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(54) **METHOD OF MULTILAYER COATING**

(57) The present invention provides a method for forming a multi-layer coating film, which is characterized by applying a cationic electrocoating on a metal-made material to be coated, heat-curing the resulting electrocoating film, applying, on the heat-cured electrocoating film, a first color base coating having a sublayer-hiding powder, applying, on the resulting coating film without substantially curing the film, a second color base coating having transparency, heating the two films of the first color base coating and the second color base coating to cure them, then applying a clear coating, and heat-curing the resulting clear coating film. According to the present invention, there can be formed a multi-layer coating film superior in finish appearance, aesthetic effect, corrosion resistance, weatherability, chipping resistance, physical properties, etc.

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**Description****Technical Field**

5 The present invention relates to a method for forming a multi-layer coating film, which can be applied at a low cost and which can form, on a metal-made substrate, especially an automobile body panel, a multi-layer coating film superior in finish appearance, aesthetic effect, corrosion resistance, weatherability, chipping resistance, physical properties, etc.

**Background Art**

Body panels of automobiles, bicycles, electric appliances, etc. wherein fine appearance is an important requirement, have hitherto been subjected to finish coating with an organic solvent type thermosetting coating capable of forming a coating film superior in smoothness, distinctness of image gloss, weatherability, etc. Usually, the coating process for such a body panel comprises applying a cationic electrocoating for providing of corrosion resistance, then applying an intermediate coating for providing of weatherability and chipping resistance, heat-curing each of the resulting two coating films, applying, as a top coat for providing of aesthetic effect, a thermosetting coating containing a coloring pigment and/or a metallic pigment (the thermosetting coating is hereinafter referred to as "color base coating"), air-drying the resulting coating film, then applying thereon a thermosetting clear coating, and heat-curing the formed two coating films simultaneously (this coating steps is a so-called two-coat one-bake method).

In recent years, the requirements for resource saving, reduction in number of operational steps, pollution control and lower application cost have become stronger. Hence, it is desired to develop a coating method not requiring the step for application of intermediate coating.

**Disclosure of the Invention**

The present inventors made an intensive study with an aim of developing a coating method which can be applied at a low cost, which can form a coating film greatly superior in finish appearance, aesthetic effect, corrosion resistance, weatherability, chipping resistance, etc., and which is advantageous in resource saving and pollution control.

30 As a result, the present inventors found out that the above aim can be achieved using no intermediate coating, by using a cationic electrocoating, two kinds of color base coatings of different functions, and a clear coating. The present invention has been completed based on the finding.

Thus, according to the present invention, there is provided a method for forming a multi-layer coating film, which is characterized by applying a cationic electrocoating (A) on a metal-made material to be coated, heat-curing the resulting electrocoating film, applying, on the heat-cured electrocoating film, a first color base coating (B) having a sublayer-hiding powder, applying, on the resulting coating film without substantially curing the film, a second color base coating (C) having transparency, heating the two films of the first color base coating and the second color base coating to cure them, then applying a clear coating (D), and heat-curing the resulting clear coating film.

40 The feature of the present invention lies in that the two color base coatings (B) and (C) both as top coat can be applied on the film of an ordinary cationic electrocoating by a two-coat one-bake method, without applying an ordinary intermediate coating on said film.

In the present method, the top coat is directly applied on the baked and cured film of a cationic electrocoating without applying an intermediate coating on said film; nevertheless, it has been found that there occurs no weather-induced peeling (the weather-induced peeling is a phenomenon in which a light passes through a top coat film and photochemically deteriorates an electrocoating film as sublayer and, as a result, intercoat adhesion failure occurs between the two films during outdoor exposure) because the first color base coating (B) has a sublayer-hiding power. Moreover, according to the present method, here can be obtained an advantage that the application cost of can be made lower because the step of applying an intermediate coating can be eliminated.

50 The present method also has a feature that since the second color base coating (C) has a color and transparency, the coating film obtained can have excellent finish appearance of fattiness, smoothness, distinctness of image gloss, depth feeling, high luster, strong metallic feeling, no mottling, etc.

Therefore, combined use of the first color base coating (B) and the second color base coating (C) according to the present invention enables formation of a novel multi-layer coating film having an aesthetic effect which has been unobtainable heretofore.

55 The present method has a further advantage that since a clear coating is applied on the heat-cured film of the color base coating, there can be used, as the clear coating, a clear coating of any type such as solvent type, aqueous type, powder type or the like.

The coating method of the present invention is hereinafter described in more detail.

Metal-made material to be coated

There is no particular restriction as to the material to be coated according to the present method, as long as the material is a metal product to which cationic electrodeposition is applicable. As the material to be coated, there can be mentioned, for example, iron, copper, aluminum, tin, zinc, other metals, alloys containing these metals, and articles which are plated or vapor-deposited with these metals. Specific examples of the material to be coated include body panels of automobiles such as passenger cars, trucks, autobicycles, buses and the like, formed using members made of the above metals. Preferably, these materials to be coated are beforehand subjected to a chemical treatment with a phosphoric acid salt, a chromic acid salt or the like.

Cationic electrocoating (A)

The cationic electrocoating (A) used in the present method is a coating to be directly applied on the above-mentioned metal-made material to be coated. There is no strict restriction as to the type of the cationic electrocoating (A), and there can be used one of various cationic electrocoatings which are known per se. Specific examples of the cationic electrocoating (A) include coatings which contain, as a main component, a water-soluble or water-dispersible resin obtained by neutralizing, with a neutralizing agent, a resin having a base value of generally about 30-200, such as epoxy resin, acrylic resin, polybutadiene resin or the like (all of these resins are modified with an amino group-containing compound) and which further contain, as necessary, a crosslinking agent (e.g. a blocked polyisocyanate or an aliphatic cyclic epoxy resin), a coloring pigment, a rust-preventive pigment, an extender pigment, a hydrophilic organic solvent, etc. As the neutralizing agent, there can be used, for example, an organic acid such as acetic acid, hydroxyacetic acid, propionic acid, butyric acid, lactic acid, glycine or the like; or an inorganic acid such as sulfuric acid, hydrochloric acid, phosphoric acid or the like. The amount of the neutralizing agent used is appropriately about 0.1-0.4 in terms of neutralization equivalent relative to the base value of the resin.

