following monomer mixture
 30 (1) (remark 5) and mixed by stirring in nitrogen gas flow, and 3 parts

of a 3 % ammonium persulfate aqueous solution was added thereto at 60°C. Then, after elevating the temperature to 80°C, a monomer emulsion comprising 79 parts of the monomer mixture (1) (remark 5), 2.5 parts of 30 % "Newcol 707SF", 4 parts of the 3 % ammonium persulfate aqueous solution and 42 parts of deionized water was added to the reactor in 4 hours by means of a quantitative pump. After finishing addition, the solution was ripened for one hour. Further, 20.5 parts of the following monomer mixture (2) (remark 6) and 4 parts of the 3 % ammonium persulfate aqueous solution were dropwise added to the reactor in a parallel way at the same time in 1.5 hour. After finishing addition, the solution was ripened for one hour and diluted with 30 parts of deionized water, followed by filtering through a nylon cloth of 200 mesh at 30°C. Deionized water was further added to this filtrate, and the solution was adjusted to a pH of 7.5 with dimethylaminoethanol to obtain an acryl resin emulsion (C1) having an average particle diameter of 0.1 μm and a non-volatile matter content of 20 %.

(Remark 5) monomer mixture (1): a mixture comprising 55 parts of methyl methacrylate, 8 parts of styrene, 9 parts of n-butyl acrylate, 5 parts of 2-hydroxyethyl acrylate, 2 parts of 1,6-hexanediol diacrylate and one part of methacrylic acid.

(Remark 6) monomer mixture (2): a mixture comprising 5 parts of methyl methacrylate, 7 parts of n-butyl acrylate, 5 parts of 2-ethylhexyl acrylate, 3 parts of methacrylic acid and 0.5 part of 30 % "Newcol 707SF".

Preparation of water based second colored paint (C):

The components described above were mixed in a blending composition shown in the following Table 2 to obtain thermosetting second colored paints a and b.

Table 2

		Second colored paint (C)	
		a	b
5	Base resin (B1)	50	50
	(B2)	50	50
	Emulsion (C1)	100	100
10	Cymel 370 (remark 1)	34	34
	Alupaste 504 AR (remark 7)	—	5
	Blue G316	5	—
	Deionized water	220	220
	Paint solid content (%)	25	25
	Viscosity (second) (remark 3)	30	30
	Light transmission ratio (remark 8)	40	40

15

Remark 7: flaky aluminum paste manufactured by Toyo Aluminum K.K.

Remark 8: light transmission ratio is a measured value in the paint film having a film thickness of 15 μm

20 4) Preparation of thermosetting water based clear paint (D):

A clear paint d was prepared in the same manner as described above, except that "Blue G316" was removed from the composition of the thermosetting water based second colored paint a.

5) Thermosetting water based clear paint (E)

25 Base resin (E1):

A reactor which was charged with 40 parts of Swasol #1000 (product of Cosmo Oil Co., Ltd.) and heated at 120°C was charged with a monomer mixture comprising 30 parts of styrene, 35 parts of butyl acrylate, 10 parts of 2-ethylhexyl acrylate, 25 parts of hydroxyethyl acrylate and 4 parts of α,α' -azobisisobutyronitrile in 3

hours by means of a quantitative pump to polymerize them. As a result thereof, obtained was an acryl resin solution (E1) having a hydroxyl group value of 120 mg KOH/g, a number average molecular weight of about 6000 and a resin solid content of 70 %.

5 60 % acryl resin non-aqueous dispersion (E2):

A reactor was charged with 58 parts of 60 % U-Van 28-60 (product of Mitsui Chemical Inc., a melamine resin solution), 30 parts of n-heptane and 0.15 part of benzoyl peroxide and heated to 95°C. Dropwise added thereto in 3 hours was a mixture comprising 15
10 parts of styrene, 9 parts of acrylonitrile, 13 parts of methyl methacrylate, 15 parts of methyl acrylate, 1.8 part of n-butyl acrylate, 10 parts of 2-hydroxyethyl methacrylate, 1.2 part of acrylic acid, 0.5 part of benzoyl peroxide, 5 parts of n-butanol, 30 parts of Shellsol 140 (remark 9) and 9 parts of n-heptane, and after one hour passed at the
15 above temperature, a mixture comprising 0.65 part of t-butyl peroctanoate and 3.5 parts of Shellsol 140 (remark 9) was dropwise added thereto in one hour. Then, stirring was continued for 2 hours while maintaining a temperature of 95°C. Subsequently, the pressure was reduced to remove 34 parts of the solvent to obtain an acryl resin
20 non-aqueous dispersion (E2) having a resin solid content of 60 % and a vanish viscosity A (Gardner bubble viscosity).