The cationic electrocoating (A) is diluted with a deionized water or the like so that the solid content becomes about 5-40% by weight, preferably about 10-30% by weight; and can be electrodeposited by an ordinary method with the pH being kept at 5-8, preferably 5.5-7. The resulting coating film can be cured at about 140-210°C, preferably at about 160-190°C. The thickness of the coating film is preferably about 10-60  $\mu\text{m}$ , particularly about 15-40  $\mu\text{m}$  as cured.

First color base coating (B)

The first color base coating (B) is a coating to be applied on the heat-cured film of the above-mentioned cationic electrocoating and has a sublayer-hiding power. There is no strict restriction as to the type of the first color base coating (B), and there can be used, for example, a per se known thermosetting coating of aqueous type or organic solvent type, containing a base material resin, a curing agent, a pigment and water and/or an organic solvent.

The base material resin constitutes the main component of the coating film formed by the first color base coating (B) and is appropriately a resin for coating which is excellent in weatherability, transparency, etc. and which is soluble or dispersible in water or organic solvents. There can be mentioned, for example, an acrylic resin, a polyester resin, an epoxy resin and a urethane resin.

As the acrylic resin, there can be mentioned, for example, a resin having an acid value of about 0-100, preferably about 5-30 and a hydroxyl value of about 20-200, preferably about 40-120, which is obtained by copolymerizing an  $\alpha,\beta$ -ethylenically unsaturated carboxylic acid, a functional group (e.g. hydroxyl group, amide group or methylol group)-containing (meth)acrylic acid ester, and other copolymerizable monomer(s) [e.g. functional group-free (meth)acrylic acid ester, substituted or unsubstituted styrene and/or olefin].

As the polyester resin, there can be used a resin obtained by subjecting a polybasic acid, a polyhydric alcohol and a modified oil to ordinary condensation. As the epoxy resin, there can be mentioned, for example, an epoxy ester resin obtained, for example, by a process which comprises reacting epoxy group with an unsaturated fatty acid to synthesize an epoxy ester and adding an  $\alpha,\beta$ -unsaturated acid to the unsaturated group of the epoxy ester, or by a process which comprises esterifying the hydroxyl group of epoxy ester with a polybasic acid such as phthalic acid or trimellitic acid.

As the urethane resin, there can be mentioned a high-molecular resin obtained by reacting the above-mentioned acrylic resin, polyester resin or epoxy resin with a diisocyanate compound. The resin is used mainly as a water-dispersible resin.

When an aqueous type coating is used as the first color base coating (B), there can be used, as the base material resin thereof, a resin having a hydrophilic group (for example, a carboxyl group, a hydroxyl group, a methylol group, an amino group, a sulfonic acid group or a polyoxyethylene bond, most typically a carboxyl group) of an amount sufficient to make the resin water-soluble or water-dispersible. The resin can be made water-soluble or water-dispersible by neutralizing the hydrophilic group to convert it into an alkali salt. In that case, the amount of the hydrophilic group (for example, carboxyl group) is not particularly restricted and can be appropriately determined depending upon to what extent

the resin is made water-soluble or water-dispersible; however, the amount can be generally about 10 or more, preferably 10-100, more preferably 15-50 in terms of acid value. As the alkaline substance used for neutralization, there can be mentioned, for example, sodium hydroxide and various amines.

The base material resin can be made water-dispersible also by subjecting the above-mentioned monomer components to emulsion polymerization in the presence of a surfactant or a water-soluble resin, or by dispersing the base material resin in water in the presence of, for example, an emulsifier. In this method of making water-dispersible the base material resin, the resin need not contain the above-mentioned hydrophilic group, or can contain the hydrophilic group in an amount smaller than that carried by the water-soluble resin.

Meanwhile, when an organic solvent type coating is used as the first color base coating (B), the coating can be prepared by dissolving or dispersing the above-mentioned base material resin (this resin need not contain the hydrophilic group but may contain it) and other coating components in an organic solvent. As the organic solvent, there can be used those ordinarily used in coatings. There can be mentioned, for example, hydrocarbon types such as toluene, xylene, hexane, heptane and the like; ester types such as ethyl acetate, butyl acetate, ethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene glycol monobutyl acetate and the like; ether types such as ethylene glycol monomethyl ether, ethylene glycol diethyl ether, diethylene glycol monomethyl ether, diethylene glycol dibutyl ether and the like; alcohol types such as butanol, propanol, octanol, cyclohexanol, diethylene glycol and the like; and ketone types such as methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, isophorone and the like.

The form of the organic solvent type coating includes a solution form, a high-solid form, a non-aqueous dispersion form, etc.

The curing agent usable in the first color base coating (B) is to crosslink and cure the base material resin three-dimensionally by heating. Specifically, an amino resin is appropriate which is obtained by subjecting melamine, benzoguanamine, urea or the like to condensation or co-condensation with formaldehyde and, as necessary, subjecting the resulting condensate or co-condensate to, for example, etherification with a lower monohydric alcohol. A polyisocyanate compound or a blocked polyisocyanate compound is also appropriate.

The pigment usable in the first color base coating (B) is to allow the coating film formed by the first color base coating (B) to have a sublayer-hiding power. Specific examples of the pigment are metallic pigments such as aluminum powder, bronze powder, copper powder, tin powder, lead powder, zinc powder, iron phosphide, pearl-like metal-coated mica powder, mica-like iron oxide and the like; rust-preventive pigments such as zinc chromate, strontium chromate, calcium chromate, lead cyanamide, calcium plumbate, zinc phosphate and the like; coloring pigments such as titanium dioxide, carbon black, Phthalocyanine Blue, Phthalocyanine Green, Carbazole Violet, anthrapyridine, Azo Orange, Yellow, Flavanthrone Yellow, Isoindoline Yellow, Azo Yellow, Indanthrone Blue, Di Brom Anthanthron Red, Perylene Red, Azo Red, Anthraquinone Red, Quinacridone Red, Violet and the like; and extender pigments such as barium oxide powder, precipitated barium sulfate, barium carbonate, gypsum, clay, silica, white carbon, diatomaceous earth, talc, magnesium carbonate, alumina white, gloss white, satin white, mica powder and the like. These pigments can be used singly or in combination of two or more kinds.

Desirably, the first color base coating (B) contains, as the pigment component, a metallic pigment and/or a coloring pigment selected from the above-mentioned pigments.

The first color base coating (B) can further contain a dye, as necessary. Desirably, the dye is one superior in light resistance, solubility in water and organic solvent, etc. As specific examples of the dye, there can be mentioned azo dyes such as monoazo dye, polyazo dye, metal complex azo dye, pyrazolone azo dye, stilbene azo dye and thiazole azo dye; anthraquinone dyes such as anthraquinone derivative and anthrone derivative; indigoid dyes such as indigo derivative and thioindigo derivative; phthalocyanine dyes; carbonium dyes such as diphenylmethane dye, triphenylmethane dye, xanthene dye and acridine dye; quinoneimine dyes such as azine dye, oxazine dye and thiazine dye; methine dyes such as polymethine (or cyanine) dye and azimethine dye; quinoline dyes; nitro dyes; nitron dyes; benzquinone or naphthoquinone dyes; naphthalimide dyes; and Perinone dyes. These dyes can be used singly or in combination of two or more kinds.

The proportions of the above individual components in the first color base coating (B) are not strictly restricted and can be determined appropriately depending upon, for example, the purpose of the use of the coated article. However, the preferable proportions of the base material resin and the curing agent are 60-90% by weight, particularly 70-85% by weight (the former) and 40-10% by weight, particularly 30-15% by weight (the latter) based on the total weight of the two components.

The pigment can be used in an appropriate combination depending upon the desired level of sublayer-hiding power, the desired color of the base coating (B), etc. The suitable amount of the pigment used is such that the transmittance of light having a wavelength within a range of 400-700 nm of a cured film of 30  $\mu\text{m}$  in thickness which was formed from the first color base coating is generally 5% or less, preferably 3% or less. The specific amount of the pigment used differs depending upon the kind of the pigment and cannot be determined in a particular range, but can be generally 1-250 parts by weight, preferably 5-150 parts by weight per 100 parts by weight of the resin solid content (the total amount of the base material resin and the curing agent).

Incidentally, in the present specification, the light transmittance of coating film is an average spectral transmittance obtained when a coating is applied on a glass sheet so as to give a film of particular thickness as cured, the resulting coating film is cured, the resulting material is immersed in a hot water of 60-70°C, the coating film is peeled from the glass sheet and dried, and the dried film is subjected to measurement by a recording spectrophotometer (Model EPS-3T, a product of Hitachi, Ltd.) using a light having a wavelength of 400-700 nm.

The first color base coating (B) can be applied according to an ordinary method. The coating (B) can be applied, for example, by adding, to the coating, deionized water and/or an organic solvent and, as necessary, additives such as thickener, antifoaming agent and the like to adjust the solid content to 10-70% by weight, preferably 15-55% by weight and the viscosity to 10-60 seconds, particularly 12-30 seconds (Ford Cup #4/20°C) in the case of a solvent type coating and to 200-5,000 cp/6 rpm, particularly 300-3,000 cp/6 rpm (B type viscometer) in the case of a water-soluble or water-dispersible coating, and applying, by spray coating or the like, the resulting material on the cured coating film of the cationic electrocoating (A) so as to form a coating film of, for example, about 5-60 µm, preferably about 8-25 µm in thickness as cured. In the present method, it is preferred that the first color base coating (B) is applied, the resulting coating film is air-dried at room temperature by air blowing or the like without substantially curing the film, and then the second color base coating (C) is applied.

#### Second color base coating (C)

The color base coating (C) is a coating to be applied on the film of the first color base coating (B) and has transparency. The kind of the coating (C) is not strictly restricted. As the coating (C), there can be used a per se known thermosetting coating of aqueous type or organic solvent type containing a base material resin, a curing agent, a pigment and water and/or an organic solvent.

Each individual component of the coating (C) can be selected from the specific examples of each component mentioned in the first color base coating (B).

The second color base coating (C) can as well contain a dye as necessary. As the dye, there can be used at least one of the specific examples mentioned in the first color base coating (B).

In the second color base coating (C), the proportions of the individual components are not strictly restricted and can be determined appropriately depending upon the purpose of the use of the coated article. However, the proportions of the base material resin and the curing agent can be generally 60-90% by weight, particularly 70-85% by weight (the former) and generally 40-10% by weight, particularly 30-15% by weight (the latter) all based on the total weight of the two components.

The second color base coating (C) preferably contains, as the pigment component, a metallic pigment and/or a coloring pigment. Desirably, the total content of the pigment is relatively low so that the film formed by the second color base coating (C) can have transparency and the color of the first color base coating can be seen through said film. It is generally preferable that the total content of the pigment is lower than the total content of the pigment in the first color base coating (B).

Specifically, the desired amount of the pigment used is such that the transmittance of light having a wavelength within a range of 400-700 nm of a cured film of 30 µm in thickness which was formed from the second color base coating is 6-95%, particularly 10-90%, more particularly 20-80%. The amount of the pigment used differs depending upon the kind of the pigment and cannot be specified in a particular range; however, it is preferable that the amount is generally 0.01-100 parts by weight, particularly 0.1-80 parts by weight per 100 parts by weight of the resin solid content (the total amount of the base material resin and the curing agent) and that the amount is smaller than that in the first color base coating (B).

The second color base coating (C) can be applied according to an ordinary method. The coating (C) can be applied, for example, by adding, to the coating, deionized water and/or an organic solvent and, as necessary, additives such as thickener, antifoaming agent and the like to adjust the solid content to 10-70% by weight, preferably 20-60% by weight and the viscosity to 10-60 seconds, particularly 13-40 seconds (Ford Cup #4/20°C) in the case of a solvent type coating and to 200-5,000 cp/6 rpm, particularly 300-3,000 cp/6 rpm (B type viscometer) in the case of a water-soluble or water-dispersible coating, and applying, by spray coating or the like, the resulting material so as to form a coating film of, for example, about 10-70 µm, particularly about 15-50 µm in thickness as cured. In the present method, it is preferred as mentioned previously that the first color base coating (B) is applied, the resulting coating film is air-dried at room temperature by air blowing or the like without substantially curing the film, and then the second color base coating (C) is applied. After the application of the second color base coating (C), heating is conducted at a temperature of about 80-170°C, preferably about 120-160°C for about 3-40 minutes, preferably about 10-30 minutes, whereby the first color base coating (B) and the second color base coating (C) can be cured simultaneously. For the heating, there can be used a method ordinarily used, such as hot-air heating, infrared heating, high-frequency heating or the like.