(Remark 9): trade name, hydrocarbon base solvent, product of Shell Chemical Co., Ltd.

Preparation of thermosetting water based clear paint (E):

25 Mixed were 57 parts of the acryl resin solution (E1) of 70 %, 50 parts of the 60 % acryl resin non-aqueous dispersion (E2), 30 parts of Cymel 303 (remark 10), 4 parts of a 25 % dodecylbenzenesulfonic acid solution and 0.5 part of BYK-300 (remark 11), and the viscosity was adjusted to 30 seconds (Ford cup #4/20°C) with Swasol
30 #1000 (remark 12) to obtain a clear paint e having a resin solid content of 55 %.

Remark 10: trade name, monomeric melamine resin manufactured by Mitsui Cytec Industries Co., Ltd.

Remark 11: trade name, surface controlling agent manufactured by BYK Chemie Japan

5 Remark 12: trade name, aromatic hydrocarbon base solvent manufactured by Cosmo Oil Co., Ltd.

2. Examples

Examples 1 to 3

The first colored paints (B)-a, b and c which were adjusted
10 to a viscosity of 25 seconds (Ford cup #4/20°C) were applied respectively on the whole surface of the electrodeposited steel plate at a relative humidity of 75 % RH by means of an air spray so that the film thickness became 20 µm, and the steel plate was left standing at a room temperature for about 5 minutes. Then, the second colored
15 paints (C)-a and b which were adjusted to a viscosity of 30 seconds (Ford cup #4/20°C) were applied respectively on the uncured paint film surface of the first colored paint in a lower half of this coated steel plate at a relative humidity of 75 % RH by means of an air spray so that the film thickness became 15 µm, and the steel plate
20 was left standing at a room temperature for about 5 minutes. Thereafter, the thermosetting water based clear paint (D)-d was applied thereon at a relative humidity of 75 % RH by means of an air spray so that the film thickness became 5 µm, and the steel plate was left standing at a room temperature for about 3 minutes, followed by
25 heating at 140°C for 30 minutes to cross-link and cure a three layer paint film comprising the first colored paint, the second colored paint and the clear paint at the same time.

Then, the thermosetting clear paint (E)-e which was adjusted to a viscosity of 30 seconds (Ford cup #4/20°C) was applied
30 by means of an air spray so that the film thickness became about 45 µm in terms of a cured film thickness, and the steel plate was left

standing at a room temperature for about 5 minutes, followed by heating at 140°C for 30 minutes to cross-link and cure the paint film.

3. Performance test results

The performance tests of the composite layer paint films obtained in the examples described above were carried out, and the results thereof are shown in Table 3.

The tests were carried out by the following methods.

Flatness:

Determined by means of a tension meter (manufactured by RENAULY Co., Ltd.). It is meant that the larger the value is, the more excellent the flatness is.

Distinctness of image:

Determined by means of an image gross measuring instrument NSIC (manufactured by Suga Test Instrument Co., Ltd.). It is meant that the larger the value is, the more excellent the distinctness of image is.

Water resistance:

The sample coated plate was immersed in warm water of 40°C for 240 hours, and then the state of the coated surface was visually evaluated.

○: nothing abnormal observed

△: defects such as poor gloss and blistering are slightly observed

×: defects such as poor gloss and blistering are notably observed

Table 3

5			Example		
			1	2	3
	Electrodeposition paint (A)		Elecron #9400		
		Baking condition	175°C, 20 minutes		
		Film thickness (μm)	20	20	20
10	First colored paint (B)		a	b	c
		Baking condition	room temperature 5 minutes		
		Film thickness (μm)	20	20	20
	Second colored paint (C)		a	a	b
		Baking condition	room temperature 5 minutes		
Film thickness (μm)		15	15	15	
15	Clear paint (D)		d	d	d
		Baking condition	140°C, 30 minutes		
		Film thickness (μm)	5	5	5
	Clear paint (E)		e	e	e
		Baking condition	140°C, 30 minutes		
Film thickness (μm)		45	45	45	
Performance test results					
Flatness		20	21	21	
Distinctness of image		78	80	81	
Water resistance		○	○	○	

CLAIMS:

1. A coating method for a car body, comprising:
applying an organic solvent base thermosetting first colored paint (B) containing a neutralized product of a polyvalent carboxylic acid resin having an acid value of 5 to 100 mg KOH/g and an amino resin on both interior and exterior parts of a car body on which a cation electrodeposition paint (A) is applied to cure paint films thereof by heating,
applying in order a thermosetting water based second colored paint (C) and a thermosetting water based clear paint (D) on the exterior part,
then curing the three layer paint films of said paints (B), (C) and (D) at the same time by heating, and
further applying a thermosetting clear paint (E) on the exterior part to cure a paint film thereof by heating.
2. The method as described in claim 1, wherein the first colored paint (B) forms a paint film of a solid color or a metallic tone having a base covering property.
3. The method as described in claim 1, wherein the polyvalent carboxylic acid resin in the first colored paint (B) is selected from:
 - i) an acryl resin or vinyl resin having a number average molecular weight of 5000 to 40000 obtained by copolymerizing a carboxyl group-containing polymerizable monomer, a hydroxyl group-containing polymerizable monomer and other polymerizable monomers, and
 - ii) a polyester resin prepared by subjecting a polyhydric alcohol and a polybasic acid to esterification reaction in an excess state of the acid component.
4. The method as described in claim 1, wherein the polyvalent carboxylic acid resin in the first colored paint (B) has an acid

value falling in a range of 10 to 50 mg KOH/g.

5. The method as described in claim 1, wherein the polyvalent carboxylic acid resin in the first colored paint (B) has a hydroxyl group, and a content of the hydroxyl group falls in a range of 10 to 200 mg KOH/g in terms of a hydroxyl group value.
6. The method as described in claim 1, wherein the amino resin in the first colored paint (B) is selected from resins obtained by condensation or copolycondensation of melamine, benzoguanamine, triazine base compounds, urea and dicyandiamide with formaldehyde, and resins obtained by modifying them with modifiers.
7. The method as described in claim 6, wherein the amino resin in the first colored paint (B) is a melamine-formaldehyde resin.
8. The method as described in claim 1, wherein the first colored paint (B) contains the neutralized product of the polyvalent carboxylic acid resin falling in a range of 50 to 90 % and the amino resin falling in a range of 10 to 50 % based on the total solid matter weight of the neutralized product of the polyvalent carboxylic acid resin and the amino resin.
9. The method as described in claim 1, wherein the first colored paint (B) forms a paint film in which a single paint film (thickness of the cured paint film: 30 μm) has a light transmission ratio of 5 % or less in a wavelength falling in a range of 400 to 700 nm.
10. The method as described in claim 1, wherein the first colored paint (B) is applied so that the film thickness becomes about 2 to about 60 μm in terms of a cured paint film thickness.
11. The method as described in claim 1, wherein the first colored paint (B) is applied on the electrodeposited paint film surfaces of both interior part and exterior part of the car body and left standing at a room temperature to 100°C or lower for 1 to 10 minutes, and then the thermosetting water based second colored paint (C) is

applied on an uncured paint surface of the first colored paint (B) on the exterior part.

12. The method as described in claim 1, wherein the second colored paint (C) contains a water-soluble or water-dispersible acryl resin, vinyl resin or polyester resin having a cross-linking functional group and forms a paint film of a solid color or a metallic tone.

13. The method as described in claim 1, wherein the second colored paint (C) forms a paint film in which a single paint film (thickness of the cured paint film: 15 μm) has a light transmission ratio of 5 % or less in a wavelength falling in a range of 400 to 700 nm.

14. The method as described in claim 1, wherein the second colored paint (C) is applied so that the film thickness becomes about 5 to about 25 μm in terms of a cured paint film thickness.

15. The method as described in claim 1, wherein in prior to coating of the thermosetting water based clear paint (D), both paint films of the first colored paint (B) and the second colored paint (C) are pre-dried at a temperature of about 50 to about 100°C.

16. The method as described in claim 1, wherein the water based clear paint (D) is a water based liquid paint which forms a colorless, transparent or colored, transparent paint film.

17. The method as described in claim 1, wherein the water based clear paint (D) is applied so that the film thickness becomes about 5 to about 30 μm in terms of a cured paint film thickness.

18. The method as described in claim 1, wherein the clear paint (E) is a liquid paint of an organic solvent solution type, a nonaqueous dispersion type (NAD) or a powder slurry type, or a powder paint which forms a colorless, transparent or colored, transparent paint film.

19. The method as described in claim 1, wherein the clear paint (E) is applied so that the film thickness becomes about 5 to

about 60 μm in terms of a cured paint film thickness.

20. A car body coated by the method as described in any of claims 1 to 19.