Clear coating (D)

According to the present invention, a clear coating (D) can be applied on the film of the second color base coating (C) so that the multi-layer coating film formed is further improved in aesthetic effect, finish appearance, weatherability, chemical resistance, water resistance, moisture resistance, etc. As the clear coating (D), there can be used a coating capable of forming a colorless or color transparent film. Specifically, there can be used a per se known thermosetting coating of water-soluble or water-dispersible type, organic solvent type or powder type, containing a base material resin and a curing agent as the main components and further containing, as necessary, a coloring pigment, a metallic pigment, a dye, etc. in such amounts that the transparency of the coating film formed is not substantially impaired.

The base material resin and curing agent usable in the water-soluble or water-dispersible coating and the organic solvent type coating, and the organic solvent usable in the organic solvent type coating can be selected from the specific examples mentioned in the first color base coating (B). The proportions of the base material resin and the curing agent are preferably those also mentioned in the first color base coating.

The water-soluble or water-dispersible clear coating or the organic solvent type clear coating can be applied according to an ordinary method, by adding, to the coating, deionized water and/or an organic solvent and, as necessary, additives such as thickener, anti-foaming agent and the like to adjust the solid content to about 10-95% by weight, preferably about 30-80% by weight and the viscosity to 10-70 seconds, preferably 15-40 seconds (Ford Cup #4/20°C) in the case of a solvent type coating and to 200-5,000 cp/6 rpm, preferably 300-3,000 cp/6 rpm (B type viscometer) in the case of a water-soluble or water-dispersible coating, and applying, by spray coating or the like, the resulting material so as to form a coating film of, for example, about 10-70  $\mu\text{m}$ , particularly about 15-50  $\mu\text{m}$  in thickness as cured. The coating film formed can be cured by heating at a temperature of about 80-170°C, preferably about 120-160°C for about 20-40 minutes. For the heating, there can be used a method ordinarily used, such as hot-air heating, infrared heating, high-frequency heating or the like.

Meanwhile, the powder coating usable as the clear coating (D) is composed mainly of a base material resin and a curing agent as the main components. As the base material resin, there can be mentioned, for example, an acrylic resin, a polyester resin, a fluoroplastic, an urethane resin and their modifications (e.g. a graft polymer) all having at least one crosslinkable functional group selected from hydroxyl group, carboxyl group, glycidyl group, etc. These resins are merely illustrations and the base material resin is not restricted thereto. The base material resin preferably has a glass transition temperature of generally 40°C or more, particularly 50-120°C, more particularly 60-100°C. There is no particular restriction as to the composition, molecular weight, etc. of the base material resin, and they can be appropriately selected depending upon the purpose of the use of the coated article.

The curing agent is a component used to three-dimensionally crosslink and cure the base material resin by heating. As the curing agent, there can be used, for example, an alkoxymethylolmelamine, a blocked polyisocyanate compound, an epoxy compound, an isocyanurate compound or an aliphatic dibasic acid.

The proportions of the base material resin and the curing agent are most preferably such that the above-mentioned functional group of the base material resin and the functional group of the curing agent become about equimolar.

The powder coating may further contain, as necessary, additives for coating, such as fluidity-controlling agent, ultraviolet absorber, light stabilizer and the like.

The powder coating can be obtained ordinarily by melt-kneading the above components, cooling the melt-kneaded material, and grinding it into appropriate particle diameters.

The method by which the powder coating is applied, is not particularly restricted, and there can be used an appropriate application method for powder coating, such as electrostatic spray coating, fluidized dip coating or the like.

The film thickness at which the powder coating is applied, is not particularly restricted, either; however, the film thickness is generally appropriate to be 20-200  $\mu\text{m}$ . It is preferable to apply the powder coating at a film thickness of particularly 20-120  $\mu\text{m}$  so as to give a finished coating film superior in smoothness, distinctness of image gloss, luster, fattiness, etc. The curing temperature of the film of the powder coating can be taken at the curing temperature of the powder coating, for example, about 120-180°C, preferably about 130-170°C.

Examples

The present invention is hereinafter described more specifically by way of Examples. In the followings, "parts" and "%" refer to "parts by weight" and "% by weight", respectively.

## 1. Preparation of samples

## 1) Cationic electrocoating (A)

## (A-1)

"Electron #9200"(product of Kansai Paint Co., Ltd., trade name, polyamine-modified epoxy resin-blocked polyisocyanate type) was diluted with deionized water or the like so as to give a solid content of about 16% by weight. The resulting material was electrodeposited by an ordinary method while the pH was maintained at 5.5-8.0. The thickness of the coating film formed was about 20  $\mu\text{m}$  in terms of cured film thickness. The coating film was cured at about 175°C.

## 2) Second color base coatings (B)

## 50% acrylic resin solution (S-1)

30 parts of methyl methacrylate, 59 parts of ethyl acrylate, 10 parts of hydroxyethyl acrylate and 1 part of acrylic acid were polymerized by an ordinary process, in the presence of a polymerization initiator,  $\alpha,\alpha'$ -azobisisobutyronitrile, in a mixed solvent of xylene/n-butanol = 70/30, whereby was obtained an acrylic resin solution (S-1) having a weight-average molecular weight of 25,000 and a resin solid content of 50%.

## 20% aqueous acrylic resin dispersion (W-1)

In a reactor were placed 140 parts of deionized water, 2.5 parts of 30% "Newcol 707SF" (surfactant, product of Nippon Nyukazai Co., Ltd.) and 1 part of a monomer mixture (1) shown below. The reactor contents were stirred in a nitrogen gas current. Thereto was added 3 parts of a 3% aqueous ammonium persulfate solution at 60°C. The resulting mixture was heated to 80°C. Into the reactor was fed, in 4 hours by the use of a metering pump, a monomer emulsion consisting of 79 parts of the following monomer mixture (1), 2.5 parts of 30% "Newcol 707SF", 4 parts of a 3% aqueous ammonium persulfate solution and 42 parts of deionized water. The resulting mixture was then subjected to aging for 1 hour. Into the reactor were dropwise and simultaneously fed, at 80°C in 1.5 hours, 20.5 parts of a monomer mixture (2) shown below and 4 parts of a 3% aqueous ammonium persulfate solution. The resulting mixture was then subjected to aging for 1 hour, then diluted with 30 parts of deionized water, and filtered through a 200-mesh nylon cloth at 30°C. To the filtrate was added deionized water, and the resulting mixture was adjusted to pH 7.5 using dimethylaminoethanol to obtain a 20% aqueous acrylic resin dispersion (W-1) having an average particle diameter of 0.1  $\mu\text{m}$  and a nonvolatile content of 20%.

## Monomer mixture (1)

Methyl methacrylate	55 parts
Styrene	10 parts
n-Butyl acrylate	9 parts
2-Hydroxyethyl acrylate	5 parts
Methacrylic acid	1 part

## Monomer mixture (2)

Methyl methacrylate	5 parts
n-Butyl acrylate	7 parts
2-Hydroxyethyl acrylate	5 parts
Methacrylic acid	3 parts
30% "Newcol 707SF"	0.5 part

27% aqueous melamine resin dispersion (M-1)

Into a 2-liter four-necked flask equipped with a thermometer, a stirrer and a reflux condenser were placed 126 parts of melamine, 225 parts of 80% paraformaldehyde (product of Mitsui Toatsu Chemicals, Inc.) and 592 parts of n-butanol. The mixture was adjusted to pH 9.5-10.0 using a 10% aqueous sodium hydroxide solution and then subjected to a reaction at 80°C for 1 hour. Thereto was added 888 parts of n-butanol. The resulting mixture was adjusted to pH 5.5-6.0 using a 5% sulfuric acid solution and subjected to a reaction at 80°C for 3 hours. After the completion of the reaction, the reaction mixture was neutralized with a 20% aqueous sodium hydroxide solution to pH 7.0-7.5. Then, vacuum concentration was conducted at 60-70°C to remove n-butanol. The residue was filtered to obtain a hydrophobic melamine resin. Nonvolatile content = 80%; dilution in water-methanol mixed solvent (weight ratio: 35/65) = 3.6%; weight-average molecular weight = 800.

The melamine resin was placed in a vessel under stirring so that the solid content became 25 parts. Thereto was added 20 parts of an aqueous acrylic resin solution (a 50% aqueous solution a resin made from n-butyl acrylate, methyl methacrylate, styrene, 2-hydroxyethyl methacrylate and acrylic acid). While the resulting mixture was stirred using Disper of 1,000-1,500 rpm, 80 parts of deionized water was slowly added thereto. Thereafter, stirring was conducted for 30 minutes to obtain an aqueous melamine resin dispersion (M-1) having a solid content of 27% and an average particle diameter of 0.11  $\mu\text{m}$ .

(B-1)

50% acrylic resin solution (S-1)	150 parts
88% Cymel 370 (Note 1)	28 parts
Pigment component-1 (Note 2)	30 parts
Dibutyl acid phosphate	0.3 part

The mixture of the above materials was subjected to viscosity adjustment with a mixed solvent consisting of 30 parts of toluene, 20 parts of isobutyl alcohol, 30 parts of cellosolve acetate and 20 parts of butyl cellosolve, so as to have a viscosity of 20 seconds (Ford Cup #4/20°C), whereby a first color base coating (B-1) of solvent type was obtained. The pigment content of the coating (B-1) was 26.5 parts by weight per 100 parts by weight of the resin solid content (the base material resin and the curing agent); the total content of the metallic pigment and/or the coloring pigment was 6.5 parts by weight per 100 parts by weight of the resin solid content (the base material resin and the curing agent); and the light transmittance of the coating film formed was 0.1% or less when measured for a cured film of 30  $\mu\text{m}$  thickness.

(Note 1) 88% Cymel 370: trade name of Mitsui Cyanamid Ltd., contains 55% (as solid content) of a mono-ring substance of methoxylated methylol-melamine containing both methoxy group and methylol group.

(Note 2) Pigment component-2: a pigment component consisting of 10 parts of "Alumipaste N-1700NL" (product of Toyo Aluminum K.K., trade name, aluminum content = 65%) and 20 parts of barium sulfate.

(B-2)

20% aqueous acrylic resin dispersion (W-1)	325 parts
27% aqueous melamine resin dispersion (M-1)	131 parts
Pigment component-2 (Note 3)	10 parts
Deionized water	171 parts
"Acrysol ASE-60"(Note 4)	3 parts
Dimethylaminoethanol	0.3 part

The mixture of the above materials was subjected to viscosity adjustment with deionized water so as to have a viscosity of 30 seconds (Ford Cup #4/20°C), to obtain a first color base coating (B-2) of aqueous type. The pigment content of the coating (B-2) was 6.5 parts by weight per 100 parts by weight of the resin solid content (the base material



resin and the curing agent); the total content of the metallic pigment and/or the coloring pigment was 6.5 parts by weight per 100 parts by weight of the resin solid content (the base material resin and the curing agent); and the light transmittance of the coating film formed was 0.1% or less when measured for a cured film of 30  $\mu\text{m}$  thickness.

5 (Note 3) Pigment component-2: "Alumipaste N-1700NL" (trade name, product of Toyo Aluminum K.K., aluminum content = 65%).

(Note 4) Acrysol ASE-60: trade name, product of Rohm and Haas Co., thickener.

(B-3)

10

50% acrylic resin solution (S-1)	150 parts
88% Cymel 370 (Note 1)	28 parts
Pigment component-3 (Note 5)	23 parts
Dibutyl acid phosphate	0.3 part

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20 The mixture of the above materials was subjected to viscosity adjustment with a mixed solvent consisting of 30 parts of toluene, 20 parts of isobutyl alcohol, 30 parts of cellosolve acetate and 20 parts of butyl cellosolve, so as to have a viscosity of 20 seconds (Ford Cup #4/20°C), whereby a first color base coating (B-3) of solvent type was obtained. The pigment content of the coating (B-3) was 23 parts by weight per 100 parts by weight of the resin solid content (the base material resin and the curing agent); the total content of the metallic pigment and/or the coloring pigment was 3 parts by weight per 100 parts by weight of the resin solid content (the base material resin and the curing agent); and the light transmittance of the coating film formed was 0.1% or less when measured for a cured film of 30  $\mu\text{m}$  thickness.

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(Note 5) Pigment component-3: a pigment component consisting of 3 parts of carbon black and 20 parts of barium sulfate.

30

(E-1) (for comparison)

35

50% acrylic resin solution (S-1)	150 parts
88% Cymel 370 (Note 1)	28 parts
Pigment component-4 (Note 6)	28 parts
Dibutyl acid phosphate	0.3 part

40

The mixture of the above materials was subjected to viscosity adjustment with a mixed solvent consisting of 30 parts of toluene, 20 parts of isobutyl alcohol, 30 parts of cellosolve acetate and 20 parts of butyl cellosolve, so as to have a viscosity of 20 seconds (Ford Cup #4/20°C), whereby a color base coating (E-1) of solvent type for comparison was obtained. The pigment content of the coating (E-1) was 28 parts by weight per 100 parts by weight of the resin solid content (the base material resin and the curing agent); the total content of the metallic pigment and/or the coloring pigment was 8 parts by weight per 100 parts by weight of the resin solid content (the base material resin and the curing agent); and the light transmittance of the coating film formed was 0.1% or less when measured for a cured film of 30  $\mu\text{m}$  thickness.

45

50 (Note 6) Pigment component-4: a pigment component consisting of 3 parts of carbon black, 5 parts of "Infinite Color YBG-06-SK3" (pearlescent pigment, product of Shiseido Co., Ltd., trade name) and 20 parts of barium sulfate.

55

## 3) Second color base coatings (C)

## (C-1)

50% acrylic resin solution (S-1)	150 parts
88% Cymel 370 (Note 1)	28 parts
Pigment component-5 (Note 7)	3 parts
Dibutyl acid phosphate	0.3 part

The mixture of the above materials was subjected to viscosity adjustment with a mixed solvent consisting of 30 parts of toluene, 20 parts of isobutyl alcohol, 30 parts of cellosolve acetate and 20 parts of butyl cellosolve, so as to have a viscosity of 20 seconds (Ford Cup #4/20°C), whereby a second color base coating (C-1) of solvent type was obtained. The pigment content of the coating (C-1) was 2.2 parts by weight per 100 parts by weight of the resin solid content (the base material resin and the curing agent); the total content of the metallic pigment and/or the coloring pigment was 2.2 parts by weight per 100 parts by weight of the resin solid content (the base material resin and the curing agent); and the light transmittance of the coating film formed was 10% when measured for a cured film of 30 μm thickness.

(Note 7) Pigment component-5: "Alumipaste 891K" (trade name), product of Toyo Aluminum K.K., aluminum content = 72%.

## (C-2)

20% aqueous acrylic resin dispersion (W-1)	325 parts
27% aqueous melamine resin dispersion (M-1)	131 parts
Pigment component-5 (Note 7)	3 parts
Deionized water	171 parts
"Acrysol ASE-60" (Note 4)	3 parts
Dimethylaminoethanol	0.3 part

The mixture of the above materials was subjected to viscosity adjustment with deionized water so as to have a viscosity of 30 seconds (Ford Cup #4/20°C), to obtain a second color base coating (C-2) of aqueous type. The pigment content of the coating (C-2) was 2.2 parts by weight per 100 parts by weight of the resin solid content (the base material resin and the curing agent); the total content of the metallic pigment and/or the coloring pigment was 2.2 parts by weight per 100 parts by weight of the resin solid content (the base material resin and the curing agent); and the light transmittance of the coating film formed was 70% when measured for a cured film of 30 μm thickness.

## (C-3)

50% acrylic resin solution (S-1)	150 parts
88% Cymel 370 (Note 1)	28 parts
Pigment component-6 (Note 8)	1.5 parts
Dibutyl acid phosphate	0.3 part

The mixture of the above materials was subjected to viscosity adjustment with a mixed solvent consisting of 30 parts of toluene, 20 parts of isobutyl alcohol, 30 parts of cellosolve acetate and 20 parts of butyl cellosolve, so as to have a viscosity of 20 seconds (Ford Cup #4/20°C), whereby a second color base coating (C-3) of solvent type was obtained. The pigment content of the coating (C-3) was 1.5 parts by weight per 100 parts by weight of the resin solid

content (the base material resin and the curing agent); the total content of the metallic pigment and/or the coloring pigment was 1.5 parts by weight per 100 parts by weight of the resin solid content (the base material resin and the curing agent); and the light transmittance of the coating film formed was 10% when measured for a cured film of 30  $\mu\text{m}$  thickness.

(Note 8) Pigment component-5: "Infinite Color YGB-06-SK3" (pearlescent pigment, product of Shiseido Co., Ltd., trade name).

#### 4) Clear coatings (D)

##### (D-1)

25 parts of methyl methacrylate, 25 parts of ethyl acrylate, 36.5 parts of n-butyl acrylate, 12 parts of 2-hydroxyethyl acrylate, 1.5 parts of acrylic acid and 2.5 parts of a polymerization initiator ( $\alpha, \alpha'$ -azobisisobutyronitrile) were polymerized in xylene to obtain an acrylic resin solution having a resin solid content of 60%. The resin had a hydroxyl value of 58 and an acid value of 12. The resin was mixed with "U-Van 20SE" (hydrophobic melamine resin, product of Mitsui Toatsu Chemicals, Inc., nonvolatile content = 60%, weight-average molecular weight = 3,000-4,000) in a solid content weight ratio of 75:25. The resulting mixture was subjected to viscosity adjustment with an organic solvent to a viscosity of 25 seconds (Ford Cup #4/20°C), to obtain a clear coating (D-1) of solvent type.

##### (D-2)

20% aqueous acrylic resin dispersion (W-1)	325 parts
27% aqueous melamine resin dispersion (M-1)	131 parts
Deionized water	171 parts
"Acrysol ASE-60" (Note 4)	3 parts
Dimethylaminoethanol	0.3 part

The mixture of the above materials was subjected to viscosity adjustment with deionized water so as to have a viscosity of 30 seconds (Ford Cup #4/20°C), to obtain a clear coating (D-2) of aqueous type.

##### (D-3)

Into a flask were fed 40 parts of methyl methacrylate, 30 parts of n-butyl methacrylate, 30 parts of glycidyl methacrylate, 10 parts of styrene, 1 part of tert-butyl peroxide (polymerization initiator) and 2 parts of potassium oleate soap (surfactant). They were heat-polymerized by suspension polymerization. The resulting copolymer (glass transition temperature = about 60°C) was dried. 100 parts of the copolymer was melt-kneaded with 25 parts of decamethylenedicarboxylic acid and 1 part of a film surface conditioner by the use of a heated kneader at 120°C for 10 minutes. The kneaded material was cooled and then ground by the use of a grinder to obtain a clear coating (D-3) of powder type having particle diameters of about 20-150  $\mu\text{m}$ .

## II. Examples and Comparative Examples

### Examples 1-5

A steel plate, which had been subjected to a surface treatment with "Bonderite #3030" (product of Nihon Parkerizing Company Limited, zinc phosphate treatment agent), was immersed in a bath of the cationic electrocoating (A-1), and electrodeposition was conducted according to an ordinary method. The thickness of the coating film formed was about 20  $\mu\text{m}$  as cured. The electrocoated steel plate was pulled up from the bath, water-washed, and heated to about 175°C to cure the electrocoating film. Then, on the cured electrocoating film was applied, by air spraying, the first color base coating (B-1) or (B-3) of solvent type having a viscosity (Ford Cup #4/20°C) of 20 seconds or the first color base coating (B-2) of aqueous type having a viscosity (Ford Cup #4/20°C) of 30 seconds so as to give a coating film of about 20  $\mu\text{m}$  thickness as cured. The resulting material was allowed to stand at room temperature for about 10 minutes.

Then, on the uncured film of the first color base coating was applied, by air spraying, the second color base coating

(C-1) or (C-3) of solvent type having a viscosity (Ford Cup #4/20°C) of 20 seconds or the second color base coating (C-2) of aqueous type having a viscosity (Ford Cup #4/20°C) of 30 seconds so as to give a coating film of about 30  $\mu\text{m}$  thickness as cured. The resulting material was allowed to stand at room temperature for about 10 minutes and then heated at 140°C for 30 minutes to crosslink and cure the films of the first color base coating and the second color base coating simultaneously.

Then, on the cured film of the second color base coating was applied, by air spraying, the clear coating (D-1) of solvent type having a viscosity (Ford Cup #4/20°C) of 25 seconds or the clear coating (D-2) of aqueous type having a viscosity (Ford Cup #4/20°C) of 25 seconds so as to give a coating film of about 40  $\mu\text{m}$  thickness as cured, or was applied, by electrostatic powder coating, the clear coating (D-3) of powder type so as to give a coating film of 50  $\mu\text{m}$  thickness as cured. The resulting material was allowed to stand at room temperature for about 10 minutes and then heated under the baking conditions shown in Table 1 appearing later, to give rise to crosslinking and curing.

#### Comparative Example 1

On the cured electrocoating film obtained above was applied, by air spraying, a solvent type intermediate coating "TP-37" (product of Kansai Paint Co., Ltd., trade name) having a viscosity (Ford Cup #4/20°C) of 20 seconds so as to give a film of about 30  $\mu\text{m}$  thickness as cured. The resulting material was allowed to stand at room temperature for about 10 minutes and then heated at 140°C for 30 minutes.

Then, on the cured film of the intermediate coating was applied, by air spraying, the first color base coating (B-1) of solvent type having a viscosity (Ford Cup #4/20°C) of 20 seconds so as to give a film of about 15  $\mu\text{m}$  thickness as cured. The resulting material was allowed to stand at room temperature for about 10 minutes.

Then, on the uncured film of the first color base coating was applied, by air spraying, the clear coating (D-1) of solvent type having a viscosity (Ford Cup #4/20°C) of 25 seconds so as to give a film of about 40  $\mu\text{m}$  thickness as cured. The resulting material was allowed to stand at room temperature for about 10 minutes and then heated at 140°C for 30 minutes to crosslink and cure the films of the first color base coating and the second color base coating simultaneously.

#### Comparative Example 2

On the cured electrocoating film obtained above was applied, by air spraying, the first color base coating (C-1) of solvent type having a viscosity (Ford Cup #4/20°C) of 20 seconds so as to give a film of about 18  $\mu\text{m}$  thickness as cured. The resulting material was allowed to stand at room temperature for about 10 minutes. Then, on the uncured film of the second color base coating (C-1) was applied, by air spraying, the clear coating (D-1) of solvent type having a viscosity (Ford Cup #4/20°C) of 25 seconds so as to give a film of about 40  $\mu\text{m}$  thickness as cured. The resulting material was allowed to stand at room temperature for about 10 minutes and then heated at 140°C for 30 minutes to give rise to crosslinking and curing.

#### Comparative Example 3

An operation was conducted in the same manner as in Example 1 except that (C-1) was used as the first color base coating and (B-1) was used as the second color base coating.

#### Comparative Example 4

An operation was conducted in the same manner as in Comparative Example 1 except that (E-1) was used as the first color base coating.

### III. Performance test results

The multi-layer coating films obtained in the above Examples and Comparative Examples were subjected to performance tests. The results thereof are shown in Table 1.

#### Test methods

##### Flat-area finish

Measured by the use of a tester for distinctness of image gloss, Model PGD-IV (marketer: JAPAN COLOUR RESEARCH INSTITUTE). A larger value indicates higher distinctness of image gloss.

### Outdoor durability

A coated plate was subjected to accelerated exposure for 200 hours in a sunshine weatherometer (light amount: 1,100 KJoule/m<sup>2</sup>.hr) and then immersed in hot water of 40°C for 24 hours. This procedure was taken as 1 cycle and repeated 25 times (25 cycles). Then, at the surface of the resulting plate were formed 100 squares each of 2 mm x 2 mm according to JIS K 5400 8.5.2 (cross-cut test method); a tape was stuck thereon and peeled; the extent of peeling appearing in squares was examined according to the following standard.

○: There is no intercoat adhesion failure.

X: There is partial or complete peeling between the electrocoating film and the base coating film.

### Chipping resistance

Using a gravelometer (product of Q Panel Co.), 500 g of No. 7 crushed stones were sprayed onto a coating film at an angle of 45° at an air pressure of 0.3 MPa at -20°C to apply an impact to the coating film. Then, a pressure-sensitive tape was stuck onto the coating film and quickly peeled, after which the extent of film peeling in the vicinity of the scars generated by the impact was examined.

○: There is no or substantially no film peeling in the vicinity of scars.

△: There is distinct film peeling in the vicinity of scars.

X: There is striking film peeling in the vicinity of scars.

### Brilliance feeling

A coated plate was visually examined according to the following standard.

◎: Very good brilliance feeling.

○: Good brilliance feeling.

X: Poor brilliance feeling.

### Intensity of interference color

A C\* value at an incident angle of 45° and a receiving angle of 15° was measured using MA68 of X-Rite Co. A larger value indicates a higher aesthetic effect.

### Flip-flop property

Alignment of aluminum was examined by the use of "Alcope" (name of metallic feeling tester produced by Kansai Paint Co., Ltd.). A larger value indicates superior aluminum alignment.

Table 1

		Examples					Comparative Examples			
		1	2	3	4	5	1	2	3	4
Coating steps	Application of electro-coating	A-1	A-1	A-1	A-1	A-1	A-1	A-1	A-1	A-1
	Baking conditions (Note)	①	①	①	①	①	①	①	①	①
	Film thickness ( $\mu$ )	20	20	20	20	20	20	20	20	20
	Application of intermediate coating	-	-	-	-	-	TP-37	-	-	TP-37
	Baking conditions (Note)	-	-	-	-	-	②	-	-	②
	Film thickness ( $\mu$ )	-	-	-	-	-	30	-	-	30
	First color or base coating (B)	B-1	B-2	B-3	B-1	B-1	B-1	-	C-1	E-1
	Baking conditions (Note)	No baking	No baking	No baking	No baking	No baking	No baking	-	No baking	No baking
	Film thickness ( $\mu$ )	15	15	15	15	15	15	-	15	15
	Application of top coat	C-1	C-2	C-3	C-1	C-1	-	C-1	B-1	-
Evaluation	Symbol of coating	②	②	②	②	②	-	No baking	②	-
	Baking conditions (Note)	30	30	30	30	30	-	30	30	-
	Film thickness ( $\mu$ )	D-1	D-1	D-1	D-2	D-3	D-1	D-1	D-1	D-1
	Clear coating (D)	②	②	②	②	③	②	②	②	②
	Baking conditions (Note)	40	40	40	40	40	40	40	40	40
	Film thickness ( $\mu$ )	1.0 $\leq$	1.0 $\leq$	1.0 $\leq$	1.0 $\leq$	1.0 $\leq$	0.8	0.6	0.7	0.8
	Flat-area finish	O	O	O	O	O	O	X	O	O
	Outdoor durability	O	O	O	O	O	O	X	X	X
	Chipping resistance	◎	◎	◎	◎	◎	◎	◎	◎	◎
	Brilliance feeling	-	-	70	-	-	-	-	-	-
	Intensity of interference color	1.7	1.8	-	1.8	1.8	1.5	1.3	1.5	-
	Flip-flop value	-	-	-	-	-	-	-	-	-

(Note) Baking conditions: ① 175°C x 20 minutes, ② 140°C x 30 minutes, ③ 160°C x 30 minutes

## Industrial Applicability

The present method is a coating method which is applied at a low cost, which gives a coating film very superior in finish appearance, aesthetic effect, corrosion resistance, weatherability, chipping resistance, etc. and which is advanta-

geous in resource saving and pollution control; and can be extensively utilized in coating of automobiles, bicycles, electric appliances, etc.

## Claims

1. A method for forming a multi-layer coating film, which is characterized by applying a cationic electrocoating on a metal-made material to be coated, heat-curing the resulting electrocoating film, applying, on the heat-cured electrocoating film, a first color base coating having a sublayer-hiding powder, applying, on the resulting coating film without substantially curing the film, a second color base coating having transparency, heating the two films of the first color base coating and the second color base coating to cure them, then applying a clear coating, and heat-curing the resulting clear coating film.
2. A method according to Claim 1, wherein the first color base coating contains a metallic pigment and/or a coloring pigment.
3. A method according to Claim 1, wherein the first color base coating has a light transmittance of 5% or less when made into a cured film of 30  $\mu\text{m}$  thickness.
4. A method according to Claim 1, wherein the first color base coating has a light transmittance of 3% or less when made into a cured film of 30  $\mu\text{m}$  thickness.
5. A method according to Claim 1, wherein the first color base coating contains pigment(s) in an amount of 1-250 parts by weight per 100 parts by weight of the resin solid content.
6. A method according to Claim 1, wherein the first color base coating is applied so as to give a cured film of 5-60  $\mu\text{m}$  thickness.
7. A method according to Claim 1, wherein the second color base coating contains a metallic pigment and/or a coloring pigment.
8. A method according to Claim 1, wherein the second color base coating has a light transmittance of 6-95% when made into a cured film of 30  $\mu\text{m}$  thickness.
9. A method according to Claim 1, wherein the second color base coating has a light transmittance of 10-90% when made into a cured film of 30  $\mu\text{m}$  thickness.
10. A method according to Claim 1, wherein the second color base coating contains pigment(s) in an amount of 0.01-100 parts by weight per 100 parts by weight of the resin solid content.
11. A method according to Claim 1, wherein the second color base coating is applied so as to give a cured film of 10-70  $\mu\text{m}$  thickness.
12. A method according to Claim 1, wherein the two films of the first color base coating and the second color base coating are heated at a temperature of 80-170°C to cure them.
13. A method according to Claim 1, wherein the clear coating is a water-soluble coating, a water-dispersible coating, an organic solvent type coating or a powder coating.
14. A coated article obtained by a method set forth in Claim 1.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP96/01119

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl<sup>6</sup> B05D1/38

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl<sup>6</sup> B05D1/00-1/42

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

Jitsuyo Shinan Koho	1926 - 1996
Kokai Jitsuyo Shinan Koho	1971 - 1996
Jitsuyo Shinan Keisai Koho	1994 - 1996

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 3-193898, A (Kansai Paint Co., Ltd.), August 23, 1991 (23. 08. 91) (Family: none)	1 - 14
A	JP, 4-161274, A (Kansai Paint Co., Ltd.), June 4, 1992 (04. 06. 92) (Family: none)	1 - 14
A	JP, 5-194811, A (Dainippon Ink and Chemicals, Inc.), August 3, 1993 (03. 08. 93) (Family: none)	1 - 14
A	JP, 5-269432, A (Kansai Paint Co., Ltd.), October 19, 1993 (19. 10. 93) (Family: none)	1 - 14

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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July 22, 1996 (22. 07. 96)

Date of mailing of the international search report

July 30, 1996 (30. 07. 96)

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